



沈阳材料科学国家研究中心 Shenyang National Laboratory for Materials Science





3月28日, 沈阳材料科学国家研究中心建设运行管理委员会及 学术委员会第一次会议在北京召开。



2019年3月,在TMS第148届年会上,卢柯 院士被授予"Acta Materialia金质奖章"。



5月18日-19日, SYNL举办"公众科学日"活动。



6月25日, SYNL组织召开"不忘初心、牢记使命" 主题教育系列活动。









4月24日-27日,"李薰讲座奖"获得者、英国剑桥大学 Bhadeshia Harshad教授访问SYNL并开展合作交流。

6月4日-7日, "李薰讲座奖"获得者、美国中佛罗里达大 学Seal Sudipta教授访问SYNL。



6月13日-18日, "李薰研究奖"获得者、日本名古屋大学 9月13日-18日, "李薰讲座奖"获得者、荷兰代尔夫特理 Ohno Yutaka教授访问SYNL。 工大学Brück Ekkes教授访问SYNL。





9月25日-27日,"李薰讲座奖"获得者、维 也纳大学Kresse Georg教授访问SYNL。

前



"沈阳材料科学国家研究中心"(简称SYNL),定位于创建国际 一流的综合性材料基础研究平台,在已经形成优势学科基础上,进一步 交叉融合,开展材料科技领域的前瞻性、战略性、前沿性学科交叉基础 研究。

2019年,在科技部、中科院、辽宁省、沈阳市等有关部门领导的 大力支持下,经过全体员工、学生的共同努力,SYNL 建设不断取得进 步,如期完成年度既定规划任务。在材料素化、百吨级不锈钢环构筑成 形、庞压卡效应、金属硫族化合物碳纳米管复合柔性热电薄膜材料与器 件、基于纤维素基元晶体的高性能Pd单原子催化剂等方面取得了新的 进展。在重大原创成果产出以及推动经济社会发展等方面均取得了很好 的成绩,得到了科技界以及各级政府部门的充分肯定。

本年度主要回顾了过去一年SYNL整体建设及运行的基本情况,总结与记载了主要研究活动,包括:科学研究成果、经费资助、国际交流与合作、研究生教育等内容,全面展示2019年SYNL各项建设工作成效。

最后,借此报告制作的机会,我谨代表SYNL全体工作人员,向在 过去一年里给予我们各项工作大力支持的各级领导和各界朋友表示衷心 的感谢。同时,我们也将继续努力工作,不断提升自身的创新能力与国 际竞争力,为中国材料科学事业的发展做出贡献。

沈阳材料科学国家研究中心主任

ph. (卢柯)

2020年3月于沈阳

FOREWORD

The Shenyang National Laboratory for Materials Science (SYNL) visions itself as a world leading comprehensive platform for basic materials research. Leveraging on the established preponderant disciplines, SYNL furthers the merging of disciplines to carries out visionary, strategic and cutting-edge interdisciplinary basic research in the field of materials science and technology.

With the support of Ministry of Science and Technology (MOST), Chinese Academy of Sciences (CAS), Liaoning province and Shenyang city, and through the efforts of all the colleagues and graduate students, SYNL has made significant progress in research activites, represented by the planification of materials, the 150 ton austenitic stainless steel ring manufactured using additive forging technology, the discovery of colossal barocaloric effects, the flexible thermoelectric thin film and microdevice for energy harvesting and on-chip cooling as well as the high performance Pd single atomic catalyst based on cellulose elementary crystals.

In this report, we summarize the principal research activities in SYNL during the past calendar year, including the research highlights, publications, funding situation, international collaborations and education of graduate students, etc.. It provides not only a record of the progress in SYNL but also a picture to understand the laboratory in the community of materials science for those who are interested in it. Your comments and suggestions on this report are highly welcome.

On behalf of the Director I would like to thank our staff and students for the excellent work performed in all divisions throughout the year 2019.

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(K. LU) Director of SYNL Shenyang, March 2020



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1 基本概况 GENERAL INTRODUCTION



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学术委员会 EMIC COMMITTEE	主任:薛其坤 man: XUE Qikun		技术支援部 Technical Support Division 科技管理办公室 Technology Administration Office	办公室 SYNL Office	东北大学联合研究分部 stern University Joint Division 重子材料联合研究分部 turn Materials Joint Division	
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1.2 建设运行管理委员会(12人)

主任:

李树深 中国科学院

副主任: 左 良 中国科学院金属研究所 高瑞平 国家自然科学基金委员会

委员:

- 卢 柯 中国科学院金属研究所
- 王大南 辽宁省科技厅
- 赵日刚 沈阳市科技局
- 单 义 沈阳市浑南区人民政府
- 郑晓年 中国科学院条件保障与财务局
- 王 颖 中国科学院前沿科学与教育局
- 杨金龙 中国科学技术大学
- 吕 坚 香港城市大学
- 孙 军 西安交通大学

1.2 MANAGEMENT COMMITTEE (12)

Director:
LI Shushen (CAS ^a)
Vice-director:
ZUO Liang (IMR ^b)
GAO Ruiping (National Natural Science Foundation of China)
Committee Members:
LU Ke (IMR)
WANG Danan (Department of Science & Technology of Liaoning Province)
ZHAO Rigang (Shenyang Bureau of Science and Technology)
SHAN Yi (The People's Government of Hunnan
District, Shenyang)
ZHENG Xiaonian (CAS)
WANG Ying (CAS)
YANG Jinlong (University of Science and Technology of China)

LU Jian (City University of Hong Kong)

SUN Jun (Xi'an Jiaotong University)

(^aCAS: Chinese Academy of Sciences)

(^bIMR: Institute of Metal Research, Chinese Academy of Sciences)

1.3 学才	、委员会	(12人)	1.3 ACADEMIC COMMITTEE (12)
主任 :	薛其坤	清华大学	Director: XUE Qikun (Tsinghua University)
副主任:	刘锦川	香港城市大学	Vice-director: LIU Chain-Tsuan (City University of Hong Kong)
	卢柯	中国科学院金属研究所	LU Ke (IMR ^a)
委员: (ル	〈 姓氏首字	母为序)	Committee Members:
	安立佳	中国科学院长春应用化学研究所	AN Lijia (Changchun Institute of Applied Chemistry, CAS^{b})
	Brechet Yves	法国格勒诺布尔综合理工大学	BRECHET Yves (Université Grenoble-Alpes, France)
	Gleiter Herbert	德国卡尔斯鲁厄理工学院	GLEITER Herbert (Karlsruher Institut für Technologie, Germany)
	刘维民	中国科学院兰州化学物理研究所	LIU Weimin (Lanzhou Institute of Chemical Physics, CAS)
	李依依	中国科学院金属研究所	LI Yiyi (IMR)
	汪卫华	中国科学院物理研究所	WANG Weihua (Institute of Physics, CAS)
	叶恒强	中国科学院金属研究所	YE Hengqiang (IMR)
	张清杰	武汉理工大学	ZHANG Qingjie (Wuhan University of Technology)
	张 泽	浙江大学	ZHANG Ze (Zhejiang University)

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1.4 人员结构 (PERSONNEL STRUCTURE)

截至2019年底,SYNL现有固定人员348人,在读研究生661人,同比分别增加20%和59%;客座研究 人员55人。固定人员中,科研人员293人(其中研究员/教授117人,副研究员/副教授/高级工程师/高级实 验师147人),专业技术人员43人,管理人员11人;具有博士学位人员269人(占人员总数77.3%)。



图1 2017-2019年科研人员总数



≤30岁 31~45岁46~60岁 ≥61岁

图2 固定人员年龄分布



图3 固定人员专业技术职务分布

1.5 杰出人才(TALENTS)



叶恒强 中国科学院院士



李依依 中国科学院院士



卢 柯 中国科学院院士



成会明 中国科学院院士



刘锦川 美国国家工程院院士



吕 坚 法国国家技术科学院 院士

国家高层次人才特殊计划			成会明 李殿中	任文才 肖伯律	
			张志东 任文才		马宗义 陈星秋
优秀青年基金					
	卢马卢胡 京 卫 (20人)	李殿明 前 尊 天 民			张广平 孙东明 张莉莉

(*以入选时间为序)



1.6 科研任务 (SCIENTIFIC RESEARCH PROJECTS)

2019年,国家研究中心承担各类竞争性研究项目近560项,到位经费总额27700余万元,其中省部级 以上项目403项(占总数的73.3%),国家重点研发计划47项、国家自然科学基金-重大研究计划7项、国 家自然科学基金-重点项目5项、国家自然科学基金-杰出青年科学基金5项、国家自然科学基金-创新研究 群体2项、中国科学院战略性先导科技专项3项、国际合作项目14项、国内大型企业合作项目115项。

项目来源	科技部	基金委	中科院	国防需求	其他
课题(项)	54	163	79		226
	6791	3762	3716	5578	7855

表1 国家研究中心在研课题构成情况



1.7 科研产出(SCIENTIFIC RESEARCH ACHIEVEMENTS)

2019年,国家研究中心在国内外重要学术期刊及会议上发表学术论文470篇,其中被SCI检索收录论 文449篇。发表论文中,在Science上发表论文1篇,Nature发表2篇;在Science及Nature子刊发表13篇。截 止2020年3月20日,国家研究中心共发表论文6265篇,总被引频次219502。

2019年,国家研究中心共申请国家发明专利136项,获得授权发明专利89项。

2019年,研究人员荣获各类学术奖励及荣誉35项,其中,卢柯院士荣获材料科学与工程终身成就奖 (Acta Materialia Gold Medal); 李依依院士荣获辽宁省科学技术最高奖; 马秀良研究员当选亚太材料科 学院院士; 王京阳研究员当选美国陶瓷学会会士 (Fellow of the American Ceramic Society); 李昺研究员荣 获日本中子学会青年研究奖。

科研成果方面,马宗义团队的"金属材料的搅拌摩擦焊接与加工基础研究"荣获辽宁省2019年度自 然科学一等奖;贾金锋教授(上海交通大学)的"拓扑量子材料制备与量子特性的实验研究"以及王敬 丰教授(重庆大学)的"镁基功能材料的功能特性与力学性能协同调控的基础研究"均荣获教育部自然 科学二等奖。

2019年,国家研究中心有36人在127个国际学术组织和学术期刊任职,包括担任Science周刊的评审编辑,担任Acta Materialia, Scripta Materialia, Carbon, Metallugical and Materials Transactions A期刊的编辑以及 Energy Storage Materials, Graphene Technology, Corrosion Communications, Nano Materials Science期刊的主编和执行副主编。

2019年,国家研究中心共培养的研究生73人获得博士学位,37人获得硕士学位,同比分别增长38%、 147%。其中,2人的学位论文入选"中国科学院优秀博士学位论文";另有2人学位论文入选"中国科技 大学优秀博士学位论文";3人获"中国科学院院长奖学金特别奖",1人获"中国科学院院长奖学金优 秀奖"。

1.8 学术交流与开放共享(ACADEMIC EXCHANGE AND INSTRUMENT SHARING)

国家研究中心坚持对外开放、鼓励高水平的合作研究。现有博士后、联合培养研究生等各类流动研 究人员合计131人;2019年共接待国内外来访和短期工作的专家学者97人次,接待国内外来访专家学者97 人次,接待国内外各界来宾参观1582人。通过"李薰讲座奖"、"来访学者报告"等方式,邀请国内外 高水平的学者来国家研究中心讲学、进行学术交流,共做学术报告72人次。

2019年,国家研究中心承担了与英国、法国、美国等国家和地区的国际合作项目14项。主办/承办了 "The Third International Conference on Energy Storage Materials (ICEnSM 2019)"等26次国际和国内会议。 国家研究中心研究人员共参加国际、国内学术会议480人次,其中国际会议215人次,受邀做国际会议报 告140人次,受邀国内会议报告175人次。

为更好的吸引国内外的优秀青年学者,国家研究中心在2019年正式推出"SYNL青年论坛"。青年论 坛是国家研究中心在沈阳定期(暂定一年两次)举办的非营利性的学术论坛,主要邀请海内外材料领域 或与材料交叉融合密切学科领域中的杰出青年学者进行学术交流,有效地宣传国家研究中心的软硬件实 力,创造合作机会。

首届青年论坛于11月30日至12月1日在沈阳召开首届青年论坛。首届青年论坛围绕"热电材料与器件"以及"介观电子器件与量子输运"两个方向,共邀请到国内30余家科研院校共47位青年学者,奉献40多场精彩的学术报告,并进行深入广泛的学术交流。同时也吸引来自辽宁省内10余家高校及科研院所共100多位老师和学生参加,同时还有来自企业界的代表参会,共聚一堂,共谋发展。



图5国家研究中心"首届青年论坛"

国家研究中心重视科学传播工作,重点对外宣传所取得的研究进展及科学成果,展示建设成果。 纳米金属机械稳定性的反常晶粒尺寸效应、不锈钢环形大锻件等成果在中央电视台、人民日报、科技日 报、中国科学报、新华网等主要媒体刊载;国家研究中心成果不断得到材料领域新媒体关注,累计报道 50余次;辽宁日报等地方媒体持续关注国家研究中心建设进展,累计报道近20次。此外,还不断地对外 开展科普工作,韩拯研究员"纳米积木,一百万种可能"在SELF格致论道讲坛做主讲展示;依托自有公 众号持续科普,累计刊发科普文章合计30余篇。

"公众科学日"是品牌科普活动,通过这个平台既向社会公众传播了科学知识,弘扬了科学精神, 也展示了最新的科研成果,增进了公众对国家研究中心的了解。2019年5月18日至19日,在为期两天的 公众开放日活动中,国家研究中心所属各研究部及公共技术服务部共接待包括东北育才、沈阳市第二中 学、沈阳市十七中学、沈阳外国语学校、东北大学的学生,以及社会公众1500余人。 通过"材料学认知"、"神奇的新材料"、"材料与美丽中国"、"材料是人类文明进步阶梯"等 展区不仅介绍了材料科普知识,也以生动活泼的形式向社会公众展示了新型净水材料、先进炭材料、磁 性材料、陶瓷材料、热电材料、仿生材料、光催化材料、涂层材料等科研成果。



图6 国家研究中心2019年度公众开放日

1.9 固定资产(FIXED ASSETS)

2019年,国家研究中心仪器设备平台建设初具规模。在平台建设规划,管理运行,理化分析能力拓展以及与大科学装置联合,新分析测试中心基础设施布局等多方面均取得了新的进展。

2019年度投入超过3500万元购置包括球差和高分辨透射电镜, X射线微聚焦荧光谱仪;添置了热机 械性能、微动疲劳等材料服役性能试验机;以及热分析、激光热导仪和液相色质联用谱仪等理化测试分 析关键设备。完善改进自主研制的高温洛氏硬度仪测试装备拟通过标准组织认证。

2019年,国家研究中心公共平台提供研究与服务机时达15万小时,年培训学生与科研人员1432人 次,用于样品制备的关键设备、透射电镜、扫描电镜、X射线衍射仪和性能测试的大型设备的运行时间达 到10万小时,电镜类设备年度平均机时达2559小时,为标准负荷1800小时的142%,保持了高负荷运行状 态。部分电镜用于科研机时超过4500小时,接近饱和。设备运行效率保持在高水平,设备机时资源真正 实现共享管理。服务于国家研究中心科研工作的同时,为航天、交通、大学、研究机构以及地方高科技 企业等外部用户提供了及时准确的分析测试与咨询服务。

类别	设备 台数	设备总价值 (亿元)	平均每台仪器 研究工作机时 (小时)	平均每台仪器 服务工作总机时 (小时)	机时率 (%)
数值			1394	141	85.3

表2 国家研究中心30万元以上设备使用情况





1.10 年度数字(SYNL IN NUMBERS)

348 科研人员

包括中外院士7人、研究员/教授 117人。在培研究生661人,年度 毕业博士研究生72人。

3.97亿元,同比增长 3.97亿元,同比增长 31%。

资助经费



SYNL申请发明专利136项, 授权发明专利89项。截止2019 年,SYNL累计授权发明专利 781项。



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SYNL

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到SYNL进行短期工作,累计1582人前来参观。 36人在127个国际学术组织和学术期刊任职。



97

国内外学者

其中, 英文期刊448篇, 中文 期刊22篇。



315 _{会议邀请报告}

其中,受邀国际会议报告140 篇,受邀国内会议报告175 篇。



其中,获得国际荣誉与奖励6 人次,获得国内荣誉与奖励32 人次。

荣誉奖励







机时

同比增长46%,各类科研仪器 总值5.55亿元,30万元以上设 备323台。 2019年获得经费资助情况 (单位:万元)

1.11 经费情况(FINANCIAL SUPPORTS)

总金额: 39701.59







SYNL





2.1 材料素化

材料特别是大宗结构材料发展长期依赖合金 化,带来资源依赖、成本攀升、回收利用困难等问 题。纳米金属科学家工作室基于前期纳米金属结构 稳定性的研究结果,创新性地提出利用跨尺度调控 材料中的稳定界面替代合金化,实现材料素化。

材料素化旨在利用缺陷调控替代合金化,实 现材料性能提升。调控缺陷的一个瓶颈问题是材料 中缺陷的稳定性往往低于合金元素,在材料加载或 加热等条件下各类缺陷聚集、合并、并相互转化, 导致材料性能退化。大幅增加材料中晶界数量至纳 米尺度,晶界的稳定性显著下降。利用晶界替代合 金化需要提高晶界的稳定性。塑性变形的纳米金属 在临界尺寸下表现出的很高的热和机械稳定性为跨 尺度调控界面奠定了基础。调控界面替代合金化还 依赖材料强化方式的转变,传统材料的强化无论是 固溶强化、弥散强化还是细晶强化,都是通过增加 合金中位错滑移的障碍而实现,位错滑移的阻力越 大、强化效果越明显。而临界晶粒尺寸下大量界面 的引入,由于位错在晶内的弓出变出困难,使得位 错增殖也被抑制。材料的强化方式从抑制位错滑移 转变为抑制位错增值。界面的高稳定性和强化机制 的改变使得不采用合金元素而通过跨尺度构筑与稳 定界面调控,大幅度提升材料强度成为可能。代表 性论文发表于Science 364 (2019) 733。

Doing more with less

The performance of materials is often improved by stabilizing interfaces between grains by alloying with other elements. Plainified materials accomplish this goal by tailoring stable interfaces with fewer or no alloying elements, which can improve resource sustainability.



图1 材料素化原理示意图。



图2直径15.6m奥氏体不锈钢支承环。

2.2 百吨级不锈钢环构筑成形

2019年3月12日,利用自主国际首创的金属构 筑成形技术,与合作企业共同轧制成功世界最大无 焊缝奥氏体不锈钢整体环形锻件。该环件直径达 15.6米,重达150吨,首次实现了百吨级金属坯分 级构筑成形,这也是目前世界上直径最大、重量最 大的整锻式不锈钢环形件。

该巨型环件的特点是整体无焊缝,均质化程 度高,组织均匀性好,将应用于我国第四代核电机 组,其成功研制将有力地保障我国核工业领域重大 装备的建设。作为我国第四代核电机组核心部件的 支承环,不但是压力容器边界、安全屏障,而且结 构上承受7000吨重量,是整个堆容器的"脊梁"。 以往此类巨型锻件国外均采用多段小坯组焊方式制 造,不仅加工周期长、成本高,而且焊缝位置的材 料组织性能薄弱,给核电机组运行埋下安全隐患。 历经十多年的艰苦努力,研发了原创的金属构筑成 形技术并揭示了构筑界面的愈合机制和组织演化机 理,突破了大锻件"以大制大"思路的局限,开发 出表面活化、真空封装、多向锻造、分级构筑、整 体轧环等系列关键技术,彻底消除了多层金属间的 界面,使支承环锻件构筑界面位置与基体金属在成 分、组织、性能上完全一致,实现了"以小制大" 的新型加工制造,大幅提升品质的同时降低了制造 成本。该技术被评价为大构件制造领域的一项变革 性创新,已在水电、风电、核电等领域应用,对于 推动我国高端装备的快速发展,保障重大装备核心 材料的自主可控发挥了重要作用。研究成果在中央 电视台、《人民日报》、《科技日报》等媒体上报 道,并入选"壮丽70年"共和国发展成就巡礼。



图3具有庞压卡效应的塑晶材料的最大等温熵变与其他材料的对比。

2.3 发现并命名庞压卡效应

制冷技术在当今社会工农业生产、日常生活 等多个领域均起到了至关重要的作用。目前制冷主 要依赖传统的气体压缩制冷技术,普遍使用具有强 烈温室效应的制冷剂,直接贡献了社会总碳排放量 的7.8%;而联合国统计数据表明全球每年25-30% 的电力被用于制冷应用,这则意味着巨大的能源消 耗。因此,要在制冷领域落实中央创新驱动发展的 要求,就必须培育颠覆性技术,从源头上解决高能 耗高排放的难题。

2019年,研究人员在塑晶 (plastic crystals) 材 料里发现了固体庞压卡效应 (colossal barocaloric effect),基于该物理效应有望发展出高效、环 保、无碳排放的固态制冷新技术。塑晶是一类高 度无序的固体材料,其有机分子或者无机结构单 元的取向完全无序,但是质心位置却构成了长程 有序的晶格。研究人员选择新戊二醇(英文名: neopentylglycol, 缩写为NPG; 分子式: C₅H₁₂O₂; IUPAC名称为2,2-Dimethylpropane-1,3-diol) 为模型 材料、运用高压热测量技术、高压中子散射技术、 高压同步辐射X射线衍射技术等,揭示了塑晶材料 出现庞压卡效应的深层次物理机制。代表性塑晶 材料的等温熵变(描述制冷材料的关键物理量)已 经接近甚至超过目前商业使用的液体制冷剂,且 所需驱动压力极低,且材料十分廉价,具有十分 诱人的应用前景(图3)。该项研究发表于Nature 567 (2019) 506。该杂志同期还刊登了评述性短文 "Refrigeration based on plastic crystals" 来阐述该 项工作的内涵和意义。

2.4 金属硫族化合物/碳纳米管复合柔性热电薄膜 材料与器件

研究人员利用亚纳米尺度的碳管束沟槽限制扩

散和诱导有序形核以及薄膜材料的温度选择性晶面 生长机理,首次制备出具有高度有序显微特征的金 属硫族化合物/SWCNT复合自支撑热电薄膜材料。

该复合材料具有纳米孔隙结构,金属硫化物 具有高度薄膜面织构,相邻纳米晶粒间为小角度取 向倾转晶界。高度有序的显微结构能降低其对于载 流子的散射作用,提高电导率,多尺度缺陷起到散 射声子降低热导率的作用,从而协同提高材料热电 性能。高度有序的微观结构、赋予复合材料良好的 热电性能。实验证明,这种利用SWCNTs管束沟槽 诱导纳米晶体有序生长的机制同样适用于其他半导 体和金属材料体系,这种有序结构对于材料的物理 化学性能具有重要影响。进一步分子动力学模拟研 究揭示了利用弱键合原子面间的相对位移是提高材 料柔性性能的普适性机制。基于该复合材料成功制 备了柔性微型热电薄膜器件原型件,实现了平面结 构热电器件微纳区域精准控温和毫瓦级环境能量收 集的技术突破。同时,该项研究成果在柔性半导体 材料和器件领域具有广泛的应用前景,相关结果 发表于Nature Materials 18 (2019) 62, Acs applied materials & interfaces 11 (2019) 38075

2.5 基于纤维素基元晶体的高性能Pd单原子催化 剂

Suzuki偶联反应是一种在有机合成工业中的重 要反应,并在制药工业中扮演重要角色。Pd催化剂 是Suzuki反应的核心,然而现有商用Pd催化剂中过 高的Pd使用量,不仅造成了过高的使用成本,同时 从催化剂中流失的Pd也会造成产物污染。已有文献 报道指出,只有将催化剂的钯载量降低至低于100 ppm水平,这些反应才能变得更具经济吸引力和安 全性。

为此,研究人员选择了自主开发的纤维素基元 晶体 (CECs) 作为Pd催化剂的载体,将接近0价的



图4金属硫化物-碳纳米管复合柔性热电薄膜材料和微型热电器件结构与性能测试。

Pd原子以低配位数原位固定在特定的晶面上,获得 了一种兼具高活性和高稳定性的Pd-CECs单原子催 化剂。利用X射线吸收谱,确定了Pd的配位方式及 价态信息。通过研究Pd-CECs与反应物的中间体信 息,确定了该催化剂可以作为Suzuki反应发生的催 化平台。通过EXAFS对氧化加成中间体的表征可 以确定,对卤代烃的活化可以在Pd-CECs上原位发 生,避免了Pd在反应过程中的流失。同时,CECs 作为载体可以使苯硼酸类中间体活化,进一步提高 反应的转化率。该催化剂可以适用于多个种类的反 应物,并可以实现公斤级的催化反应应用,在20 L 的小试级反应体系下,可以获得超过15000000的转 化数和超过300000 h⁻¹的反应速度。



图5 (a) Pd单原子稳定方式示意图; (b) Pd-CECs在MXene上的HAADF-STEM照片; (c) Pd-CEC与Pd标准品的X射线近边吸收谱对比(含一阶导数); (d) Pd-CEC与Pd标准品的X射线扩展边吸收谱的R空间变化谱图。

2.1 Plainification of Materials

Extensive alloying makes material development more resource-dependent. Alloyed materials with complicated compositions become more difficult to synthesis and to recycle. With increasing alloying, material cost continues to spiral while property enhancements level off. The sustainability of materials, especially metals, has gained more and more attentions. Researchers proposed to advance material properties by plainification to reduce alloying in material development, which means tailoring stable interfaces at different length scales instead of alloying. The newly proposed strategy intends to lower materials cost and increase their resource-independence and recyclability, therefore advancing material sustainability.

Alloying changes material properties by modifying the microstructures of the host element. Alloying can create strong phases with robust interfaces to block dislocation motion, solid solutions with internal stress to make dislocation slip more sluggish, or both kinds of microstructures. However, tailored microstructures can be created without changing the chemical composition of a material, often by processing the material to alter the regions between crystallites-the grain boundaries (GBs). Because GBs impede dislocation motion, decreasing the crystallite size (grain refinement) can harden both metals and alloys.

Doing more with less

The performance of materials is often improved by stabilizing interfaces between grains by alloying with other elements. Plainified materials accomplish this goal by tailoring stable interfaces with fewer or no alloying elements, which can improve resource sustainability.



Fig. 1: Planification of Materials.

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Although with sound principle, plainification of metals is facing challenges due to the intrinsic instability of microstructures at the nanometer scale where property variations are dramatically elevated. Recent studies revealed that nano-sized grains in pure copper and nickel produced from plastic deformation exhibit notable thermal and mechanical stability against coarsening below a critical grain size, thanks to an autonomous grain boundary relaxation to low-energy states (Science (2018), Phys. Rev. Lett. (2019)). This finding offers new possibilities for developing stable nanostructured metals and alloys with novel properties, foundation of the material plainification strategy. Stabilization of nanoscale grains in metals takes advantage of their ability to suppress dislocation nucleation, providing a strengthening mechanism that is distinct from the conventional way of resisting dislocation slip.

The novel strengthening mechanism highlights new opportunities of plainification for greatly advancing material properties by tailoring stable interfaces at different length scales with fewer or no alloying elements. See *Science* 364 (2019) 6442 for more details.

2.2 150 ton Austenitic Stainless Steel Ring Manufactured Using Additive Forging Technology

On March 12, 2019, the austenitic stainless steel supporting ring with the world's largest diameter (15.6 meters) and the largest weight (150 tons) was successfully rolled in Jinan using the additive forging technology proposed by SYNL. This huge rolled ring is manufactured without welding, so it has good microstructural uniformity. It will be used in China's fourth-generation nuclear power plants. Its successful development will effectively protect China's nuclear industry equipment implementation. As the core component of a nuclear power plant, the support ring not only serves as the boundary and safety barrier of the pressure vessel, but also serves as the "backbone" of the entire vessels, thus bearing 7,000 tons of weight. In the past, the supporting rings were manufactured by multi-piece billet welding, which not only has a long manufacturing processing and high cost, but also has weak structural properties at the welding position, thereby laying a hidden safety hazard for the operation of nuclear power plant. After more than ten years of research,



Fig. 2: Austenitic stainless steel supporting ring with a diameter of 15.6 meters.

researchers first proposed the idea of additive forging in the world. This technology uses multiple small-sized homogenized slabs as the basis material. By means of surface activation, vacuum sealing, and high-temperature deformation, the bonding interfaces are completely healed and its mechanical properties have no difference than that of the basis material. As homogenized slabs are used, the homogeneous large forging is obtained. Additive forging technology has been evaluated by many experts as a transformative and innovative technology in the field of large forging manufacturing. It has been widely used in hydropower, wind power, nuclear power and other fields. Additive forging technology has played an important role in promoting the rapid development of high-end equipment in China and ensuring the independence and controlling of the manufacturing of the core equipment. The research results were widely reported by *CCTV News*, *People's Daily*, and *Science* and *Technology Daily*.

2.3 Discovery of Colossal Barocaloric Effects

According to the UN statistics, 25 to 30 percent of the world's electricity is consumed for refrigeration. Current refrigeration technology mostly involves the conventional vapour compression cycle, but the materials used in this technology are of growing environmental concern because of their large global warming potential. As a result, both the research community and industries are devoting to exploiting environment-friendly, efficient refrigeration technology.

As a promising alternative, refrigeration technologies based on solid-state caloric effects have been attracting attention in recent decades. These effects are described by the isothermal entropy changes (Δ S) and the caloric effects of current leading materials are characteristic of entropy changes of dozens of joules per kilogram per kelvin. In addition, unpractically large driving fields are also required. These limited performances are the obstacle to the application.

Recently, researcher and collaborators have performed pressure-dependent differential scanning calorimetric measurements, high-resolution neutron scattering, and



Fig.3: QENS measurements at ambient pressure (a) and 286 MPa (b), obtained at 325 K with E_i =2.64 meV. INS measurements at ambient pressure (c) and 286 MPa (d), obtained at 325 K with E_i =23.72 meV.

synchrotron X-ray diffraction on neopentyl glycol (NPG) as the prototype material. It was found that this material exhibited the maximum entropy changes of 389 J kg⁻¹K⁻¹, achieved at applied pressure of 45.0 MPa. This value is one order of magnitude larger than those of current leading caloric materials, as shown in Figure. More important, the entropy changes exceed one half of the maximum at 15.2 MPa, which is very beneficial to the practical application. Accessing large-scale facilities in Japan (J-PARC and SPring-8) and Australia (ANSTO) to utilize neutron scattering and synchrotron X-ray diffraction techniques, the team revealed that the constituent molecules of NPG are extensively orientationally disordered on the lattices and these materials are intrinsically very deformable. As a result, a tiny amount of pressure is able to suppress the extensive orientational disorder to induce the phase transitions to the ordered state and thus huge pressureinduced entropy changes are obtained. These two merits make plastic crystals the best barocaloric materials so far. In Fig. 3, plastic crystals reported in this study are compared to other leading caloric materials.

This research has established the microscopic scenario on colossal barocaloric effects of plastic crystals and also suggested that plastic crystals are an emerging class of caloric materials, which might benefit the design of better caloric materials and solid-state refrigeration technology in the future.

2.4 Flexible Thermoelectric Thin Film and Microdevice for Energy Harvesting and On-chip Cooling

Inorganic chalcogenides are traditional highperformance thermoelectric materials. However, they suffer from intrinsic brittleness and it is very difficult to obtain materials with both high thermoelectric ability and good flexibility. Here, researchers report a flexible thermoelectric material comprising highly ordered Bi, Te, nanocrystals anchored on a single-walled carbon nanotube (SWCNT) network, where a crystallographic relationship exists between the $Bi_{3}Te_{3} < \overline{1210} >$ orientation and SWCNT bundle axis. This material has a power factor of ~1,600 µWm⁻¹K⁻² at room temperature, decreasing to 1,100 µWm⁻¹K⁻² at 473 K. With a low in-plane lattice thermal conductivity of 0.26 ± 0.03 Wm⁻¹K⁻¹, a maximum thermoelectric figure of merit (ZT) of 0.89 at room temperature is achieved, originating from a strong phonon scattering effect. A prototype of TE micro-module consisting of eight hybrid p-n-couples is demonstrated, which achieves a maximum output power density of ~5.7 mWcm⁻² under 30 K temperature difference and a maximum cooling of ~22 K at the target region with a



Fig. 4: Bi₂Te₃-SWCNTs flexible hybrid and micro-device characterization.

SYNL

heat absorption density of ~54 W cm⁻², exhibiting great advantages in microelectronics. Our results may pave the way for a bright future for flexible TE devices in the booming energy market.

2.5 High Performance Pd Single Atomic Catalyst Based on Cellulose Elementary Crystals

Suzuki coupling reaction is an important reaction in the organic synthesis industry and plays an important role in the pharmaceutical industry. The Pd catalyst is the core of the suzuki reaction. However, the excessive use of Pd in the existing commercial Pd catalysts not only causes excessive use costs, but also the Pd lost from the catalyst will also cause product pollution. It has been reported in the literature that these reactions can become more economically attractive and safer only if the palladium loading of the catalyst is reduced to a level below 100 ppm. To this end, we have selected independently developed cellulose element crystals (CECs) as the support for Pd

catalysts. Pd atoms close to 0 valence are fixed in situ on a specific crystal plane with a low coordination number, and a kind of Pd-CECs monoatomic catalyst with high activity and high stability. The X-ray absorption spectrum was used to determine the coordination mode and valence information of Pd. By studying the intermediate information of Pd-CECs and reactants, it was confirmed that the catalyst can be used as a catalytic platform for suzuki reaction. Through the characterization of oxidative addition intermediates by EXAFS, it can be confirmed that the activation of halogenated hydrocarbons can occur in situ on Pd-CECs, which prevents the loss of Pd during the reaction. At the same time, CECs as a carrier can activate phenylboronic acid intermediates and further improve the conversion rate of the reaction. The catalyst can be applied to multiple types of reactants, and can realize kilogramscale catalytic reaction applications. Under a 20 L smallscale reaction system, it reached the high reaction rate along with high turnover number at the level of 300,000 h⁻¹ TOF and 15,000,000 TON in kg scale.



Fig. 5: (a) Scheme of stabilization single Pd atoms; (b) HAADF-STEM image of Pd/CECs on MXene; (c) Normalized Pd Kedge XANES spectra of Pd_1 /CEC and Pd foil (inset: calculated first derivative curves); (d) EXAFS spectra of Pd_1 /CEC (blue line) and Pd foil (red line) at the Pd R-space.

3 研究工作报告 SCIENTIFIC REPORTS




3.1 材料动力学研究部

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研究组负责人(5人)

- 李 毅 (构筑金属材料)
 卢 磊 (块体纳米金属的力学行为)
 马宗义 (金属基复合材料)
 张海峰 (非晶合金及其复合材料)
- 王建强 (非晶态合金涂层)

3.1.1 研究工作简述

本研究部着重关注金属结构材料研究中与动力学相关的若干关键科学问题;探讨该材料形成及结构 演化过程中的基础科学问题;建立材料在跨尺寸、多尺度下结构与性能间的关联,开创材料制备新工艺 以及新材料设计和创新;开发具有独特结构和功能的新材料,实现材料基础研究和应用有机结合的研究 目标。

2019年度,本研究部的重要进展有:

(1) 评估了梯度结构Ni的变形和断裂行为,研究发现①梯度结构Ni具有高断裂韧性,显示出强度和韧性的最佳组合。梯度材料在拉伸至断裂的过程中消耗的塑性功明显高于纯粗晶和纯纳米晶材料。②梯度材料的断裂韧性和变形行为与梯度方向有关。粗晶到纳米晶梯度方向上的起始断裂韧性(K_{IIc})比纳米晶到粗晶梯度方向的起始断裂韧性要高,其R曲线与纯粗晶Ni类似,显示出强度和韧性的最佳组合。上述的研究成果为梯度材料的实际应用提供理论基础。

(2) 首次对纯钛采用水下搅拌摩擦焊(FSW),有效克服了纯钛FSW过程中的工具磨损和过热问题,得到具有超细晶结构的高质量接头,焊接系数达到100%。在此基础上系统地研究了纯钛水下FSW 过程中的变形模式、晶粒细化机制及两者关系。为钛及钛合金高质量焊接和超细晶构件制备提供了新思路。

(3)利用双电极体系测量涂层在干湿交替环境中的阻抗谱行为,利用传输线等效电路模型分析涂层的腐蚀行为、评价涂层腐蚀寿命,解决了实际服役条件的干湿交替环境中涂层腐蚀监测、寿命评价难题,为涂层工程化应用打下了扎实基础。

(4) 系统研究了Ti基非晶内生β-Ti复合材料不同微观组织对拉伸性能的影响规律。设计了成分为 Ti_{41.8}Zr_{33.5}Cu_{6.9}Co_{1.2}Bel_{6.6} (BT35-50-Co1)的非晶复合材料。该非晶复合材料表现出了优异的综合性能, 包括高的屈服强度、较大的拉伸塑性、优异的拉伸加工硬化能力以及优异的非晶基体玻璃形成能力。

(5) 继发现纳米孪晶金属与历史无关的稳定循环响应特征后,发现了经预拉伸变形后纳米孪晶Cu 样品具有明显的循环响应不对称性:即循环变形过程中最大拉伸应力显著高于最小压缩应力的绝对值, 这与沉积态样品的拉压对称行为截然不同。该发现为深入理解纳米孪晶金属的疲劳行为及设计抗疲劳纳 米结构具有指导意义。

3.1.1.1 梯度材料的断裂韧性

研究表明梯度结构在一定程度上打破材料"强 度和塑性"的倒置关系,获得优异的强塑性结合。 但是作为工程结构材料,须显示出可接受的断裂韧 性。但是一般而言:强度和塑性是由材料的整体变 形控制的全局机械响应,而断裂韧性是裂纹尖端 "局部"微观结构变形的机械响应结果,断裂韧性 裂纹尖端参与的变形区域比拉伸整体变形体积小多 个数量级。因此,尽管通过构建梯度结构可以实现 材料强度和塑性的优异组合,是否保证其断裂韧性 同样优越,是一个亟待解决的关键科学问题。因 此,揭示梯度结构中微观结构的不均匀性对裂纹的 启裂和扩展阻力的影响具有非常重要的意义。

本研究评估了梯度结构Ni的变形和断裂行为。 我们研究发现,(1)梯度结构Ni具有高断裂韧 性,显示出强度和韧性的最佳组合。梯度材料在拉 伸至断裂的过程中消耗的塑性功明显高于纯粗晶和

纯纳米晶材料。(2)梯度材料的断裂韧性和变形 行为与梯度方向有关。粗晶到纳米晶梯度方向上的 起始断裂韧性 (K_{IIc}) 比纳米晶到粗晶梯度方向的 起始断裂韧性要高,其R曲线与纯粗晶Ni类似,显 示出强度和韧性的最佳组合。裂纹扩展初期在粗晶 区域会发生钝化、表现为韧性断裂。在裂纹扩展后 期,在纳米晶区域诱发脆性裂纹,发生不稳定的脆 性断裂。由于裂纹扩展过程是韧性断裂向脆性断裂 的转变过程,因此在安全应用上需要慎重考量。另 一方面,当裂纹沿纳米晶到粗晶梯度方向扩展时, 也表现出优于纯纳米晶Ni的起始断裂韧性(Kuo) 和R曲线,并且裂纹尖端的韧性是不断增加。此 外,当裂纹的扩展到达粗晶区域时,裂纹尖端发生 钝化。表明纳米晶到粗晶的梯度方向,是脆性断裂 向韧性断裂的转变过程,具有优异安全应用前景。 我们的研究成果为梯度材料的实际应用提供理论基 础。相关研究成果见Mate. Today 32 (2020) 94。



图1 粗晶,纳米晶,粗晶→纳米晶梯度结构,以及纳米晶→粗晶梯度结构金属Ni的力学性能。(a)拉伸应力-应变曲线;(b) 断裂韧性J值和裂纹扩展长度Δa的关系图;(c)拉伸时抗拉强度 vs. 塑性应变能;(d) 抗拉强度 vs. 断裂韧性值;(e) 抗拉强度 vs. Δa=~1 mm时的断裂韧性。

3.1.1.2 水下搅拌摩擦焊制备高质量细晶结构纯钛 接头及其微观演变机制

由于搅拌摩擦焊 (FSW) 过程中塑性变形的 瞬时性和复杂性, 澄清各类金属FSW变形模式难度 极大。因此, 长时间以来, 研究者仅将FSW过程中 金属的变形模式当成"黑匣子"来研究其微观演变 机制, 从而导致了片面的结论。随着铝合金FSW取 得巨大商业成功, FSW研究拓展到钢铁、钛合金等 高熔点材料和复合材料等难焊材料。钛及钛合金由 于化学活性高、热导差等原因,在常规FSW过程中 极易因工具磨损和过热问题难取得无缺陷接头。针 对上述问题,本研究首次对纯钛采用水下FSW, 有效克服了纯钛FSW过程中的工具磨损和过热问 题,得到超细晶结构的高质量接头,焊接系数达到 100%。在此基础上,系统地研究了纯钛水下FSW 过程中的变形模式、晶粒细化机制及两者关系。研 究表明,纯钛在水下FSW过程中的变形和再结晶机 制为{10T2}孪晶,基、柱面<a>滑移和锥面<a+c>滑 移在不同变形阶段开动,并与位错吸收相关的连续



图2 纯钛水下搅拌摩擦焊高质量接头的制备及其变形过程中的微观组织演变。

动态再结晶演变机制。本研究还揭示了孪晶-位错 交互、位错吸收、晶界迁移和织构对晶粒细化的作 用,澄清了变形温度和晶粒取向对变形机制的潜在 影响。以上结果为钛及钛合金的高质量焊接和超细 晶构件的制备提供了新思路,并为理解金属FSW过 程中的微观演变机制提供了新的参考。相关研究工 作见Acta Mater. 166 (2019) 371。

3.1.1.3 干湿交替环境中铁基非晶合金涂层腐蚀行 为研究

铁基非晶合金涂层在多种极端苛刻环境下,如 海洋环境、冲刷环境及其他腐蚀磨损环境中表现出 优异的防护性能。在这些苛刻的实际服役条件下, 铁基非晶合金涂层更多遭受干湿交替循环侵蚀而非 单纯地浸泡于腐蚀介质中。由于干湿交替循环条件 下存在溶液电阻大、参比电极不稳定和电极表面电 流分布不均匀等特点,造成涂层腐蚀准确测定及理 解一直是该领域的难题。

本工作利用双电极体系测量涂层在干湿交替环 境中的阻抗谱行为,利用传输线等效电路模型分析 涂层的腐蚀行为、评价涂层腐蚀寿命,成功解决了 以上难题。研究发现,涂层在濒临干燥的状态下氧 传输变快,腐蚀速率最大。涂层孔隙内外的氧浓度 差加速孔隙内部的腐蚀,引发涂层在孔隙中发生局 部腐蚀,最终导致涂层失效。整体上来说,铁基非 晶合金涂层在干湿交替环境中具有较高的耐腐蚀性 能,有效保护基体免于侵蚀。该工作解决了实际服 役条件的干湿交替环境中涂层腐蚀监测、寿命评价 难题,为涂层工程化应用打下了扎实基础。相关研 究成果发表在*Electrochim. Acta* 319 (2019) 966。

3.1.1.4 Ti基非晶内生复合材料的拉伸力学性能优化

本工作系统研究了Ti基非晶内生β-Ti复合材料 不同微观组织对拉伸性能的影响规律。发现随着内 生β相颗粒尺寸的增加,非晶复合材料具有较大的 拉伸塑性和更优的加工硬化能力。发现β-Ti相的稳 定性显著影响非晶复合材料的拉伸力学性能:内生 稳定β相的非晶复合材料屈服后很快呈现加工软化 特点;内生亚稳β相的非晶复合材料屈服后表现出 明显的锯齿行为,拉伸塑性较差;内生可形变诱发 相变β相的非晶复合材料表现出最大拉伸塑性和优 异的拉伸加工硬化能力。随着内生β-Ti体积分数增 加,非晶复合材料塑性增加, 屈服强度逐渐降低。

因此,具有优异力学性能的非晶复合材料, 其内生β-Ti相应该具有较大的颗粒尺寸、适当的结 构亚稳定性、较低的体积分数。因为、较大的颗粒 尺寸可以导致较大的拉伸塑性;适当的亚稳定性, 可以保证发生形变诱发相变,导致较大的塑性和加 工硬化能力; 较低的体积分数可以保证非晶复合材 料具有较高的强度。基于上述发现设计了成分为 Ti418Zr335Cu69Co12Be166 (BT35-50-Co1)的非晶复合 材料。该非晶复合材料中内生β相的平均尺寸约为 16微米,体积分数仅为38%。该合金的拉伸屈服强 度为~1380 MPa,均匀变形应变为5.2%,并且在屈 服后呈现加工硬化能力,见图4。与目前开发的非 晶复合材料相比、该非晶复合材料表现出了优异的 综合性能,包括高的屈服强度、较大的拉伸塑性、 优异的拉伸加工硬化能力以及优异的非晶基体玻璃 形成能力。相关成果发表在Acta Mater. 168 (2019) 24



图3 干湿交替环境中铁基非晶合金涂层腐蚀示意图。



图4 Ti_{41.8}Zr_{33.5}Cu_{6.9}Co_{1.2}Be_{16.6} (BT35-50-Col) 非晶复合材料微观组织和拉伸力学性能; (a) BT35-50-Col直接凝固150g合金锭与 其(b)XRD谱和(c)微观组织; (d)拉伸应力应变曲线; (e)拉伸破坏后样品的XRD谱。

3.1.1.5 预变形纳米孪晶Cu的非对称性循环响应

纳米孪晶结构金属具有超高强度、良好塑性以 及优异的高/低周疲劳性能,特别是在变应变幅条 件下表现出与历史无关的独特稳定循环响应特征, 展示出潜在的应用前景。实际上,金属构件往往经 历复杂预变形加工工艺(如冲压成型等),由于引入 位错等缺陷因而显著影响其服役过程中的疲劳行 为。然而,有关预变形历史对于纳米结构金属的疲 劳行为的影响却鲜有报道。

继发现纳米孪晶金属与历史无关的稳定循环 响应特征后,本工作发现经预拉伸变形后纳米孪晶 Cu样品具有明显的循环响应不对称性:即循环变 形过程中最大拉伸应力显著高于最小压缩应力的绝 对值,这与沉积态样品的拉压对称行为截然不同。 随循环周次或应变幅增加、循环不对称性逐渐降 低。在较大塑性应变幅疲劳时,预变形纳米孪晶 Cu很快就恢复对称循环响应(图5)。分子动力学模 拟和微观结构分析表明,循环响应不对称性主要与 预变形阶段在孪晶片层内产生的高密度贯穿位错有 关。在循环变形时,与预拉伸方向相同的拉伸阶段 会导致贯穿位错在孪晶界面内的拖尾扩展,能量增 加,因此需要更高的拉伸应力;但在压缩阶段,孪 晶界面内贯穿位错拖尾长度缩短,降低能量,因此 压缩时所需的应力显著减小。在较大应变幅循环变 形时,相邻孪晶片层内的贯穿位错在往复运动过程 中容易发生拖尾相互连接,形成高度关联项链状位 错结构。由于结构对称,关联位错沿孪晶界往复运 动,并且运动阻力的方向性减弱,从而导致预变形 纳米孪晶结构的非对称循环响应转变为对称循环响 应(图5)。该发现为深入理解纳米孪晶金属的疲劳 行为及设计抗疲劳纳米结构具有指导意义。相关工 作发表在Acta Mater. 175 (2019) 477。



图5 拉伸预变形纳米孪晶Cu的疲劳性能和循环变形机制。 (a) 不同应变幅 $\Delta \varepsilon_{pl}$ /2时NT-Cu的应力-应变滞回环;(b, c) 不同应变幅下循环70周次后纳米孪晶结构,表明小应变幅条 件下为不对称结构的贯穿位错,引起不对称循环响应;大 应变幅疲劳时贯穿位错连接形成具有对称结构的关联位错 (CND),引起对称循环响应。



3.1 Materials Kinetics Division

DIVISION HEAD: LI Yi

RESEARCH GROUP LEADERS: (5)

LI Yi (Architectured Materials) LU Lei (Mechanical Behavior of Bulk Nano Structured Metals) MA Zongyi (Metal Matrix Composites) ZHANG Haifeng (Amorphous Alloys and Composites) WANG Jianqiang (Amorphous Metallic Coatings)



3.1.1 Summary of Scientific Activities

Materials Kintetics Division explores materials and material processes from the perspective of kinetics, one of the key fundamental fields of materials science. We focus on the kinetic processes in terms of understanding basic aspects of phase transformation and structure-property relationship in heterogeneous structures of multi-scale and of developing novel technologies for materials processing and manufacturing. Our goal is to develop advanced materials, covering amorphous metals and alloys, nano-metals and alloys and their composites for engineering applications, contributing to achieve a positive impact on the lives of people from home and abroad.

The main achievements over last one year are as following:

(1) A systematic study has been recently carried out to evaluate the fracture properties and crack propagation process in gradient structured (GS) nickel, involving grain size gradients from ~30 nm to 4 μ m. The team found that an optimized combination of high strength and high toughness can be achieved in the gradient structured material. Scientists also found that CG \rightarrow NG gradient structure, where a pre-existing crack initiates from CG zone and propagates into NG zone, displays the best combination of strength and toughness properties; with largest degree of R-curve toughening behavior, similar to the CG material. On the other side, the NG \rightarrow CG gradient structure, where a pre-existing crack initiates from NG zone and propagates into CG zone, exhibits a degree of R-curve toughening in excess of the NG structure, but less than that of the CG \rightarrow NG gradient structure. This study seeks not only to develop a mechanistic understanding of the fracture behavior of GS materials, but also may provide practical guidelines for the use of such materials in safety-critical applications.

(2) We used submerged FSW technology to effectively overcome the tool wear and overheat problem for the first time, and successfully produce a defect-free ultrafine-grained Ti joint with a joint efficiency of 100%. The deformation modes, grain refinement mechanisms and their relationships during FSW were systematically investigate. This study provides a new method of fabricating high-quality joints and ultrafine-grained bulk Ti materials, and also provides a new reference for understanding the microstructural evolution mechanism during FSW.

(3) The corrosion evolutions of the coatings under wet-dry cyclic conditions were investigated by EIS on a twoelectrode cell. Accurate R_{ct} was obtained through fitting EIS results using a modified transmission line equivalent circuit model and a landscape map of R_{ct} was constructed for a panoramic investigation on coating corrosion. This work proposed an accurate method for the electrochemical measurements and life evaluations of the coatings under wet-dry cyclic conditions.

(4) The effects of different microstructure of Ti-based bulk metallic glass composites (BMGCs) containing in-situ formed β -Ti crystals on their tensile properties were systematically investigated. A BMGC with a composition of Ti_{41.8}Zr_{33.5}Cu_{6.9}Co_{1.2}Be_{16.6} was then designed. This BMGC exhibits a yield strength as high as ~1380 MPa and a uniform elongation of 5.2% accompanying remarkable work-hardening capacity. As compared with the previously reported BMGCs, this BMGC possesses an excellent combination of properties, including high yield strength, large tensile plasticity, good work-hardening capacity and extraordinary glassy forming ability of the glassy matrix.

(5) Gradient nanograined (GNG) materials with the spatially graded distributed grain sizes from nano-meter in the surface to micron scale in the core exhibit a combined enhancement of mechanical properties, such as high strength, considerable ductility. In this study, GNG Cu with a thin superficial GNG layer is found to exhibit an unprecedented combination of cyclic properties during cyclic loading: doubling both low-cycle fatigue life and high-cycle fatigue limit, compared to its homogenous CG counterparts. The present results offer unique pathways to mitigate fatigue damage using gradient nanostructure in many practical applications.

3.1.1.1 Exceptional Damage-Tolerance of Gradient Metallic Materials

Nature always inspires material scientists to seek ways to enhance the mechanical properties of engineering structural materials from the structure-property relations in natural materials.

For example, bamboo stems possess a gradient structure that comprises a decreasing density of vascular bundles from their exterior inwards the center, leading to enhanced flexibility yet overall strength and stiffness. Using the inspiration of such natural materials, there have now been several attempts to replicate these gradient structures to create structural metallic materials with similarly favorable combinations of properties.

Although excellent combinations of strength and ductility can be achieved with gradient structures, it's a challenge to guarantee that the fracture resistance will be similarly superior, as it is the local microstructure that affects the fracture toughness of the materials

A systematic study has been recently carried out to evaluate the fracture properties and crack propagation process in gradient structured (GS) nickel, involving grain size gradients from \sim 30 nm to 4 µm.

The team found that an optimized combination of high strength and high toughness can be achieved in the gradient structured material, compared to the ultrahigh-strength nano-grained (NG) and low-strength coarse-grained (CG) uniformed grain-sized structures. Scientists also found that CG \rightarrow NG gradient structure, where a pre-existing crack initiates from CG zone and propagates into NG zone, displays the best combination of strength and toughness properties; with largest degree of R-curve toughening behavior, similar to the CG material. Once crack extension approaches the end of gradient structure, however, unstable brittle fracture can occur as the crack encounters the nano-sized grains. Therefore, the CG \rightarrow NG gradient structure represents a characteristic transition from ductile fracture to brittle fracture.

On the other side, the NG \rightarrow CG gradient structure, where a pre-existing crack initiates from NG zone and propagates into CG zone, exhibits a degree of R-curve toughening in excess of the NG structure, but less than that of the CG \rightarrow NG gradient structure. However, it is less susceptible to outright fracture as the propagation of brittle cracks in the nano-grains of the early part of the gradient region become arrested once they reach the coarser-grained regions due to excessive crack-tip blunting. Therefore, the NG \rightarrow CG gradient structure represents a characteristic transition from brittle fracture to ductile fracture, which might be preferred for some safety-critical applications.

This study seeks not only to develop a mechanistic understanding of the fracture behavior of GS materials, but also may provide practical guidelines for the use of such materials in safety-critical applications.

This work has been published in *Mater. Today* 32 (2020) 94, collaborating with researchers from UC Berkeley.



Fig. 1: Evolution of the deformation and fracture modes in the crack-tip region for the CG (a-d) and NG (e-g) specimens. In situ SEM images of (a) the pre-crack tip in CG specimen and in CG-to NG and NG-to-CG.



3.1.1.2 Fabrication of High-quality Ti Joint with Ultrafine Grains Using Submerged Friction Stir Welding Technology and Its Microstructural Evolution Mechanism

To clarify the deformation mode of various metals during friction stir welding (FSW) is rather difficult due to the instantaneity and complexity of the plastic deformation process during FSW. Therefore, for a long time, the researchers have treated it as a "black box" to study microstructural evolution mechanisms during FSW, resulting in one-sided conclusions. Since a significant commercial success has been achieved for the FSW of Al alloys, FSW has now developed to apply in high-melting point materials such as steels, Ti alloys and hard-to-weld composite materials. Among them, obtaining defect-free welds of Ti and its alloys has been largely hindered by the tool wear and overheat problem due to their high reactivity and low thermal conductivity.

In this work, we used submerged FSW technology to effectively overcome the tool wear and overheat problem for the first time, and successfully produce a defect-free ultrafine-grained Ti joint with a joint efficiency of 100%. The transmission electron microscopy with a two-beam diffraction technique, electron backscatter diffraction and finite element simulation are utilized to systematically investigate the deformation modes, grain refinement mechanisms and their relationships during FSW. It was found that the deformation and recrystallization mechanisms of Ti during FSW were associated with the domination of $\{10\overline{1}2\}$ twins, basal, prismatic <a> slip and pyramidal <a+c> slip at different deformation stages, and continuous dynamic recrystallization related to the dislocation absorbing. Also, the contribution of twin-dislocation interaction, dislocation absorption. grain boundary migration and texture on the ultimate ultrafine-grained microstructure, and the underlying effect of temperature and orientation on the deformation mechanisms were clarified. This study provides a new method of fabricating high-quality joints and ultrafinegrained bulk Ti materials, and also provides a new reference for understanding the microstructural evolution mechanism during FSW. More detailed description can be found in Acta Mater. 166 (2019) 371.



Fig. 2: Temperature distribution and deformation mechanism during submerged friction stir welding of pure Ti.

3.1.1.3 Insight into the Corrosion Evolution of Febased Amorphous Coatings under Wet-dry Cyclic Conditions

Understanding the corrosion behavior of Fe-based amorphous coatings under wet-dry cyclic conditions is of pretty importance for coating applications in marine environments. However, it is extremely difficult to unravel corrosion features under wet-dry cyclic conditions by conventional electrochemical measurements as the solution resistance is very high.

In this work, the corrosion evolutions of the coatings under wet-dry cyclic conditions were investigated by EIS on a two-electrode cell. Accurate R_{ct} was obtained through fitting EIS results using a modified transmission line equivalent circuit model and a landscape map of R_{et} was constructed for a panoramic investigation on coating corrosion. The results show that the corrosion rate increases rapidly when the solution film over the coating become very thin due to fast oxygen transport under ultrathin solution film. It is deduced that an oxygen concentration gradient can form between--- the inside and the outside of coating pores when the solution film over the coating is very thin, which further promotes the localized corrosion in the pores. In general, the substrate is well protected by the coatings against corrosion under wet-dry cyclic conditions. This work proposed an accurate method for the electrochemical measurements and life evaluations of the coatings under wet-dry cyclic conditions.

3.1.1.4 Optimization of Tensile Properties of Tibased Metallic Glass Composites

The effects of different microstructure of Ti-based bulk metallic glass composites (BMGCs) containing in-situ formed β -Ti crystals on their tensile properties were systematically investigated. With increasing the particle size of the β phase, the BMGCs exhibit a higher tensile plasticity and a higher work-hardening capacity. It was found that the phase stability of the β phase plays a vital role on tensile properties of BMGCs: BMGCs containing a stable β -Ti phase undergo a tensile worksoftening behavior after yielding. BMGCs containing a metastable β -Ti phase exhibit a poor tensile plasticity with severe serrated deformation after yielding. BMGCs containing a phase-transformable β -Ti phase show the best tensile plasticity as well as work-hardening capacity. With increasing the volume fraction of the β phase, the yield strength of BMGCs decreases although their tensile plasticity increases.

Therefore, in order to obtain an excellent combination of properties of BMGCs, the β -Ti phase should have a larger particle size, an appropriate phase metastability and a relatively low fraction. This is because a larger particle size can result in a larger tensile plasticity; an appropriate metastability can lead to deformation-induced phase transformation and cause an improved tensile plasticity as well as work-hardening capacity; and a low fraction can bring a high yield strength of the composites. A BMGC



Fig. 3: Landscape map of the parameter Rct for the Fe-based AMCs under wet-dry cyclic conditions fitted through the modified transmission line equivalent circuit model.



Fig. 4: BT35-50-Co1 possesses an excellent combined properties, including the high yield strength and the large cast size, as compared with the reported BMGCs in literature.

with a composition of $Ti_{41.8}Zr_{33.5}Cu_{6.9}Co_{1.2}Be_{16.6}$ (BT35-50-Co1) was then designed. The average particle size of β phase is about 16 µm, and the volume fraction is only 38%. This BMGC exhibits a yield strength as high as ~1380 MPa and a uniform elongation of 5.2% accompanying remarkable work-hardening capacity. As compared with the previously reported BMGCs, this BMGC possesses an excellent combination of properties, including high yield strength, large tensile plasticity, good work-hardening capacity and extraordinary glassy forming ability of the glassy matrix (see Fig.4).

3.1.1.5 Improved Fatigue Resistance of Gradient Nanograined Cu

Numerous metallic components suffer from fatigue damage and failure, arising from the vast accumulation of very small irreversible plastic microstrain under cyclic loading. Dislocation activity associated with the formation dislocation patterns occur in conventional coarse grained (CG) metals, thereby causing local surface roughening, early cracking and inferior high-cycle fatigue limit. Intensive studies over past 30 years have indicated homogeneously refining CG into the ultra-fine (UFG) and nano-scale (NG) can greatly enhances strength and fatigue limit by suppressing dislocation activities. However, uniform grain size reduction always causes a very shorter low-cycle fatigue life and pronounced cyclic softening of UFG and NG metals. Such inferior fatigue resistance arises from microstructural instability and cyclic-deformationinduced local damage accumulation, such as that produced by shear banding and/or abnormal grain coarsening.

Recently, gradient nanograined (GNG) materials with the spatially graded distributed grain sizes from nanometer in the surface to micron scale in the core exhibit a combined enhancement of mechanical properties, such as high strength, considerable ductility. In this study, GNG Cu with a thin superficial GNG layer is found to exhibit an unprecedented combination of cyclic properties during cyclic loading: doubling both low-cycle fatigue life and high-cycle fatigue limit, compared to its homogenous CG counterparts (Fig.5). Specially, cyclic stability at constant stress amplitude is maintained in GNG Cu after a short initial hardening stage, in distinct contrast to the cyclic hardening of CG metals and cyclic softening of UFG metals under strain control. Such superior fatigue resistance stems from the unique homogeneous grain coarsening and the progressive homogenization of an initially gradient nanostructure through ordered cyclic plastic strain transmission from CG core to GNG surface layer, which effectively suppresses both strain localization and surface roughening concurrently (Fig.1). This unique fatigue mechanism is fundamentally distinct from traditional persistent strain-localizing fatigue behaviors in homogeneous structures, associated with large local surface roughening. The present results offer unique pathways to mitigate fatigue damage using gradient nanostructure in many practical applications (The details see Acta Mater. 166 (2019) 56).



Fig. 5: Graded surface nanostructure and its fatigue properties. Cross-sectional EBSD image of GNG/CG Cu produced via surface mechanical grinding treatment (a) and that after repeated loading until failure over 2,600 cycles at $\Delta_{et}/2$ of 0.5% (b). (c) Dependence of the high-cycle fatigue life (N_f) on the stress amplitude ($\Delta\sigma/2$)/tensile strength (σ_{UTS}) under stress control. (d) Cyclic stress response ($\Delta\sigma/2$) at total strain amplitude ($\Delta_{et}/2$) of 0.29% and 0.5%, respectively. (e) Correlation between the fatigue endurance limit (σ_{-1}) and the transition life ((2N_f)_f) of GNG/CG Cu.





3.2 材料结构与缺陷研究部

OPb OSr ● Ti OO

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- 陈春林 (扫描透射电镜微分相衬成像)

3.2.1 研究工作简述

本研究部主要以电子显微技术为主要研究手段,在原子尺度探究晶体材料的结构与缺陷,主要涵盖:材料界面与缺陷的超高分辨电子显微学;低维铁电功能材料;金属形变动力学的定量电子显微学; 扫描透射电镜微分相衬成像技术;材料结构与缺陷理论计算。

本年度工作以电子显微技术为主要分析手段,以晶体材料的结构与缺陷为主要研究内容,立足对 材料科学中经典的基本科学问题的进行再认识并获得新理解,探索材料科学中的重大前沿性基础科学问 题,为发展高性能金属结构材料以及先进功能材料提供原子尺度的结构信息。本年度在诸如晶体材料结 构与缺陷的倒易空间解析及实空间的原子结构图谱、基于铁电极化的量子材料构筑及其亚埃尺度结构特 性、腐蚀介质条件下的材料电子显微学、扫描透射电镜微分相衬成像技术的理论与应用研究、金属形变 动力学的定量电子显微学研究、金属结构材料原子尺度界面结构设计及性能调控、材料结构与缺陷的理 论计算等多个方面相继取得具有重要国际影响力的研究成果。

在低维铁电材料研究方面,利用精密脉冲激光沉积技术,精确调节激光能量和频率等生长参数,成 功地在SrTiO₃(111)单晶衬底上制备出全共格[111]PbTiO₃高指数铁电薄膜,揭示出[111]PbTiO₃薄膜具有异 常的弹性响应特性和相组成;发现薄膜单胞体积和块体值相比被压缩4%以上,导致了一种具有铁电自发 极化值大于50 μCcm²的单斜[111]PbTiO₃铁电相的产生,且表现出零泊松比的特性。此外,在亚稳超硬材 料相变研究方面,发现三维缺陷网络对材料相变的显著抑制作用,突破了人们对材料缺陷与相变关系的 传统认识;在全片层Ti-6Al-4V中的孪晶及系列扭折机理方面的研究中,从根本上阐释了全片层Ti-6Al-4V 合金的微观韧性起源,从而为新型钛合金的优化与设计提供了理论指导;在电子显微学方法方面,提出 一种新的具有一定普适性的制备单原子层二维金属的方法。

3.2.1.1 具有零泊松比的电极化超薄铁电体

目前,生长在[001]这类低指数取向衬底上的 钙钛矿氧化物薄膜已有了系统的研究。相比之下, 高指数取向(如[111]取向)单晶衬底面外对称性较 低,对钙钛矿氧化物薄膜的应变及对称性调控具有 更多的灵活性,能够在更深程度打破界面及薄膜的 对称性,诱导引入新的界面结构及新的物理性能。 然而,高指数取向钙钛矿氧化物其表面具有强的极 性、严重的表面重构、以及高的表面能。这些因素 限制了高指数取向钙钛矿功能氧化物薄膜的制备及 新结构与性能关系探索。

利用精密脉冲激光沉积技术,精确调节激光能 量和频率等生长参数,成功地在SrTiO₃(111)单晶衬 底上制备出全共格[111]PbTiO₃高指数铁电薄膜。X 射线衍射和原子尺度像差校正透射电子显微学研究 表明,薄膜的共格外延性和强铁电极化特性,揭示 出[111]PbTiO₃薄膜具有异常的弹性响应特性和相组 成。该铁电薄膜面内受到衬底约为2%的压应,变 而面外[111]取向晶格却几乎没有弹性形变,薄膜 单胞体积和块体值相比被压缩4%以上,导致了一 种具有铁电自发极化值大于50 μCcm⁻²的单斜[111] PbTiO₃铁电相的产生,且表现出零泊松比的特性。 这一结果对探索新型高指数取向钙钛矿氧化物薄膜 及其建立结构与性能关系具有重要意义,对设计新 型抗压抗剪切薄膜材料具有重要价值。相关研究结 果发表在Adv. Funct. Mater. 29 (2019) 1901687上。



图1 生长于SrTiO₃(111)衬底的单斜极化PbTiO₃相。 (a) 6 nm [111]PbTiO₃ 薄膜的BF-STEM原子像,注意其中的氧原子 成像。此处图像经过衬度翻转处理。红框区域示意Ti-O (δ_{Ti-O})离子位移导致的铁电极化特征。(b) 铁电极化矢量的 二维图(δ_{Ti-O})。

3.2.1.2 亚稳超硬材料的相变研究

纤锌矿型氮化硼是硬度接近于金刚石的超硬 材料,有望在许多应用领域中替代金刚石。然而, 纤锌矿型氮化硼是一种高压亚稳相,在常压下极易 转变为六角氮化硼。如何在常温常压下稳定纤锌矿 型氮化硼是个具有挑战性的问题,相关机理尚不清 楚。

本研究利用扫描透射电子显微术与第一性原 理计算相结合的方法系统地研究了纤锌矿型氮化硼 中的缺陷结构及其对材料相变的影响。电子显微学 研究发现,纤锌矿型氮化硼中基面上的层错与棱柱 面上的倒反畴界相交在一起,从而形成一个三维缺 陷网络。层错与倒反畴界相交形成了数量众多的 "层错-倒反畴界结"。第一性原理计算表明三维 缺陷网络可显著抑制锌矿型氮化硼向六角氮化硼的 相变,极大地提高了材料的稳定性。传统相变理论 认为材料中的结构缺陷具有较高的能量、易于偏析 杂质原子,通常是材料相变的易形核位置,会促进 相变的发生。然而,本研究发现的三维缺陷网络对 材料相变的显著抑制作用,突破了人们对材料缺 陷与相变关系的传统认识。相关成果发表在P. Natl. Acad. Sci. USA 116 (2019) 11181上。

3.2.1.3 全片层Ti-6AI-4V中的孪晶及系列扭折

Ti-6Al-4V合金作为应用最广泛的钛合金,具 有三种典型的组织结构:全片层结构,全等轴结构 以及双态结构。其中,全片层结构的Ti-6Al-4V合 金因其优异的断裂韧性和抗疲劳裂纹扩展性能而被 大量应用于航空航天结构件。

认识全片层Ti-6Al-4V合金优异韧性的起源对 进一步提升合金性能有重要意义。前人把全片层 Ti-6Al-4V合金的高断裂韧性归因于其片层状的结 构,但对于其片层结构在微观尺度如何影响韧性仍 不得而知。

我们利用透射电子显微镜,尝试从原子尺度揭 示了全片层Ti-6Al-4V合金的微观韧性起源。研究 发现:随着疲劳裂纹的扩展,裂纹尖端的孪晶大量 增多并连续扩展从而有利于释放裂纹尖端的应力。 实验证实这些孪晶是在α/β两相界面处形核的, 而Ti-6Al-4V合金α/β两相界面处台阶状的原子尺 度结构促进了孪晶的形核;同时发现孪晶与β相交 互作用诱导β相产生扭折,扭折后的β相使得应力 能够连续传递,从而促使了孪晶在β相的另一侧界 面处形核并连续扩展。

该工作揭示了Ti-6Al-4V合金中孪晶的形核机



图2 (a)高质量六角氮化硼单晶的照片; (b) 合成的纤锌矿型氮化硼晶体呈现黑色, (c, d) 层错 (ISF) 和倒反畴界 (IDB) 交叉区域的HAADF像(c)和相应的ABF像(d)。两组垂直的平面缺陷交叉在一起形成了"层错-倒反畴界结"。



图3 α/β 界面处的孪晶形核以及孪晶从α相到β相的穿过 机制。 (a) $[0001]_{\alpha}||[101]_{\beta}$ 方向下α/β 两相界面的高分辨高 角环形暗场扫描透射图像,图像显示α/β 界面处存在着明 显的原子尺度台阶状结构;(b)实验观察到变形孪晶从α/β 界面处产生并终止于α/β 界面;(c)<a>型位错分解诱导孪 晶形核的示意图,示意图显示 T₄⁻¹ 和 T₅⁻¹ 孪晶分别在P4和P5 面上形核。以及基面<a>型位错在不同晶体学面上分解产生 不同的孪生位错及驻留位错的反应示意图;(d)疲劳变形后 $[2\overline{110}]_{\alpha}//[11\overline{1}]_{\beta}$ 方向下孪晶与β相交互作用区域的明场透射 电镜图像;(e)孪晶从α相到β相的穿过机制示意图。

制及其与β相的交互作用机制,从根本上阐释了全 片层Ti-6Al-4V合金的微观韧性起源,从而为新型 钛合金的优化与设计提供了理论指导。相关研究结 果发表在Acta Mater. 181 (2019) 479上。

3.2.1.4 二维Au薄膜以及Au纳米条带

二维金属由于维度的急剧降低和电子结构的巨 大变化,具有与块体金属截然不同的性质。比如, 理论计算指出,单原子层密排结构的金具有极低的 可见光吸收率和良好的金属导电性,是理想的透明 导体材料。为了验证金的这一性能,我们开展了制 备无衬底二维金的方法的研究。对于金属材料,由 于金属键的各向同性,很难通过剥离法制备单原子 厚度的无衬底二维金属。

根据不同元素脱合金所需的入射电子束能量 不同,我们利用透射电子显微镜原位电子束脱合金 法,对AuAg合金进行原位脱Ag,制备得到了面积 达到57 nm²的单原子层无衬底二维Au薄膜以及Au 纳米条带。更值得注意的是,宽度小于0.9 nm的锯 齿状单原子层Au纳米条带是铁磁性的,且磁性与 纳米条带的宽度有密切相关,这对于通常没有磁 性的Au来说是十分罕见的。此外,我们进一步对 二维Au薄膜和纳米条带测量,得到了不同配位数 (从3到12)与金属原子间距的关系。本工作提出 了一种新的具有一定普适性的制备单原子层二维金 属的方法:由具有不同knock-on能量的元素组成的 固溶体合金通过选择合适的入射电压刻蚀即可。相 关研究结果发表在Nano Lett. 19 (2019) 4560上。



图4 (a-c)单层金膜的电子显微像; (d-f)金膜厚度的确定; (g) 电子束刻蚀制备单层金膜的示意图。

SYNI

3.2.1.5 石墨烯在金属表面上物理与化学混合吸附 现象的微观机理研究

石墨烯由于独特的电学性质、突出的力学强度 和良好的热导性被认为是理想的金属基复合材料增 强相。石墨烯和金属间的界面结合对复合材料的性 能起着重要作用。但是,关于石墨烯和金属间的界 面结合机理尚不十分明了。

我们借助第一原理理论计算方法对石墨烯吸附 在三种金属的(111)、(110)和(100)等低指数表面上 的微观机理进行了详细的研究。研究发现,石墨烯 吸附在金属(110)和(100)表面后会产生不同程度的 褶皱,而吸附在(111)表面未产生褶皱。石墨烯吸 附在Ni(111)、Co(111)、Ni(110)、Co(110)和Cu(110) 表面是化学吸附,而吸附在Cu(111)表面是物理吸 附。有趣的是,石墨烯吸附在Ni(100)、Co(100) 和Cu(100)表面都形成了物理与化学混合方式的吸 附。分波电子态密度与电荷差分密度分析表明,石 墨烯发生化学吸附时,碳和金属原子间发生了强烈 的轨道耦合效应,在成键原子之间产生了大量的电 荷积累;物理吸附时,碳和金属原子间未发生轨道 耦合效应,仅发生极少的电荷转移;物理与化学混 合吸附时,一部分的碳和金属原子间发生了强烈的 轨道耦合效应,产生大量的电荷积累,而其它部分 的碳和金属原子间未发生轨道耦合效应,只有极少 的电荷积累。本工作解释了石墨烯和金属间的界面 结合机制,对石墨烯的制备及石墨烯在复合材料 中的应用具有很好参考价值。以上结果发表在RSC Advances 9 (2019) 32712。



图5 物理与化学混合吸附界面的差分电荷密度和投影电子态密度。

3.2 Materials Structure and Defect Characterization Division



DIVISION HEAD: MA Xiuliang

RESEARCH GROUP LEADERS: (5)

MA Xiuliang (Ultra-high Resolution Transmission Electron Microscopy of Interficial Structures) DU Kui (Quantitative Electron Microscopy Investigation on Kinetics of Materials Deformation) ZHU Yinlian (Low Dimensional Ferroelectric Functional Materials) WANG Shaoqing (Theoretical Study of Material Structure and Defects) CHEN Chunlin (Differential Phase Contrast Scanning Transmission Electron Microscopy)



3.2.1 Summary of Scientific Activities

By means of transmission electron microscopy, we focus on material structures and defect characterization, address some unclarified fundamental issues in materials science, explore the frontier problems in materials science, and provide atomic-scale information for developing high-performance engineering alloys and advanced functional materials. In 2019, we made some progress in several aspects.

(1) We fabricated ultrathin $PbTiO_3$ films grown on a $SrTiO_3(111)$ substrate with atomically defined surfaces. High resolution scanning transmission electron microscopy and X-ray diffraction reveal that the as-grown [111]PbTiO_3 films are coherent with the substrate and compressively strained along all in-plane directions. In contrast, the out-of-plane lattices are almost unchanged compared with that of the bulk $PbTiO_3$, resulting in 4% contraction in unit cell volume and a nearly zero Poisson's ratio. Fabricating oxide films through [111] epitaxy may facilitate the formation of new phase components and exploration of novel physical properties for future electronic nano-devices.

(2) We fabricated millimetre-sized w-BN bulk crystals via the hexagonal-to-wurtzite phase transformation at high pressure and high temperature.

(3) We clarified the underlying mechanisms of interface-related deformation modes at an atomic scale in fully lamellar Ti-6Al-4V alloys.

(4) We fabricated free-standing monolayer Au membranes by in situ dealloying of Au-Ag alloy.

(5) We investigated in details the microscopic adsorption mechanism of graphene on the low-index metal surfaces such as the (111), (110) and (100) surfaces of Ni, Co and Cu by first-principles calculation.

3.2.1.1 Ultrathin Ferroelectric Film with a Nearly Zero Poisson's Ratio

[111]-oriented perovskite oxide films exhibit unique interfacial and symmetry breaking effects, which are promising for novel quantum materials as topological insulators and polar metals. However, due to strong polar mismatch and complex structural reconstructions on (111) surfaces/interfaces, it is still challenging to grow high quality [111] perovskite heterostructures let alone explore the as-resultant physical properties. Here we report a fabrication of ultrathin PbTiO, films grown on a SrTiO, (111) substrate with atomically defined surfaces, by pulsed laser deposition. High resolution scanning transmission electron microscopy and X-ray diffraction reveal that the as-grown [111]PbTiO₃ films are coherent with the substrate and compressively strained along all in-plane directions. In contrast, the out-of-plane lattices are almost unchanged compared with that of the bulk PbTiO₃, resulting in 4% contraction in unit cell volume and a nearly zero Poisson's ratio. Ferroelectric displacement mapping reveals a monoclinic distortion within the compressed [111]PbTiO₃, with a polarization larger than 50 μ Ccm⁻². The present



Fig. 1: Experimental evidence for the low symmetry polar PbTiO₃ phase grown on SrTiO₃(111). (a) BF-STEM image of the 6 nm [111]PbTiO₃ film showing O²⁻ columns. Contrast is inverted here to ease visual inspection. The red box area is magnified as an inset, which displays the significant Ti-O (δ_{Ti-O}) displacement. (b) The δ_{Ti-O} displacement vector maps based on (a).

findings, as further corroborated by phase field simulations and first principle calculations, differ significantly from the common [001]-oriented films. Fabricating oxide films through [111] epitaxy may facilitate the formation of new phase components and exploration of novel physical properties for future electronic nano-devices.

3.2.1.2 Phase Transformations in Metastable Superhard Material

Wurtzite boron nitride (w-BN) is a fascinating superhard material with a hardness next to diamond, rendering it a candidate material to replace diamond. However, w-BN is a high-pressure metastable phase, which tends to recover to the h-BN phase after releasing pressure. How to stabilize w-BN at atmospheric pressure is a challenging subject and the related mechanism remains unclear.

In this study, we fabricate millimetre-sized w-BN bulk crystals via the hexagonal-to-wurtzite phase transformation at high pressure and high temperature. By combining transmission electron microscopy and *ab-initio* molecular dynamics simulations, we reveal a stabilization mechanism for w-BN, i.e. the metastable high-pressure phase can be stabilized by three-dimensional networks of planar defects which are constructed by a high density of intersecting (0001) stacking faults and $\{10\overline{1}0\}$ inversion

domain boundaries. The three-dimensional networks of planar defects segment the w-BN bulk crystal into numerous nanometer-sized prismatic domains with the reverse crystallographic polarities. Our findings unambiguously demonstrate the retarding effect of crystal defects on the phase transformations of metastable materials, which breaks the common knowledge that the crystal defects in materials will facilitate the occurrence of phase transformations.

3.2.1.3 Twins and Sequential Kinks in Fully Lamellar Ti-6AI-4V Alloys

Fully lamellar Ti-6Al-4V alloys comprise bodycentered cubic (BCC) β lamellae in large-sized, hexagonal close-packed (HCP) α colonies, presenting outstanding toughness. Although it is generally considered that α/β interfaces play a key role in plastic deformation connected to the toughness, the interface effects have not been revealed so far. In this work, we studied underlying mechanisms of interface-related deformation modes at an atomic scale. After the cyclic loading, {1102} deformation twins were observed in the vicinity of fatigue crack surfaces. Moreover, the α/β interface structures before and after cyclic loading deformation were characterized via transmission electron microscopy (TEM). The initial α/β



Fig. 2: (a) Photograph of the high-purity h-BN bulk crystal, (b) As-synthesized w-BN bulk crystal appearing a black color. (c) HAADF and (d) ABF STEM images showing the intersection of the (0001) ISF and (0110) IDB. The two orthogonal planar defects penetrate each other and construct an ISF-IDB junction.



interfaces are consisting of $(01\overline{1}0)_{\alpha} || (\overline{1}21)_{\beta}$ terrace plane and $(\overline{1}100)_{\alpha} || (\overline{1}01)_{\beta}$ ledge plane, which can be explained by the terrace ledge kink model. TEM investigations reveal that deformation twins nucleated at the α/β interface and the corresponding nucleation is ascribed to the dissociation of $\langle a \rangle$ type dislocations in basal plane. The type of deformation twins is determined by the atomic scale α/β interface structure. More importantly, these twins can continuously propagate through multiple β phase lamella. The continuous propagation of twinning is accomplished through double kinking mechanism. In this way, the plastic deformation associated with twinning in α phases



Fig. 3: Twin nucleation from the α/β interface and the twinning transmission mechanism from α to β. (a) HR HAADF-STEM image of interface structure along $[0001]\alpha||[101]\beta$ direction showing obvious ledge terrace planes; (b) deformation twinning is observed starting and terminating at the α/β interface; (c) A schematic of the twinning nucleation mechanism from <a> type dislocations dissociation, showing the formation of T₄⁻¹ and T₅⁻¹ twin variants at the P₄ and P₅ planes. Schematic of reaction of basal <a> type dislocations at different planes into different twin dislocations and residual dislocations; (d) BF-TEM morphology of a typical twin-β interaction area viewed along $[2\overline{110}]_{\alpha}/[111]_{\beta}$ direction after fatigue deformation. (e) Schematic illustrations of twinning transmission from α to β.

and sequential kinking in β phases can contribute a lot to fracture toughness of fully lamellar Ti-6Al-4V. (*Acta Mater.* 181(2019) 479)

3.2.1.4 Two-dimensional Au Membrane and Nanoribbon

Two-dimensional (2D) materials, such as graphene, nitride, and transition metal dichalcogenides have triggered enormous enthusiasm for research owing to their attractive mechanical, optical, electronic, and chemical properties. A common feature in these 2D materials is strong intralayer covalent bonding and weak interlayer van der Waals bonding. Atomic-thick flakes can be prepared using exfoliation methods by breaking weak interlayer interactions. However, in metals, the bonding is metallic and more isotropic, and normally, it is impossible to exfoliate metallic materials to form monatomic-thick membrane. Thus far, few reports have demonstrated fabrication of monolayer metal membranes, whether it is through surface diffusion on graphene or direct etching of 2D metal selenide. Under those circumstances, the properties of metal membranes are heavily influenced by carbon atoms at the edges of graphene pores. Meanwhile, the size of defect-free monolayer metal membranes is limited for fabrication from 2D metal selenides. Despite the difficulties, if 2D membranes can be synthesized, they should exhibit distinct properties from their 3D counterparts attributed to the reduction in dimension and dramatic changes of electronic structures. For example, theoretical calculations have suggested enhanced magnetic moment in free-standing monolayer Hf and Fe. Theory has predicted that closely packed monolayer Au membrane has low visible-light absorption and good conductivity, with great potential for an ideal transparent conducting material with advantages over graphene. Before validating the theory, it is crucial to find ways to synthesis free-standing monolayer Au membranes.

In this work, we fabricated free-standing monolayer Au membranes by in situ dealloying of Au–Ag alloy. Regarding of the crystal orientation of different grains, all the Au membranes maintain a closely packed hexagonal lattice and remain robust under electron beam irradiation. Moreover, monolayer Au nanoribbons with both zigzag and flat edges are observed. The zigzag-edged nanoribbons



Fig. 4: (a-c) Electron micrographs of fabricated monolayer Au membranes; (d-f) The thickness determination; (g) The fabrication of a monolayer Au membrane by in situ dealloying of Au-Ag alloy.

with width between 0.65 and 0.9 nm are ferromagnetic with magnetic moments of 0.38–0.51 μ B per unit cell, according to first-principles calculations. Based on direct measurement from atomic resolution images of monolayer and bilayer Au membranes, the bond length between atoms decreases linearly as coordination number decreases.

This study demonstrates a new approach to fabricate monolayer metal membranes and nanoribbons. Freestanding monolayer membranes or nanoribbons of metals can be fabricated from bulk solid solution alloys, which comprise atoms with distinctly different knock-on energies, by in situ dealloying.

3.2.1.5 Microscopic Mechanism of Chemical and Physical Adsorption of Graphene on the Metal Surfaces

Graphene is considered as an ideal reinforcement phase of metal matrix composites due to its excellent electrical, mechanical and thermal properties. Interfacial bonding between graphene and metal plays an important role in the properties of composites. However, the mechanism of interfacial bonding between graphene and metal needs to be further explored.

In this study, we investigated in details the microscopic adsorption mechanism of graphene on the low-index metal surfaces such as the (111), (110) and (100) surfaces of Ni, Co and Cu by first-principles calculation. The results show the graphene sheet has a different degree of buckling after graphene is adsorbed on the (110) and (100) surfaces, while the graphene sheet has no buckling when graphene is adsorbed on the (111) surface. The adsorption of graphene on the Ni(111), Co(111), Ni(110), Co(110) and Cu(110) surfaces is chemical adsorption, while the adsorption of graphene on the Cu(111) is only physical adsorption. Interestingly, the adsorptions of graphene on the (100) surfaces of Ni, Co and Cu are all physical and chemical mixed adsorption. The projected density of states and the differential charge density results show there are strong orbital coupling effect and a large amount of charge accumulation between carbon and metal atoms in the chemical adsorption while there are almost no orbital coupling effect and charge accumulation between carbon and metal atoms in the physical adsorption. In addition, there are a strong orbital coupling effect and a large amount of charge accumulation between carbon and metal atoms in some parts while there are almost no orbital coupling effect and charge accumulation between carbon and metal atoms in other parts of the surface in the physical and chemical mixed adsorption. The interface bonding mechanisms between graphene and these metals are fully clarified in this study. The results will provide help for the preparation of graphene and its application in the R & D of composite materials.



Fig. 5: Differential charge density and projected density of states at physical and chemical mixed interface.



3.3 纳米金属材料研究部

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3.3.1 研究工作简述

本研究部主要聚焦研究金属材料中的纳米结构,探索纳米尺度下金属材料的独特性能及结构-性能关系,发展具有优异性能和使役行为的新一代金属材料。主要在新型纳米结构设计、新型纳米结构金属可 控制备与跨尺度构筑、以及新型纳米结构金属的结构表征、力学行为、使役行为、物理与化学行为、功 能特性等方面开展研究。研究领域包括:极限尺寸纳米金属、变形纳米孪晶、纳米金属使役行为、纳米 金属化学行为等。

2019年度,本研究部取得的主要进展有:

(1) 在纯金属Cu、Ni、Ag中发现纳米金属机械稳定性的反常晶粒尺寸效应。即,准静态拉伸变形时,随着晶粒尺寸从亚微米减小至纳米量级,晶界迁移先逐渐增强,而当晶粒尺寸小于临界值时,晶界迁移逐渐受到抑制。这为提高纳米晶机械稳定性开辟了新的途径,同时也为发展纳米晶制备工艺创造了条件。

(2) 基于纳米金属的高热稳定性和机械稳定性,提出利用稳定界面调控替代合金化实现材料素化的策略,深化材料素化的科学基础。

(3) 发现了极小尺寸下纯镍中面心立方向密排六方的相转变。

(4) 发现随层错降低纳米晶拉伸变形机制由晶粒长大向变形孪生转变,分析了变形机制由晶粒长 大向变形孪生转变的临界晶粒尺寸。

(5) 研究了梯度纳米结构316L不锈钢的疲劳行为,发现梯度结构可提高钢的强度,并协调一定幅度的塑性变形、以及促进形变诱导马氏体形成,从而抑制疲劳裂纹的萌生和扩展,提升材料在应力和应变控制下的疲劳性能。

(6)利用纳米孪晶结构提高304不锈钢的抗氢脆性能。发现纳米孪晶304不锈钢中束状的纳米孪晶 能有效缓解氢致局部塑性变形,同时氢原子作用下的位错与孪晶界反应所生成的大量不全位错能提供额 外的加工硬化能力。

3.3.1.1 纳米金属机械稳定性的反常晶粒尺寸效应

纳米金属在机械变形时容易发生晶界迁移, 导致晶粒长大,使得纳米材料发生软化和应变局域 化,这种现象在拉伸、压缩、压痕等变形条件下均 有大量实验和计算模拟结果的报道。机械驱动晶界 迁移不仅破坏材料的性能,也给利用塑性变形制备 纳米晶带来巨大困难。 一般认为,力作用下的晶界迁移速率与晶界 能、晶界曲率、晶界上的有效台阶等相关。晶粒尺 寸越小,迁移速率越快。研究发现对于塑性变形制 备的纳米晶Cu、Ag、Ni等不同层错能金属样品, 准静态拉伸变形时,随着晶粒尺寸从亚微米减小至 纳米量级,晶界迁移先逐渐增强,而当晶粒尺寸小 于临界值时,晶界迁移逐渐受到抑制。这一结果 与纳米晶热稳定性晶粒尺寸反常效应一致。对于



图1 (a) 纯Cu晶粒尺寸变化率($\Delta D/D_0$)随初始平均晶粒尺寸(D_0)变化关系, M-GBR和T-GBR分别表示机械诱导和热处理诱导 晶界驰豫效应; (b) 表面机械碾磨技术制备纯Ag、Cu、Ni样品 $\Delta D/D_0$ 随 D_0 变化关系。

Cu、Ag、Ni而言,实验中临界晶粒尺寸分别约为 75、80、38 nm。研究表明临界尺寸以下纳米晶在 塑性变形过程中其晶界容易发生应变诱导晶界驰 豫,而这种晶界驰豫使得晶界能降低,并且晶界开 始发生平直化,抑制了晶界迁移行为,变形机制由 晶界迁移转变为不全位错运动为主导,纳米晶机械 稳定性增强。这说明与晶界偏聚效应类似,晶粒尺 寸相关的晶界驰豫效应能对机械驱动晶界迁移起到 明显抑制作用,这为提高纳米晶机械稳定性开辟了 新的途径,同时也为发展纳米晶制备工艺提供了重 要参考。代表性论文发表于Phy Rev Lett. 122 (2019) 126101,同时被Science 364 (2019) 6443以"A size limit for softening"为题推选为亮点工作。

3.3.1.2 极小尺寸下纯镍中的FCC-HCP相变

纯镍是稳定的FCC结构,在高低温、高压下也 不会发生晶体结构的转变。研究表明,镍从低温 至熔点的温度范围内晶体结构均为FCC,而高压条 件下即使高达200GPa也没有发生相转变。通过调 整变形工艺将纯镍的晶粒尺寸细化至8nm左右,研 究发现,当晶粒尺寸细化到17 nm左右时,发生了 反常的面心立方(FCC)向密排六方(HCP)的相 变,形成了FCC和HCP结构混合的纳米晶,且形成 的HCP结构具有优异的热稳定性。结构表征表明, 晶粒细化到一定尺寸后层错变为主要的变形方式, 层错提供了FCC-HCP转变的有利形核位置,促进了 极小尺寸HCP纳米晶镍的形成。塑性变形至极小晶 粒尺寸时发生相转变的方法和机制有可能推广到其 它类似金属和合金中,为调控材料的点阵结构及性 能提供了一种新的途径。代表性论文发表于Scripta Mater. 168 (2019) 67。

3.3.1.3 梯度纳米晶Cu-AI合金拉伸变形机制研究

本工作系统研究了梯度纳米晶铜铝合金的拉伸 变形,发现随层错能降低,纳米晶拉伸变形机制由 晶粒长大向变形孪生转变,指出影响变形机制转变 的因素是层错能和纳米晶晶粒尺寸,分析了变形机 制由晶粒长大向变形孪生转变的临界晶粒尺寸。

将金属材料的晶粒尺寸减小到纳米量级后,材料的强度、硬度相比粗晶得到数倍的提升,然而材料的塑性和加工硬化率迅速下降。梯度纳米结构是提高纳米材料塑性的有效方法之一,梯度纳米晶Cu的表层纳米晶可以通过晶粒长大协调变形,使其具有很好的塑性。对于固溶体合金材料,晶界迁移受到抑制而制约了纳米晶粒长大。

在梯度纳米晶铜拉伸变形机制的研究基础上, 系统研究了梯度纳米晶铜铝合金的拉伸变形,发现 随层错能降低纳米晶拉伸变形机制由晶粒长大向变 形孪生转变,指出影响变形机制转变的因素是层错 能和纳米晶晶粒尺寸。不同于纳米晶的晶界迁移而 导致的晶粒长大,纳米晶变形孪生能够引入明显的



图2(a)(b)(d) 密排六方结构(HCP)纳米晶镍的高分辨图像;(c)(e) HCP Ni的电子衍射图,(f)相邻的FCC Ni电子衍射图。



图3 梯度纳米晶 Cu, Cu-2.2Al和Cu-4.5Al样品拉伸变形表层纳米晶晶粒尺寸随应变 (a) 和时间 (b) 的变化。

加工硬化,使梯度纳米晶铜铝合金比纯铜表现出更高的拉伸塑性。纳米晶孪生变形提高材料塑性为高强、高韧纳米结构材料设计提供了新的思路。研究工作发表在Acta Mater. 180 (2019) 231。

3.3.1.4 梯度纳米结构316L不锈钢在应力和应变控制下的疲劳行为研究

将金属材料晶粒细化为纳米晶或超细晶,可提 高其在应力控制下的疲劳性能,但往往降低其在应 变控制下的疲劳性能。本工作发展了控温表面机械 滚压处理(W-SMRT),抑制了316L奥氏体不锈钢在 形成梯度纳米结构(GNS)表层过程中的形变诱导马 氏体转变。所制备的全奥氏体相GNS层厚度为~800 μm,晶粒尺寸在最表层为~45 nm且随深度增大逐 渐增大。疲劳性能的研究表明,GNS 316L不锈钢 在应力和应变控制条件下的疲劳性能均显著提升。 如图4,在应力控制条件下,疲劳强度大幅提升, 疲劳极限由粗晶(CG)样品的180 MPa提高为GNS样 品的320 MPa;在应变控制条件下,GNS样品的疲 劳寿命也显著提升,0.1%塑性应变幅时疲劳寿命比 CG样品提高20倍左右。与之相比,等通道转角挤 压制备的纳米晶样品虽然在应力控制下的疲劳强度 大幅提升,但在0.1%塑性应变幅控制下的疲劳吞命 只有CG样品的15%左右。对循环加载过程中的结 构演化和疲劳机制分析表明,GNS层一方面提高了 316L不锈钢的强度并有效协调一定幅度的塑性变 形、另一方面促进了奥氏体基体中形变诱导马氏体 的形成,从而抑制了疲劳裂纹的萌生和扩展,造成 材料在应力和应变控制下疲劳性能的同时提升。相 关研究成果详见Acta Mater. 168 (2019) 133。



图4 梯度纳米结构316L奥氏体不锈钢与粗晶样品在 (a) 应力控制及 (b) 应变控制条件下的疲劳性能。图 (b) 中还对比了文献 中纳米晶及粗晶316L不锈钢样品的疲劳性能。

3.3.1.5 纳米孪晶奥氏体不锈钢的氢脆行为研究

奧氏体不锈钢经预应变和细化晶粒后,虽然能 有效地提升不锈钢的强度,但却会降低其抗氢脆性 能和塑性。孪晶界的界面能较低,氢不易富集且能 抑制位错运动,因而是一种潜在的能兼顾提升强度 和抑制氢脆的界面结构。然而,传统方法制备的不 锈钢的孪晶界面的密度低,氢脆的问题依然存在。 因此如何研制高强抗氢脆的奥氏体不锈钢具有很大 的挑战。

我们通过在奥氏体不锈钢中引入纳米孪晶结构

来解决这一难题。采用动态塑性变形 (DPD) 以及 后续退火处理成功地制备出了具有41%纳米孪晶组 织、32%再结晶晶粒和27%位错结构的纳米孪晶304 不锈钢,电化学充氢条件下的拉伸试验表明该合金 不仅拥有较高的强度及良好的塑性,同时具备良好 的抗氢脆性能。这主要由于纳米孪晶304不锈钢中 束状的纳米孪晶能有效缓解氢致局部塑性变形,同 时氢原子作用下的位错与孪晶界反应所生成的大量 不全位错能提供额外的加工硬化能力。相关研究成 果详见J. Alloy. Compd. 788 (2019) 1066。



图5 纳米孪晶304奥氏体不锈钢的氢脆敏感性和显微结构。(a) 典型的粗晶 (CG)、变形态纳米孪晶 (DPD) 和退火态纳米孪晶 (DPD-annealed) 样品在空气中和充氢条件下慢应变速率工程应力应变曲线;(b) DPD-annealed样品的扫描电镜电子通道衬度 图;(c) DPD-annealed样品纳米孪晶组织TEM明场像;(d) DPD-annealed样品纳米孪晶组织选区电子衍射花样。





3.3 Metallic Nano-Materials Division

DIVISION HEAD: LU Ke

RESEARCH GROUP LEADERS: (4)

LI Xiuyan (Size Limits in Metals) TAO Nairong (Strain Induced Nanotwinned Metals) WANG Zhenbo (Application Fundamentals of Nanostructured Metals) ZHANG Bo (Chemistry of Nanocrystalline Metals)



3.3.1 Summary of Scientific Activities

Research at the Metallic Nano-Materials Division focuses on discovery of novel nanostructures in metallic materials, exploration of their novel properties and structure-property relationships and development of next-generation metallic materials with superb properties and performance. The research area includes design of novel nanostructures, synthesis and structural characterization of nanograined metals, and exploration of their mechanical, physical and chemical properties, and functionalities. The current research topics are size limits in metals, strain induced nanotwinned metals, chemistry of nanocrystalline metals, application fundamentals of nanostructured metals.

3.3.1.1 Size Dependence of Grain Boundary Migration in Metals under Mechanical Loading

In classical models of mechanical properties of solids, GBs are often treated as "static" geometrical barriers to dislocation motion. Based on this, a well-known grain size dependence of strength is derived, predicting increased strength with decreased grain size, namely, the Hall-Petch relationship. However, deviating from this relationship, some nanograined metals exhibit softening with decreasing grain size. One of the fundamental reasons is that GBs move in response to mechanical loading with concomitant coarsening of nanograins, especially for pure metals, as evidenced by experiments and by atomistic simulations in a number of nanograined metals and alloys under various loading conditions such as tension, compression, and indentation, even at cryogenic temperatures. The mechanically induced GB migration not only deteriorates properties of nanograined materials but also hinders their processing by plastic deformation.

Grain size dependences of GB migration in nanograined Ag, Cu, and Ni under tension were investigated quantitatively in a wide size range by using gradient nanograined (GNG) samples which have unique strain delocalization mechanisms and enable very large tensile strains without failure in the nanograined layer. It is found that as grain size decreases from submicron, GB migration intensifies and then diminishes below a critical grain size.

In Cu samples, after tension with a strain of 0.31, the topmost nanograins with grain size of 44 ± 10 nm coarsen slightly to 48 ± 13 nm. While, in the subsurface layer coarsening is evident, from 106 ± 32 nm to 170 ± 41



Fig. 1: Longitude-sectional SEM images of the surface layers in the gradient nanograined Cu sample (Cu-1) before (a) and after tension (b), and the distributions of the measured transversal grain sizes from TEM observations at a depth of $1 \sim 2 \mu m$ (c),(d) and $\sim 30 \mu m$ (e),(f) from the surface, respectively. (g),(h) Variations of the measured transversal grain size as a function of depth from the surface before and after tension in the samples Cu-1 (grain size on the topmost surface is $44\pm10 nm$) and Cu-2 (grain size on the topmost surface is $64\pm20 nm$), respectively. (i) Relative grain size changes ($\Delta D=D_0$) as a function of depth for the two samples.



nm at a depth of 30 μ m. According to the grain size profiles measured along depth before and after tension, the change in grain size peaks at a depth of 15 μ m with corresponding grain size of 75 nm with a maximum value of 90%. It drops with a decreasing depth below 15 μ m and becomes negligible at the topmost surface. A similar grain coarsening phenomenon was also observed as the sample was tensioned at 77 K. Similar inflection point were also found in Ag and Ni samples at 80 nm and 38 nm, respectively.

The suppression of GB migration below a critical size can be attributed to GB relaxation during sample processing, which can be attributed to inhibition of full dislocations and nucleation of partials to form twins or stacking faults in nanograins. With relaxed GBs the governing deformation mechanism of nanograins shifts from GB migration to formation of through-grain twins or stacking faults. GB relaxation, analogous to GB segregation, offers a novel approach to stabilizing nanograined materials under mechanical loading. See *Phy. Rev. Lett.* 122 (2019) 126101 for more details.

3.3.1.2 Plastic Deformation Induced Hexagonal-Close-packed Nickel Nano-grains

For those FCC metals with high SFE such as Ni and Al, FCC lattice is rather stable and the FCC-HCP transformation is difficult to occur even at high temperatures or pressure, or under severe plastic deformation. No phase transition has been identified so far in FCC Ni in a wide temperature range up to its melting point and under a pressure up to 200 GPa.

It is discovered that Ni nano-grains with hexagonalclose packed lattice structure can be induced by plastic deformation. As discovered before, below 30 nm, formation of stacking faults with partial dislocations becomes dominant in nano-grained Ni, replacing dislocation slip and GB activities commonly observed in coarsegrained Ni. As grain size decreasing further, formation of multiple stacking faults in FCC nano-grains elevates their energy state and the FCC nano-grains may become thermodynamically unstable due to the increased excess energy. Below 17 nm, an FCC-to-HCP transformation occurs. Formation of hexagonal-close-packed Ni nanograins induced by plastic deformation. The finding offers



Fig. 2: (a) Grazing-incidence XRD patterns of the samples with different grain sizes in the top surface layers (20 nm and 8 nm) and the annealed sample (8 nm) at 773 K for 1 h. (b) Lattice parameters of nano-grained Ni as a function of grain size.

a novel approach to tailor lattice structures of metals that are stable in coarse-grained form. See *Scripta Mater.* 168 (2019) 67 for more details.

3.3.1.3 Tensile Deformation Mechanisms of Gradient Nanograined Cu-Al Alloys

The microstructures of the gradient nanograined Cu and CuAl samples before and after tension at different strains were systematically investigated by transmission electron microscope. It is revealed that grain coarsening dominates the plastic deformation of nanograins in the gradient nanograined Cu sample while the propensity of deformation twinning in nanograins increases in the gradient nanograined CuAl samples.

In the past decades, numerous strategies have been made by material researchers to improve the ductility and work hardening and to discover the intrinsic deformation mechanism of nanograins. Among all of the successful attempts, the gradient nanograined (GNG) structure seems to be one of the effective and powerful approaches to



Fig. 3: (a) The orientation map of nanograins at the depth of 5 μ m and (b) corresponding distribution of boundaries in the gradient nanograined Cu-4.5Al sample at the tensile strain of 0%; (c) the orientation map of nanograins at the depth of 5 μ m and (d) corresponding distribution of boundaries in the GNS/ CG Cu-4.5Al sample at the tensile strain of 35%.

suppress the strain localization and to realize the tensile ductility of the nanograined materials. In our work, a gradient nanostructured (GNS) surface layer was induced on coarse-grained (CG) Cu and CuAl alloys by means of surface mechanical grinding treatment. The GNS/CG Cu-4.5Al sample subjected to tensile tests yields at a higher strength and fails at a higher uniform elongation (~42%) in comparison with the GNS/CG Cu and Cu-2.2Al samples. The microstructures of the GNS/CG samples before and after tension at different strains were systematically investigated by transmission electron microscope. It is revealed that grain coarsening dominates the plastic deformation of nanograins in the GNS/CG Cu sample while the propensity of deformation twinning in nanograins increases in the GNS/CG CuAl samples. The experimental results suggested a transition of deformation mechanism of nanograins from grain coarsening to the partial dislocation associated deformation twinning in the GNS/CG Cu and CuAl alloys with increasing Al solute concentration. This work demonstrated that besides the nanograin coarsening, the partial dislocation associated deformation twinning

is also an effective deformation mechanism to retard the strain localization and to improve the tensile ductility of nanograins. The relevant work was published in *Acta Mater.* 180 (2019) 231.

3.3.1.4 Simultaneous Enhancement of Stressand Strain-controlled Fatigue Properties in 316L Stainless Steel with Gradient Nanostructure

As the grain sizes are refined into ultrafine/nanoscale in metallic materials, considerable enhancements in fatigue properties will be achieved under stress-controlled mode. However, the fatigue properties under strain-controlled mode usually decrease due to the lack of ductility. In the present work, a gradient nanostructured (GNS) surface layer of ~800 µm in thickness is manufactured on 316L austenitic stainless steel by means of surface mechanical rolling treatment at controlled temperature (W-SMRT, $\sim 280^{\circ}$ C). The average grain size is ~ 45 nm at the top surface and increases gradually with depth, while deformation-induced martensite (DIM) transformation is completely suppressed in the surface layer. Axial tensioncompression fatigue tests show that fatigue properties of the GNS samples are significantly enhanced under both stress- and strain-controlled modes. Fatigue limit in stresscontrolled tests increases from 180 MPa of the CG samples to 320 MPa of the GNS samples. Simultaneously, fatigue lives of the GNS samples are higher than those of the CG samples in strain-controlled tests, especially under plastic strain amplitudes < 0.25%. For example, the fatigue lives of the GNS samples are ~20 times higher than those of the CG samples at the plastic strain amplitude of 0.1%. This is different from the fatigue properties typically observed in homogenous nanostructured materials, i.e. enhanced fatigue strengths in stress-controlled tests accompanied by decreased fatigue lives in strain-controlled tests. For example, the fatigue lives of nanostructured 316L stainless steel samples prepared by equal channel angular pressing are only ~15% of those of the CG samples at the plastic strain amplitude of 0.1%. Besides contributions from the enhanced mechanical properties and suppressed formation of surface defects, analyses of fatigue mechanisms demonstrate that the promoted formation of DIM during cyclic strain plays a crucial role in enhancing fatigue properties of the GNS samples in strain-controlled tests.



Fig. 4: Cyclic stress response curves of the GNS and CG 316L stainless steel samples fatigued at different constant total amplitudes as indicated.

The formation of DIM results in a distinct secondary hardening stage and a higher strain homogeneity under cyclic deformation, leading into higher fatigue strength and endurance (Fig.4). See *Acta Mater*. 168 (2019) 133 for more details.

3.3.1.5 A Nanotwinned Austenite Stainless Steel with High Hydrogen Embrittlement Resistance

It is well documented that the strength of stainless steel can be effectively improved by pre-strain (introducing martensite into metastable austenitic stainless steel) and grain refinement, however these methods can cause the reduction of the hydrogen embrittlement (HE) resistance and the loss of plasticity. It is well known that the interface energy of twin boundary is relatively low, which can impede dislocation movement and is not the trapping site for hydrogen. Thus, twin boundary is a potential interface structure that can enhance strength and inhibit hydrogen embrittlement. However, the twin interface density of stainless steel produced by traditional method is low, which has been found to have no obvious effect on the HE resistance. Up to now, the development of austenitic stainless steel with high strength and high hydrogen embrittlement resistance is still challenging. In order to solve this problem, we successfully introduced nanotwin structure into austenitic stainless steel by dynamic plastic deformation (DPD) and subsequent annealing. The 304 stainless steel consists of 41% nano-twin structures, 32% recrystallized grains and 27% dislocation structures. The tensile tests under the condition of electrochemical hydrogen charging show that the alloy not only has a high strength and a good plasticity, but also has a good hydrogen embrittlement resistance. This is mainly due to the fact that the bundle like nano-twins in the deformed 304 stainless steel can effectively alleviate the local plastic deformation caused by hydrogen, and a large number of partial dislocations generated by the reaction of dislocations and twin boundaries under hydrogen environment can contribute to the additional work hardening. See J. Alloy. Comp. 788 (2019) 1066 for more details.



Fig. 5: (a) Engineering stress-strain curves of CG, DPD and DPD-annealed samples tested in air and hydrogen environment with a strain rate of 10^{-5} s⁻¹, schematic describing of (b) slip localization at a single TB and (c) a homogeneous distribution of stain at nanotwinned structure.

3.4 陶瓷及复合材料研究部



研究部主任: 王京阳

研究组负责人: (5人)

- 王京阳 (热障/环境障一体化陶瓷涂层)
- 李美栓 (超高温热结构材料及防护涂层)
- 王晓辉(结构陶瓷功能化)
- 张广平 (薄膜与微小尺度材料及力学行为)
- 张 洁 (先进核用陶瓷材料)



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3.4.1 研究工作简述

陶瓷及复合材料研究部研究领域主要有:新型高温结构/功能陶瓷及复合材料的多层次设计和结构 与性能关系;发展不同尺度(低维粒子、薄膜及大尺寸块体)材料的关键制备技术;研究新型陶瓷及复 合材料在热、力、氧和腐蚀等极端环境中的力学行为及热/化学稳定性;微小尺度材料及纳米复合材料制 备、材料尺寸与界面效应、材料强韧性与疲劳断裂。

本年度累计发表及合作发表46篇论文,授权/申请国家发明专利8项,在国际/国内学术会议上作30次 主旨和邀请报告。

本年度研究部以发展极端环境用高性能结构陶瓷及复合材料为目标,开展了高通量设计、多尺度可 控制备、结构组织表征和综合性能评价研究,主要工作进展如下:

(1) 系统研究了稀土硅酸盐材料受高温水蒸气和熔融氧化物(CMAS)腐蚀的典型行为,建立了腐蚀性能变化规律与稀土元素的关系,提出了高温水氧和CMAS腐蚀下稀土硅酸盐内禀惰性新机理。研究结果用于构建目前已知的最全面稀土硅酸盐抗腐蚀性能数据库,并指导航空发动机用先进环境障涂层的稀土元素优选及性能精准调控。

(2) 发展出高熵稀土硅酸盐热障/环境障涂层材料,通过稀土元素高熵效应实现关键热学和抗腐蚀 性能的协同优化。

(3) 采用超分子组装技术制备出形貌可控的氮化硼气凝胶,孔隙率98%以上,热导率(0.025W•m⁻¹/K⁻¹)比氮化硼体材料降低了5个数量级,在超高温超级隔热领域有应用前景。

(4) 采用物理气相沉积制备了化学计量可控的碳化锆,同步辐射X射线实验结合理论计算发现:亚 化学计量碳化锆中存在高浓度的第三近邻碳空位组态,且3NN空位组态热力学稳定性最高,是亚化学计 量比结构中碳空位分布的主要构型;同时,发现碳空位的存在可以提高碳化锆陶瓷抗辐照损伤能力。研 究结果为第四代核能系统用新型耐高温、抗强辐射陶瓷材料选材设计提供了基础支撑。

(5) 系统研究了空气压力对超高温陶瓷(UHTC) 1800℃以上氧化行为的影响。在1atm空气中, ZrB₂-20SiC具有良好的抗氧化性能; 但是在低压空气中 (10,5,0.5 kPa), SiC发生活性氧化形式的内氧 化,抗氧化性随之变差。通过添加MSi₂ (M=Ta, Mo和Hf), 极大地抑制了挥发性产物相的生成,改善 了ZrB₂-20SiC抗氧化性。首次基于Wagner内氧化理论定量分析了SiC发生内氧化的温度和氧分压条件,并 提出了气相SiO在氧梯度分布的氧化层中被进一步氧化成SiO₂以及在氧化层表面蒸气压差异的协同作用机 制。研究对于深入了解UHTC超高温氧化机理具有重要的理论意义和实用价值。

(6) 利用电解液中氢醌和醌之间的可逆反应,以单壁碳纳米管为媒介作为正极匹配Ti₃C₂T_x负极,使用Nafion质子交换膜分隔正负极电解液,构建了氢离子摇椅式的超级电容器。组装成全电容后电压窗口 在水系中达到了1.6V,比电容和能量密度分别达到了176 F/g和62 Wh kg⁻¹,为迈科烯的实际应用打下坚实 的基础。

(7) 揭示了Mo/W多层膜疲劳抗力与组元层单层厚度之间的规律。发现了纳米晶金互连线热疲劳性 能与线厚度与晶粒尺寸之间的规律。建立了晶界排列的随机模型,发现超细尺度Cu/W多层膜疲劳裂纹在 界面处的偏折长度随着组元层的晶粒尺寸和晶界对齐偏差的减小而减小。研发并搭建了用于评价微小尺 度高温金属部件蠕变性能的评价设备。研究了不同扫描方式和热处理方式对增材制造Inconel 718合金疲 劳性能和高温蠕变抗力的影响规律。

3.4.1.1 多功能热障/环境障涂层的成分和结构设 计与先进制备技术

系统研究了稀土硅酸盐材料受高温水蒸气和熔融氧化物(CMAS)腐蚀的典型行为,建立了腐蚀性能变化规律与稀土元素的密切关联,提出了高温水氧和CMAS腐蚀下稀土硅酸盐内禀惰性新机理。

研究结果用于构建目前已知的最全面稀土硅酸盐抗 腐蚀性能数据库,可指导航空发动机用先进环境障 涂层的稀土元素优选及性能精准调控。为了实现本 研究部在国际上创新提出的多功能热障/环境障一 体化涂层的设计思路,研究工作突破了适用于不 同等离子喷涂工艺的稀土硅酸盐粉料制备技术, 解决了国外粉体制造公司对国内的"卡脖子"禁卖限


图1稀土硅酸盐多功能热障/环境障涂层材料制备技术及损伤自监视功能成分设计。

制;随后采用PS-PVD喷涂技术,成功获得了具有 典型热障涂层柱状晶微观结构的稀土硅酸盐涂层, 相关工作尚未见文献报道;另外,采用大气等离子 喷涂技术,获得了具有典型环境障涂层致密微观结 构的稀土硅酸盐涂层。创新结合这二种涂层的微观 形貌与性能特点,将支撑航空发动机用多功能热障 /环境障一体化涂层的技术突破,发展出具有优异 热学和化学匹配性的新型耐高温涂层并在国际本领 域处于领跑地位。相关结果本年度在Corros. Sci.、 Scripta Mater.、Sci. Rep.、J. Am. Ceram. Soc.、J. Eur. Ceram. Soc.、JMST和《中国材料进展》等发表 论文9篇,申请国家发明专利3项。

3.4.1.2多组分稀土单硅酸盐热障/环障涂层材料 性能的鸡尾酒效应

基于早期对稀土硅酸盐力学、热学以及抗腐蚀性能的系统研究,优选抗水蒸气腐蚀性能优异的Ho、Er,抗CMAS腐蚀性能好的Y、Yb四种元素,制备了多组分稀土单硅酸盐 $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ 材料,并对其力学、热学及抗腐蚀性能进行研究。该材料为单相 X_2 -RE $_2SiO_5$ 均匀固溶体,HAADF-STEM及原子尺度元素分析结果表明,四种稀土元素均匀分布。

较单组分材料RE₂SiO₅(RE=Y, Ho, Er, Yb),多组分稀土硅酸盐(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})₂SiO₅热膨胀系



图2 多组分稀土单硅酸盐材料($Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4}$)₂SiO₃的HAADF-STEM及原子尺度元素分布图及其关键性能同混合定律结果 对比。

数减小11~19%, 室温热导率降低5.4~66.8%。热 膨胀系数减小,使材料的热膨胀行为更好地匹配 SiC_f/SiC基体,可以有效降低热循环过程中的热 应力;同时晶格畸变导致声子散射加剧,传热寿 命更短,降低晶格热导率,实现隔热性能优化。 在降低热导率和热膨胀系数的同时,多组分固溶 体的抗高温水蒸气腐蚀能力与单组分稀土单硅 酸盐RE₂SiO₅(RE=Y, Ho, Er, Yb)的平均值持平, 抗低熔点氧化物CMAS (CaO-MgO-AlO_{1.5}-SiO₂)腐 蚀能力优于平均水平。综合分析,多组分固溶体 (Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})₂SiO₅实现了关键热学和抗腐蚀性 能的协同优化,在多功能热/环障一体化涂层领域 有重要的应用前景,为多功能热障/环障涂层设计 提供了新思路。

3.4.1.3 新型抗强辐照陶瓷材料设计与表征

第四代核能系统固有安全性高,可持续性良 好、经济性优,是未来核能的重要突破方向。第四 代核能系统中工作环境非常严苛,燃料组件包壳和 堆芯构件等结构材料应具有优异机械性能,良好的 长时相稳定性,与冷却介质相容性好的特点;还要 承受300~1000℃的高温,100~200 dpa的强辐照剂 量。目前亟待开发面向第四代核反应堆系统应用的 新型抗强辐射结构材料。碳化错具有熔点高、耐裂 变产物腐蚀、在高温下仍具有较高热导率,中子吸 收截面低以及抗辐照优异等特点,是目前正在广泛 研究的前沿核用陶瓷材料。

碳化锆是典型的高度非化学计量比化合物, 其碳原子晶格上存在高浓度空位和较宽的成分分布 范围。本工作制备出不同化学计量比碳化锆,其晶 格常数、硬度及弹性模量随碳含量减小而降低;同 步辐射X射线实验分析结果表明亚化学计量比碳化 锆中存在高浓度的第三近邻碳空位对组态;理论计 算结果发现第三近邻 (3NN) 碳空位对组态热力学 稳定性最高,是非化学计量比结构中碳空位分布的 主要构型。进一步研究了高能Au离子强辐照条件 下不同化学计量比碳化锆显微结构的演化:与化 学计量碳化锆 (ZrC_{0.86}) 相比,亚化学计量碳化锆 (ZrC_{0.55}) 辐照非晶化抗力更优。研究结果为通过 碳空位调控及内禀点缺陷阱设计来提升抗辐照性能 提供了新思路。

3.4.1.4 ZrB₂-SiC-MSi₂超高温陶瓷在1800℃下的 内氧化行为研究

使用温度超过1600℃的超高温陶瓷 (UHTC) 在 航空航天领域有重要的应用需求。由于服役时涉及 有氧环境,对UHTC的抗氧化性能要求十分苛刻。 限于实验技术目前对UHTC的超高温氧化行为缺乏 系统研究。特别是针对空气压力 (氧分压和气体总 压)影响的研究却很少。因此,为深入了解UHTC 超高温氧化机理、发展超高温结构材料/防护涂层 新体系,系统开展这方面研究具有重要的理论意义 和实用价值。

利用具有自主知识产权的可控气氛超高温氧化 试验平台,针对ZrB₂-20SiC-xMSi₂(M=Ta,Mo和 Hf; x=0~10 vol.%)复合材料,首次系统研究了空气 压力对UHTC超高温氧化行为的影响。在1800℃下 1atm空气中,ZrB₂-20SiC具有良好的抗氧化性能;



图3 不同化学计量比ZrC_x的晶格常数 (a) 硬度及模量 (b) 随碳含量变化曲线; (c) 同步辐射X射线测得ZrC_x样品径向分布函数, 亚化学计量碳化锆中存在高浓度的第三近邻碳空位对; (d) 理论计算结果表明第三近邻 (3NN) 碳空位组态热力学稳定性最高, 是非化学计量比结构中碳空位分布的主要构型。



图4 ZrB,-20SiC-MoSi,在1800℃低压空气中氧化后典型截面形貌以及相关挥发性氧化产物的蒸汽压图。

但是在低压空气中(10, 5, 0.5 kPa),靠近氧化层/ 3.4.1.5 氢离子摇椅式超级电容器 基体界面的SiC发生活性氧化,导致在氧化层下基 体中出现SiC缺失的内氧化层、抗氧化性随空气压 力降低显著变差。添加MoSi,后明显改善了材料的 抗氧化性能,主要是抑制了10 kPa空气中发生内氧 化,大幅度减小了材料在5和10 kPa空气中的内氧 化层厚度。原因是添加MoSiz后,反应形成了稳定 的MoB,减少挥发相B₂O₃而增加保护性SiO₂的生 成。

本工作明确了空气压力对UHTC氧化行为的作 用机制,首次基于Wagner内氧化理论定量分析了 SiC发生内氧化的温度和氧分压条件,并基于热力 学分析提出了气相SiO在氧梯度分布的氧化层中被 进一步氧化成SiO。以及在氧化层表面不同压力的空 气中蒸气压差异对氧化层完整性的协同作用机制。 该项研究发表在Corros. Sci. 157 (2019) 87上。

迈科烯是三元层状化合物MAX相陶瓷的衍生 物。利用MAX相中MA之间的弱结合和A元素的化 学活性,在酸性含氟溶液中可以选择性刻蚀掉A 原子层、得到MX片层的二维材料。裸露的MX片 层与刻蚀液发生反应,在其表面形成-O、-F和-OH 等官能团(通常以T_x表示)。这种类似于石墨烯 的二维材料被称为迈科烯 (MXenes, $mTi_3C_3T_x$, Ti_2CT_x , Nb₄C₃T_x等)。迈科烯在储能、催化、传感 器、电磁屏蔽等诸多领域表现出优异的性能。特别 在电化学储能领域,展现出光明的应用前景。

此前的研究表明,迈科烯在酸性溶液中才能表 现出高的容量。这个过程主要依赖于迈科烯表面的 氧官能团同氢离子的反应,所以迈科烯是一种典型 的赝电容材料,但是基于迈科烯的对称型超级电容 器电压窗口较窄(大约0.6V),这就需要为其匹配



图5 氢离子摇椅式超级电容器工作原理图。

一个高容量的对电极来充分发挥其性能优势。

我们利用电解液中氢醌和醌之间的可逆反应, 以单壁碳纳米管为媒介作为正极匹配Ti₃C₂T_x负极, 使用Nafion质子交换膜分隔正负极电解液。由于氢 醌氧化过程失去电子时会释放氢离子进入溶液,氢 离子向负极迁移同迈科烯反应,这样便构建了氢离 子摇椅式的超级电容器。在2 mV/s的扫描速率下, 碱化处理的单壁碳纳米管的质量比电容从546 F/g提 升到了786 F/g, 而碱化后酸化氧化则达到了1080 F/ g (能量密度285 mAh/g)。组装成全电容后电压窗 口在水系中达到了1.6 V,并且比电容和能量密度 分别达到了176 F/g和62 Wh kg⁻¹。该能量密度在已 报到的文献中处于很高的水平,并且组装的全电容 具有很好的循环稳定性。将其制作成全固态柔性电 容器,两个器件串联后电压窗口达到了3 V,可以 点亮多个并联的LED灯。

3.4.1.6 扫描方式对选区激光熔化成形Inconel 718 合金力学性能影响规律研究

选区激光熔化技术 (Selective Laser Melting, SLM),因具有制造周期短、复杂形状零部件一体 化成形以及个性化定制等特点,近年来在航空航 天、交通运输、人工生物材料以及智能器件制造等 领域得到了快速发展。尽管如此,其特殊工艺所造 成的组织结构不均匀性以及存在大量微米尺度的工 艺缺陷,导致合金力学性能,尤其是疲劳性能的显 著弱化,这些已成为制约SLM成形技术工业化应用 的巨大瓶颈。为了使成形合金满足高致密度、高质 量和优异力学性能的需求,有必要对SLM成形工艺 参数、组织结构、力学性能之间的内在规律开展深 入研究。扫描方式作为SLM成形工艺参数中的一个 重要变量,研究其对合金组织结构和力学性能的影 响规律,显然具有非常重要的意义。

我们针对两种不同扫描方式制备的样品开展了 室温拉伸和室温疲劳性能测试,结果显示,扫描方 式为SS-X(双向扫描)的样品比扫描方式为SS-XY (双向扫描,每层旋转90°)的样品具有更高的拉 伸强度和室温疲劳强度。研究分别从孔洞尺寸与分 布、相组成与枝晶结构、晶粒取向以及晶粒结构四 个方面进行了综合分析,结果表明晶粒尺寸对原始 态SLM成形Inconel 718合金的室温力学性能影响更 加显著。扫描方式为SS-X的样品晶粒尺寸更加细 小,这是造成其力学性能更加优异的主要原因。研 究结果为我们通过设计不同的扫描方式进而实现增 材制造部件不同位置的组织结构和力学性能调控提 供了一定的理论指导。



图6 (a)SLM成形Inconel 718合金室温拉伸工程应力-应变曲线; (b)两种扫描方式制备的合金试样屈服强度和抗拉强度对比; (c)SLM成形Inconel 718合金室温疲劳S-N曲线。

3.4 Advanced Ceramics and Composites Division



DIVISION HEAD: WANG Jingyang

RESEARCH GROUP LEADERS: (5)

WANG Jingyang (Multifunctional Thermal and Environmental Barrier Coatings)
LI Meishuan (Ultra-High Temperature Structure Materials and Protective Coatings)
WANG Xiaohui (Functionalization of Structural Ceramics)
ZHANG Guangping (Thin Films & Small-scale Materials and Mechanical Behavior)
ZHANG Jie (Advanced Nuclear Materials)



3.4.1 Summary of Scientific Activities

The research activities of this division are focused on: multi-scale materials design and structure-property relation of advanced high-temperature structural/functional ceramics and composites; novel processing methods for bulk and low-dimensional (nano-powder and thin film) ceramics and composites; performances and thermal/chemical stability of ceramics and composites under extreme environments (high-temperature, loading, oxidation and corrosion); fabrication of small-scale materials and nanocomposites, size and interface effects, strength-ductility and fatigue & fracture properties.

In 2019, staffs in our division authored and co-authored 46 papers, applied and registered 8 Chinese patents, delivered 30 keynote and invited presentations in international and domestic academic conferences.

Our division focused on fundamental researches of advanced ceramics and composites for extreme environmental applications. We developed new strategies and conducted innovative works on high throughput materials design, novel materials processing technology, advanced microstructural characterization, and rapid property evaluation in harsh environments. Representative advancements are summarized as flowing.

(1) The general trends are disclosed for rare earth silicates corroded by high temperature water vapor and molten oxide (CMAS). A connection between corrosion behavior and rare earth (RE) species were fundamentally established. The results demonstrated a new mechanism of intrinsic corrosion inertness of rare earth silicates under high temperature hot gas and CMAS attacks. A comprehensive database of corrosion resistances was constructed and used to guide the precise design of rare earth elements in advanced thermal and environmental barrier coatings.

(2) The high entropy rare-earth silicates multifunctional thermal and environmental barrier coating materials were developed. The critical thermal and corrosion resistance properties were synergetic optimized through the high entropy effects of rare earth elements.

(3) Multilevel assembly scheme is developed for the elegant fabrication of boron nitride aerogels consisting of varied superstructures, i.e. nanoribbons composed of tiny nanocrystals and nest-like structures tangled by nanofibers. Interestingly, the resultant aerogels exhibit great contrast in their hydrophilicity, which could be attributed to the microstructure difference. The processed BN aerogel also demonstrated extremely low thermal conductivity (0.025 W^{-1} -m/K⁻¹), that provides an opportunity for its super insulator applications in UHT.

(4) Zirconium carbide with controlled stoichiometry was accomplished by Physical Vapor Deposition technique. By means of synchrotron X-ray diffraction as well as first-principle calculations, the 3^{rd} nearest neighboring carbon vacancy pairs was traced in the sub-stoichiometric zirconium carbides and the formation of 3NN VC triplet benefited to lower the energy of defective structure. Moreover, under high radiation damage level, the sub-stoichiometric $ZrC_{0.55}$ exhibited improved radiation tolerance compared with the stoichiometric $ZrC_{0.86}$. It is expected to provide ceramic material screening for Generation IV nuclear power systems.

(5) Effects of air pressure on oxidation of UHTC have been investigated. In 1atm air at 1800 °C, ZrB_2 -20SiC possessed good oxidation resistance; but in 10, 5, 0.5 kPa air, active oxidation of SiC happened adjacent to the oxide/substrate interface, a SiC-depleted layer appeared under the oxide scale, the oxidation resistance became worse with decreasing of air pressure. By adding MSi₂ (M=Mo, Ta and Hf), the oxidation resistance of ZrB_2 -20SiC composite was improved greatly, mainly due to inhibiting the formation of highly volatile products. Based on Wagner's internal oxidation theory, the critical conditions of temperature and oxygen partial pressure were analyzed quantificationally, the synergistic effect of further oxidation of SiO in oxygen gradiently - distributed oxide scale and the vapour pressure of SiO on the oxide surface on the completeness of oxide scale was proposed.

(6) We propose a strategy by integrating a negative electrode of $Ti_3C_2T_x$ MXene and a positive electrode of redoxactive hydroquinone (HQ)/carbon nanotubes. The two electrodes are separated by a Nafion film that is proton permeable in H_2SO_4 electrolyte. Upon charging/discharging, hydrogen ions shuttle back and forth between the cathode and anode for charge compensation. The proton-induced high capacitance of MXene and HQ, along with complementary working voltage windows, simultaneously enhance the electrochemical performance of the device. Specifically, the hybrid supercapacitors operate in a 1.6 V voltage window and deliver a high energy density of 62 Wh kg⁻¹. This work offers the possibility of designing high-energy-density noble-metal-free asymmetric supercapacitors for practical applications.

(7) We have found the relationship between fatigue resistance of Mo/W multilayers and the individual layer thickness. We also found the mechanism thermal fatigue behavior of the nanocrystalline metal influenced by both line thickness and the grain size. A grain-boundary-arrangement related stochastic model has been proposed to understand the fatigue cracking behavior of the Cu/W multilayers. Succeeding in establishing equipment for evaluation of creep properties of small-scale components exposed to high-temperature service conditions. We have clarified the effect of scanning strategy and heat treatment strategies on mechanical properties and high-temperature creep resistance of selective laser melted Inconel 718.

3.4.1.1 Design and Advanced Processing Technology of Multifunctional TEBC

In order to support breakthrough on multifunctional thermal and environmental barrier coating for aviation engines, we disclosed the general trends of rare earth silicates corroded by high temperature water vapor and molten oxide (CMAS). A connection between corrosion behavior and rare earth (RE) species were fundamentally established. The results demonstrated a new mechanism of intrinsic corrosion inertness of rare earth silicates under high temperature hot gas and CMAS attacks. A comprehensive database of corrosion resistances was constructed and used to guide the precise design of rare earth elements in advanced thermal and environmental barrier coatings. Our work further developed the processing techniques of RE-silicate powders for different plasma spraying technologies. This progress has solved the critical bottleneck restriction of RE-silicate powder suppliers from abroad companies. Using home-made REsilicate powders, PS-PVD and APS (atmospheric plasma spraying) technologies were developed to successfully fabricate RE-silicate coatings with the typical columnar microstructure of thermal barrier coating and the typical dense microstructure of environmental barrier coating, respectively. The present work verified our innovative concept of multifunctional TEBC and will contribute to the advancement of a new type of high-temperature resistant



Fig. 1: Database for CMAS corrosion resistances of thermal and environmental coating materials

TEBC with excellent thermal and chemical compatibility. These results have been published in 9 papers in *Corros. Sci., Scripta Mater, Sci. Rep., J. Am. Ceram. Soc., J. Eur. Ceram. Soc., JMST and Mater. China* (Chinese Journal) and applied 3 national invention patents.

3.4.1.2 Cock-tail Effects in the Properties of Multicomponent Rare Earth Silicate Thermal and Environment Barrier Coating Materials

In our previous studies, Ho and Er containing silicates showed remarkable resistance to high temperature water vapor corrosion; and Y and Yb containing silicates exhibited excellent resistance to CMAS (CaO-MgO-AlO_{1.5}-SiO₂) corrosion. Herein, equiatomic quaternary rare earth silicate multicomponent solid solution $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ were studied to explore the synergetic optimization effects of different RE elements. Dense and pure X_2 - $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ solid solution was successfully synthesized by hot press method. HAADF (High-angle annular dark-field) images directly confirmed the compositional and structural homogeneity at the atomic scale, specially four kinds of RE ions are homogenously dispersed on RE lattice sites.

Thermal expansion coefficient of $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ is 11~19% lower than those of the single constituents RE_2SiO_5 (RE=Y, Ho, Er, Yb) and closer to those of Si-based ceramics, which is good to reduce residual tensile thermal stress of as prepared coating. Meanwhile, thermal conductivity at room temperature of $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ decreases 5.4~66.8%, which is attributed to enhanced phonon anharmonic scattering

caused by lattice distortion in complex multicomponent RE-silicate. Besides, the resistances to water vapor and CMAS of $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ are close to and better than the averaged magnitudes of single-constituent RE₂SiO₅. $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$ as a multifunctional TEBC candidate with optimal and balanced properties provides new perspective on the design of TEBC by complex RE-doping route.

3.4.1.3 Design and Characterization of Advanced Radiation-resistant Ceramics

In Generation IV reactors, the structural materials will be exposed to much higher irradiation doses and operated at much higher temperatures. As a result, the lifetime displacement damage levels to core structural materials may approach 200 displacements per atom (dpa), or even higher levels in some concepts. Zirconium carbide is considered as an attractive structural material for new generation reactors operating at high temperature. Besides, zirconium carbide is a typical non-stoichiometric compound with a high carbon vacancy concentration. The microstructure evolution under high-dose irradiation was critical for the feasibility of zirconium carbides in advanced reactors

Accordingly, advanced zirconium carbides have been designed with tuning carbon vacancy characteristics. By means of synchrotron X-ray diffraction as well as First-principle calculations, the structural characteristics and stability of non-stoichiometric zirconium carbide have been identified. The microstructure evolution of zirconium carbides with different stoichiometry induced



Fig. 2: Resistance to (a) water vapor and (b) CMAS corrosion of $(Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})_2SiO_5$.



Fig. 3: Depth profiles of damage level, expressed in displacements per atom (dpa), and implanted ion concentration induced by 3 MeV Au ion irradiation in stoichiometric $ZrC_{0.86}$ and sub-stoichiometric $ZrC_{0.55}$ (Data were calculated using the SRIM code). As well as the representative microstructures of irradiated $ZrC_{0.86}$ and $ZrC_{0.55}$ under the doses of 120 and 180 dpa.

by 3 MeV Au ion irradiation were investigated, over a series of ion fluences ranging from $1 \times E^{14}$ to $2 \times E^{16}$ ions cm⁻². The highly irradiated and virgin regions could be identified as representative microstructures in irradiated ZrC_{0.86} and ZrC_{0.55} under the doses of 120 and 180 dpa, respectively. Compared with the stoichiometric ZrC_{0.86}, the sub-stoichiometric ZrC_{0.55} exhibits improved radiation tolerance. This work provides a practical strategy for the enhancement of irradiation tolerance through the novel concept of defect engineering in lattice.

3.4.1.4 Internal Oxidation of ZrB₂-SiC-MSi₂ Composites at 1800°C in Low Pressure Air

Ultra-high temperature ceramics (UHTC) have great potential applications as structural materials over 1600 [°]C in thermal protection systems and propulsion systems of future hyper-sonic aerospace vehicles. Due to serving at ultra-high temperature in oxidizing environmint, good ablation/oxidation resistance is required for UHTC. Up to now, ultra-high temperature oxidation of UHTC has not been investigated systematically because of the limitation



Fig. 4: Schematic illustrations of external / internal oxidation and various interface reactions of (a) ZrB_2 -20SiC and (b) ZrB_2 -20SiC-MoSi₂ during oxidation at 1800 °C in 0.5 and 5, 10 kPa air.

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of experimental techniques. Especially, the investigations about the effects of air pressure (i.e oxygen partial pressure) are very limited. Therefore, it is significant to further understande oxidation mechanism of UHTC at ultra-high temperatures.

By using the gas-contrable ultra-high temperature oxidation facility established in our laboratory, effects of air pressure on oxidation of ZrB,-20SiC-xMSi, (M=Ta, Mo and Hf, x=0 \sim 10 vol.%) composites at 1800°C have been investigated. In 1atm air, ZrB,-20SiC possessed good oxidation resistance; but in 10, 5, 0.5 kPa air (the corresponding oxygen partial pressure was, 2, 1 and 0.1 kPa, respectively), active oxidation of SiC happened adjacent to the oxide/substrate interface, a SiC-depleted layer appeared under the oxide scale, the oxidation resistance became worse with decreasing of air pressure. The addition of MoSi, improved the oxidation resistance of ZrB₂-20SiC composite, mainly inhibited internal oxidation in 10 kPa air, greatly reduced the thicknesses of internal oxidation layers formed in 5 and 10 kPa air. This was attributed to the reactions of MoSi₂ with ZrB₂ and highly volatile B₂O₃ to form stable MoB, causing the formation of a continuous, compact and silica-rich outer oxide layer with lower oxygen permeability.

In this work, effects of air pressure on oxidation of UHTC have been explored, the critical conditions of temperature and oxygen partial pressure were analyzed quantificationally based on Wagner's internal oxidation theory, the synergistic effect of further oxidation of SiO in oxygen gradiently-distributed oxide scale and the vapour pressure of SiO on the oxide surface in air with different pressures on the completeness of oxide scale was proposed.

This work was published in Corros. Sci. 157 (2019) 87.

3.4.1.5 Hydrogen-Ion-Rocking-Chair Hybrid Supercapacitor

MXenes have emerged as promising high-volumetriccapacitance supercapacitor electrode materials, whereas their voltage windows are not wide. This disadvantage prevents MXenes from being made into aqueous symmetric supercapacitors with high energy density. To attain high energy density, constructing asymmetric supercapacitors is a reliable design choice. Here, we propose a strategy to achieve high energy density of hydrogen ion aqueous-based hybrid supercapacitors by integrating a negative electrode of $Ti_{A}C_{A}T_{A}$ MXene and a positive electrode of redox-active hydroquinone (HQ)/carbon nanotubes. The two electrodes are separated by a Nafion film that is proton permeable in H₂SO₄ electrolyte. Upon charging/discharging, hydrogen ions shuttle back and forth between the cathode and anode for charge compensation. The proton-induced high capacitance of MXene and HQ, along with complementary working voltage windows, simultaneously enhance the electrochemical performance of the device. Specifically, the hybrid supercapacitors operate in a 1.6 V voltage window and deliver a high energy density of 62 Wh kg⁻¹, which substantially exceeds those of the state-of-theart aqueous asymmetric supercapacitors reported so far. Additionally, the device exhibits excellent cycling stability



Fig. 5: Assembly of all-solid-state MXene//CNT-HQ hybrid supercapacitors. (a) Schematic and CV curves of the two hybrid supercapacitors connected in parallel. (b) Schematic and CV curves of the two hybrid supercapacitors connected in series. (c) Two MXene//CNT-HQ hybrid supercapacitors connected in series can drive a set of green light-emitting diodes.

and the all-solid-state planar hybrid supercapacitor displays exceptional flexibility and integration for bipolar cells to boost the capacitance and voltage output. These encouraging results provide the possibility of designing high-energy-density noble-metal-free asymmetric supercapacitors for practical applications.

3.4.1.6 Effect of Scanning Strategy on Mechanical Properties of Selective Laser Melted Inconel 718

Selective laser melting (SLM) is one of the promising additive manufacturing (AM) technologies, which is capable of fabricating near-net shape metallic components with geometrically complex structures. Despite many advantages, SLM process still faces a lot of challenges that need to be addressed prior to widespread industrial application. Two main challenges are microstructure heterogeneities and randomly dispersed defects, which result in the uncertainty and degradation in mechanical properties, especially fatigue properties. To obtain the final components with high density and optimal mechanical properties, many efforts have been devoted to optimize the processing parameters, such as laser energy density, building orientation, and scanning strategy. Besides, it is urgent to build up the relationships among the process, microstructure and mechanical properties. Scanning strategy is an important variable that significantly affects the thermal history during the SLM process and further influences the specimen density, residual stress and evolution of the microstructures, ultimately changes the mechanical properties.

In this work, two types of scanning strategies of SLM, i.e. bidirectional scanning without (SS-X) and with a 90°-rotation (SS-XY) for every layer, were adopted to produce the Inconel 718 specimens. The results show that tensile strength and fatigue strength of SS-X specimens are superior to that of the SS-XY ones. Such excellent mechanical properties of the SS-X specimens at room temperature were found to mainly result from the processing-induced fine grain structures compared with void size, grain orientation or dendrite structure. The above findings would be helpful to realize site-specific control of the grain structure and mechanical properties by tailoring the scanning strategy during the SLM process.



Fig. 6: Band contrast (BC) maps showing grain structure of the (a) SS-X and (b) SS-XY specimens from the YZ cross section, insets in (a) and (b): pole figures of the SSX and SS-XY specimens, respectively, high-magnification SEM backscatter electron images of the dendrite structure of the (c) SS-X and (d) SS-XY specimens.

3.5 先进炭材料研究部



研究部主任: 成会明

研究组负责人(5人)

- 刘 畅 (碳纳米管的可控制备与应用)
- 任文才 (石墨烯等二维材料)
- 孙东明 (纳米碳基柔性电子器件)
- 李 峰 (新型电化学能源材料与器件)
- 刘 岗 (先进能量转换材料与器件)

3.5.1 研究工作简述

先进炭材料研究部的主要研究领域包括:碳纳米管、石墨烯等二维材料的制备、性能与应用;纳米 碳基柔性电子器件;新型电化学能源材料与器件;先进能量转换材料与器件;碳合金及碳-陶瓷基防隔热 复合材料。

重点开展碳纳米材料及其复合材料、高性能块体炭材料、能量存储与转换材料与器件等的制备、性 能及应用研究。力争突破先进炭材料的结构设计原理与可控制备方法等关键科学技术问题,推动其在新 能源、柔性光电器件、航空航天、国家安全等领域的实际应用。

本年度累计在国内外学术期刊上发表SCI收录论文98篇。共有45人次参加在意大利、澳大利亚、新西 兰、德国、日本、韩国、中国等地召开的国际学术会议,其中特邀报告36人次,口头报告4人次。申请国 家发明专利35项,实用新型1项,获得专利授权23项。

2019年度取得的主要研究进展包括:

(1)研制出一种氮掺杂碳包覆Ni@单壁碳纳米管双功能电催化材料,当外加1.57 V电压时,即可实现10 mA cm⁻²电流密度的全分解水,可望用于电化学分解水制氢及金属-空气电池等新型能源器件。

(2)发展了一种液态碳源淬火法,实现了纳米晶石墨烯的超快制备;提出了液/固复合基体CVD方法,制备出英寸级均一AB堆垛的双层石墨烯薄膜。推动了石墨烯等二维材料薄膜控制制备技术的发展与性能调控研究。

(3) 首次制备出一种以肖特基结作为发射结的垂直结构的硅-石墨烯-锗晶体管,使器件总延迟时间 缩短了1000倍以上,将器件的截止频率由约1.0 MHz提升至1.2 GHz,为最终实现超高速晶体管奠定了基础。

(4)发现固/固界面双电层可有效抑制离子浓度梯度及电场驱动的自放电,采用固/固界面电极构筑 了双石墨烯锂离子电容器,其兼具高能量密度、高功率密度及长循环寿命,为发展高性能超级电容器提供了新思路。

(5)制备出一种均相C/N掺杂的TiO₂材料,其光吸收边整体红移至500纳米,且电子传输能力显著提高,在波长大于450纳米的可见光下表现出光催化氧化水放氧能力。

3.5.1.1 氮掺杂碳包覆Ni@单壁碳纳米管双功能电催化材料的制备与性能

电化学分解水被认为是最有效的制氢方法之 一。但由于氢生成反应和氧生成反应的动力学缓 慢,故需使用贵金属如铂、铱、钌等作为催化剂。 但这些贵金属储量低、成本高、不可持续,因而极 大限制了电化学分解水制氢及燃料电池、金属-空 气电池等相关器件的实用化进程。

针对以上问题,我们利用浮动催化剂化学气相 沉积法制备的碳纳米管在反应器中随载气浮动,且 纳米金属催化剂供给量易于调控这一特征,直接制 备出碳包覆纳米金属颗粒锚固于单壁碳纳米管网络 的复合薄膜。具体地,以二茂镍为催化剂前驱体, 通过调控催化剂含量及优化碳纳米管生长的热力学 和动力学条件,实现了碳包覆Ni纳米颗粒锚固于单 壁碳纳米管网络复合结构的可控制备。在反应器尾 端设置不锈钢网,实现了膜厚可调的碳包覆镍/单 壁碳纳米管(Ni@C/SWCNT)复合膜的收集。将该 薄膜在NH3气氛下热处理,在包覆的碳层及单壁碳 纳米管管壁上掺杂氮原子,最终获得了氮掺杂碳包 覆Ni颗粒锚固于单壁碳纳米管网络的薄膜 (-Ni@ N-C/SWCNT)。其中,Ni颗粒的尺寸小(2-5 nm) 且分布均匀, 表面包覆的碳层基本为单层; 包覆碳层既可抑制Ni颗粒的团聚,又可通过与单 壁碳纳米管管壁的π-π相互作用提高电子传输。 研究发现氮掺杂碳包覆Ni/单壁碳纳米管复合自支 撑薄膜具有优异的氢析出和氧析出性能、其达到 10 mA cm⁻²电流密度的过电势分别为190 mV和270 mV。当外加1.57V电压时,即可实现10 mA cm⁻² 电流密度的全分解水。相关论文发表在Adv. Sci. 6 (2019) 1802177



图1 (a)NCNi/SWCNT薄膜的制备过程示意图;(b)柔性自支撑NCNi/SWCNT薄膜的光学照片;(c)本研究与已报道镍基双功 能电催化剂达到10 mA cm⁻²电流密度所需电压的比较。

3.5.1.2 纳米晶石墨烯与双层石墨烯的控制制备及 物性

晶界、层数和堆垛方式是石墨烯最重要的三 个结构特征。由于大量晶界的存在,纳米晶石墨烯 有望展现出与单晶和多晶石墨烯不同的物理化学性 质,极具理论和应用研究价值,而AB堆垛的双层 石墨烯具有电场可调的带隙、偶数分母分数量子霍 尔效应等多种新奇物性,在电子、光电子和自旋电 子学领域有重要应用前景。然而,上述两种石墨烯 材料均难以通过传统CVD方法来获得。

本研究打破CVD方法制备石墨烯薄膜的传统

思路,提出了全新的液态碳源淬火法,实现了石墨 烯薄膜的秒级超快制备,并首次制备出平均晶粒尺 寸达3.6 nm的纳米晶石墨烯,同时发现在纳米尺度 晶粒尺寸对电学性质的影响巨大,导致了带隙的打 开,而对力学性质的影响较小,与单晶石墨烯相比 仍保持了约60%的强度和模量。这种液相前驱体淬 火方法也为制备传统石墨烯材料及其他纳米晶二维 材料提供了可能。

我们提出了液/固复合基体CVD方法,以液态 Pt₃Si/固态Pt基体为例,制备出英寸级均一AB堆垛 的双层石墨烯薄膜,其具有与机械剥离的样品可比 拟的高结晶质量及优异的电学和力学性质。进一步



图2 液态碳源淬火法制备的纳米晶石墨烯及其性能。

研究发现,石墨烯晶核在液态基体表面移动所需要 克服的势垒要远低于固态基体表面,因而由固态基 体析出形成的第二层在液态基体表面会以先期形成 的第一层为模板外延形成能量上最为稳定的AB堆 垛结构。这种层间外延生长方法为制备具有特定堆 垛结构的多层石墨烯及其他二维材料提供了一个基 本策略。

上述结果在Nat. Commun.上发表论文2篇,推动了石墨烯等二维材料薄膜控制制备技术的发展与性能调控研究。

3.5.1.3 硅-石墨烯-锗高速晶体管

1947年,第一个双极结型晶体管(BJT) 诞生 于贝尔实验室,标志着人类社会进入了信息技术 的新时代。在过去的几十年里,提高BJT的工作频 率一直是人们不懈的追求,异质结双极型晶体管 (HBT)和热电子晶体管(HET)等高速器件相继



图3 硅-石墨烯-锗晶体管的设计和制备。(a) 通过垂直堆垛技 术构筑的硅-石墨烯-锗晶体管;(b) 器件光学照片(标尺:20 μm);(c) 扫描电子显微镜照片(标尺:4 μm);(d) 晶体管 截面图;(e) 器件原理示意图。

被研究报道,但难以进一步提高。石墨烯是一种性 能优异的二维材料,人们提出使用石墨烯作为基区 材料制备晶体管,其原子级厚度将消除基区渡越时 间的限制,同时其超高的载流子迁移率也有助于实 现高质量的低阻基区。已报道的石墨烯基区晶体管 普遍采用隧穿发射结,然而隧穿发射结的势垒高度 严重限制了该晶体管作为高速电子器件的发展前 景。

我们采用半导体薄膜和石墨烯转移工艺,首次 提出了以肖特基结作为发射结的垂直结构的硅-石 墨烯-锗晶体管。与已报道的隧穿发射结相比,硅 -石墨烯肖特基结表现出目前最大的开态电流(692 A cm⁻² @ 5V)和最小的发射结电容(41 nF cm⁻²),从 而得到最短的发射结充电时间(118 ps),使器件总 延迟时间缩短了1000倍以上(128 ps),可将器件的 截止频率由约1.0 MHz提升至1.2 GHz。通过使用掺 杂较重的锗衬底(0.1 Ω cm),可实现共基极增益接 近于1且功率增益大于1的晶体管。基于实验数据的 建模预示该器件具备了工作于太赫兹领域的潜力。 该项研究工作极大地提升了石墨烯基区晶体管的性 能,为未来最终实现超高速晶体管奠定了基础,相 关研究结果发表于Nat. Commun. 10(2019)4873。

3.5.1.4 炭材料固/固界面双电层的形成及其电化 学过程探索

铝双电层形成规律,特别是在有机体系下, 对材料的电化学性能发挥至关重要。固/液电极形 成的双电层电压窗口窄、自放电速率高,显著制约 了材料的能量密度及能量效率。我们利用双氟草酸 硼酸锂的还原反应,对多种炭材料进行了电化学 包覆,构筑了高离子电导及纳米级的固/固电极界 面,实现了对双电层电位区间的拓宽。通过对固/ 固电极界面的形成机理及传质过程进行深入研究, 提出了新的固/固界面双电层模型,并探讨了其电 化学过程。

与固/液界面双电层相比,固/固界面双电层由 去溶剂化的离子吸附在电极表面形成,由于离子与 表面之间减少了溶剂分子形成的溶剂壳,具有更小 的分隔距离及更强的相互作用,因此固/固界面双 电层可提高材料的比电容。通过对电化学包覆前后 的石墨烯电极进行自放电表征及分析,发现固/固 界面双电层可有效抑制离子浓度梯度及电场驱动的 自放电过程。采用固/固界面电极构筑了石墨烯锂 离子电容器,其兼具高能量密度、高功率密度及长



图4(a)各种碳电极的电化学覆层装置及充放电过程;(b)固液(SL-EDL);(c)固固(SS-EDL)界面电双层模型示意图。

循环寿命,同时能量效率也得到显著提高。

以上工作有利于促进有机电解液体系下的双电 层机理研究,为发展高性能的超级电容器提供了新 的设计思路。

3.5.1.5 具有可见光光催化氧化水活性的均相碳/ 氮掺杂TiO₂

异质原子掺杂可以改善金属氧化物光催化材料的吸光范围与电荷传输特性。传统掺杂方法要 经过金属-氧键断裂和金属-掺杂原子键形成两个步 骤,增加了调控掺杂原子含量和空间分布的难度, 限制了预期目标的实现。拓扑相变是基于与金属氧 化物含有相同基本单元的前驱体,通过改变基本单 元取向、释放额外原子制备特定形貌与结构的金属 氧化物的方法,残留的额外原子可掺杂在金属氧化 物中。通过调控拓扑相变的条件,控制额外原子的 释放过程,可以对掺杂含量和空间分布进行有效调 控。

我们以草酸钛为起始材料,在氨气(NH₃)气氛 中使其拓扑相变为锐钛矿相TiO₂,利用NH₃的还原 性抑制草酸钛中C原子的释放,并利用草酸钛层状 结构中的一维通道作为N原子掺杂的扩散通道,制 备出均相C/N掺杂的TiO₂。由于C和N的2p能级高于 O的2p,均相C/N掺杂提高了TiO₂价带顶缩小了带 隙,使其光吸收边整体红移至500纳米;同时C和 N的电负性较O更低,对电子的束缚能力低,均相 C/N掺杂显著提高了TiO₂的电子传输能力,从而使 均相C/N掺杂TiO₂在波长大于450纳米的可见光下具 有光催化氧化水放氧的能力。相关研究内容发表在 Adv. Funct. Mater. 29 (2019) 1901943。



图5 正交结构的草酸钛晶胞结构在氨气气氛中经过热处理拓扑相变为碳、氮掺杂的四方结构锐钛矿TiO2。



3.5 Advanced Carbon Division

DIVISION HEAD: CHENG Huiming

RESEARCH GROUP LEADERS: (5)

LIU Chang (Synthesis and Applications of Carbon Nanotubes) REN Wencai (Graphene and Other 2D Materials) SUN Dongming (Nanocarbon-based Flexible Electronic Devices) LI Feng (Novel Electrochemical Energy Storage Materials and Devices) LIU Gang (Advanced Eenergy Conversion Materials and Devices)



3.5.1 Summary of Scientific Activities

The research activities in the Advanced Carbon Division are focused on: Preparation, property and application of carbon nanotubes, graphenes and other 2D materials; nanocarbon-based flexible electronic devices; novel electrochemical energy storage materials and devices; advanced energy conversion materials and devices; advanced bulk carbon and carbon-based composite materials.

The main progresses made in 2019 are as follows:

(1) We prepared a single-wall carbon nanotube film decorated with N-doped carbon-encapsulated Ni nanoparticles as a bifunctional electrocatalyst. When used as anode and cathode for overall water electrolysis, a current density of 10 mA cm⁻² was achieved at an applied potential of 1.57 V, showing excellent catalytic performance and potential for use in metal-air batteries.

(2) We developed a liquid-phase quenching method that enables ultrafast growth of nanocrystalline graphene films within a few seconds. Wafer-scale continuous uniform AB-stacked bilayer graphene films were prepared on a specifically-designed liquid Pt₃Si/solid Pt substrate by chemical vapor deposition. These works push forward the control over the structure and properties of graphene and other 2D materials.

(3) A silicon-graphene-germanium transistor was fabricated. Compared with the previous tunnel emitters, the oncurrent of the Si-Gr Schottky emitter shows the maximum on-current and the smallest capacitance, leading to a delay time more than 1,000 times shorter. Thus the alpha cut-off frequency of the transistor is expected to increase from about 1 MHz by using the previous tunnel emitters to above 1 GHz by using the current Schottky emitter.

(4) We found that the self-discharge driven by ion concentration gradients and potential can be effectively restricted inside the solid/solid electric double-layers. A dual-graphene lithium ion capacitor was constructed by solid/solid interfacial electrode, which shows a high energy density and power density coupling with long cycle life and high energy efficiency. These studies will promote the understanding of electric double-layer mechanisms in organic systems and provide guidance for the design of high-performances cells.

(5) Homogeneous doping of substitutional carbon/nitrogen for oxygen in the TiO_2 decahedral plates with a dominant anatase phase is obtained for the first time. The resultant $\text{TiO}_{2-x}(\text{CN})_y$ with an unusual band-to-band visible light absorption spectrum and enhanced electron transport ability can induce photocatalytic water oxidation to release oxygen under visible light irradiation. This work provides not only a promising visible light–responsive TiO_2 photocatalyst but also an important strategy for developing other solar-driven photocatalysts.

3.5.1.1 Single-wall Carbon Nanotube Film Decorated with N-doped Carbon-encapsulated Ni Nanoparticles as a Bifunctional Electrocatalyst for Overall Water Splitting

Electrochemical water splitting is considered as one of the most reliable and efficient ways for the production of clean, renewable and sustainable hydrogen energy, which is based on two half reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Currently, the state-of-the-art catalysts are based on noble metals, including Pt, Ir and Ru. However, their low abundance, high cost and non-sustainability have seriously impeded their wide use in fuel cells, air-metal batteries and other related energy storage/conversion devices.

Here, we prepare binder-free and flexible films of Ni/SWCNT hybrid materials containing very small Ni particles encapsulated in monolayer carbon decorated on a network of high-quality SWCNTs by a one-pot floating catalyst chemical vapor deposition technique. These flexible Ni/SWCNT films are heat-treated under an NH₃ environment to dope carbon matrix with nitrogen atoms. As shown in Fig.1(a), the ultrafine nanoparticles are entirely encapsulated by a single shell of carbon and well attached on SWCNTs, which forms an interconnected network. These Ni@N-C/SWCNT free-standing films



Fig. 1: (a) Typical TEM image of the Ni@N-C/SWCNT films. (b) Photograph of an alkaline electrolyzer setup using self-standing rods of Ni@N-C/SWCNT films as anode and cathode. (c) LSV curves of Pt/C-Ir/C and Ni@N-C/SWCNT pairs on nickel foam in 1 M KOH solution for overall water splitting at a scan rate of 5 mV s⁻¹.

were used for bifunctional overall water splitting. A typical film showed overpotentials of 190 mV and 270 mV to reach a current density of 10 mA cm⁻² for HER and OER, respectively. When two free-standing Ni@N-C/SWCNT rod shaped electrodes were used as anode and cathode for overall water electrolysis, a current density of 10 mA cm⁻² was achieved at an applied potential of 1.57 V, showing excellent electrocatalytic performance.

3.5.1.2 Controlled Synthesis and Properties of Nanocrystalline Graphene and AB-stacked Bilayer Graphene

Nanocrystallization is a well-known strategy to dramatically tune the properties of materials, however, the grain size effect of graphene at nanometer scale

remains unknown experimentally because of the lack of nanocrystalline graphene samples. We report an ultrafast growth of graphene films within a few seconds by quenching a hot metal foil in liquid carbon source. Using Pt foil and ethanol as examples, four kinds of nanocrystalline graphene films with average grain sizes of ~3.6, 5.8, 8.0 and 10.3 nm are synthesized. It is found that the effect of grain boundary becomes more pronounced at nanometer scale. In comparison with pristine graphene, the 3.6-nmgrained film retains high strength (101 GPa) and Young's modulus (576 GPa), while its electrical conductivity is declined by over 100 times, showing semiconducting behavior with a bandgap of ~50 meV. This liquid-phase quenching method opens possibilities for ultrafast synthesis of typical graphene materials and other twodimensional nanocrystalline materials.



Fig. 2: A wafer size AB-stacked bilayer graphene film and its electrical property.

Large-area high-quality AB-stacked bilayer graphene films are highly desired for the applications in electronics, graphene with variable photonics and spintronics. However, the existing growth methods can only produce discontinuous bilayer stacking orders because of the nonuniform surface and strong potential field of the solid substrates used. We report the growth of wafer-scale continuous uniform AB-stacked bilayer graphene films on a specifically-designed liquid Pt,Si/solid Pt substrate by chemical vapor deposition. The films show quality, mechanical and electrical properties comparable to the mechanically exfoliated samples. Growth mechanism studies show that the second layer is grown underneath the first layer by precipitation of carbon atoms from the solid Pt, and the small energy requirements for the movements of graphene nucleus on the liquid Pt₃Si enables the interlayer epitaxy to form energy-favorable AB-stacking. This interlayer epitaxy also allows the growth of ABAstacked trilayer graphene and is applicable to other liquid/ solid substrates.

3.5.1.3 A Vertical Silicon-graphene-germanium Transistor

In 1947, the first transistor, named a bipolar junction

transistor (BJT), was invented in the Bell Laboratory and has since led to the new age of information technology. In the past decades, there has been a persistent demand for higher frequency operation for a BJT, leading to the inventions of new devices such as heterojunction bipolar transistors (HBT) and hot electron transistors (HET). The HBTs have achieved great development towards the terahertz operation, however their cut-off frequency is ultimately limited by the base transit time, while for the HETs the demand of a thin base without pinholes and with a low base resistance usually causes difficulties in material selection and fabrication. Recently, graphene has been proposed as a base material to form graphene-base transistors (GBT). Because of the atomic thickness, the graphene base is almost transparent to electron transport leading to a negligible base transit time. At the same time, the remarkably high carrier mobility of graphene will benefit the base resistance compared with a thin bulk material. So far, the GBTs generally use a tunnel emitter which emits an electron through an insulator. However, the emitter potential barrier height will limit the cut-off frequency seriously. Theoretical study has indicated that a Schottky emitter may solve this potential barrier limitation.

Here, we report a graphene-base transistor with a Schottky emitter, i.e. a silicon-graphene-germanium



Fig. 3: Schottky emitter of the Si-Gr-Ge transistor. (a) A typical I-V characteristic of the top Si-Gr emitter junction at room temperature showing an obvious rectifying behavior. (b) Temperature-dependent characteristics of the current. An Arrhenius plot at a voltage of 0.1 V gives a Schottky barrier height of 0.64 eV at room temperature. (c) Comparison of the on-currents of graphene-base transistors with different emitters. The Si-Gr Schottky emitter shows a current of 692 A cm² at 5 V. (d) Comparison of alpha cut-off frequency of graphene-base transistors with different emitters. The one with the Si-Gr Schottky emitter shows the best cut-off frequency of 1.2 GHz.

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transistor. Using semiconductor membrane and graphene transfer, we stacked three materials including an n-type top single-crystal Si membrane, a middle single-layer graphene (Gr) and an n-type bottom Ge substrate. Compared with the previous tunnel emitters, the on-current of the Si-Gr Schottky emitter shows the maximum on-current and the smallest capacitance, leading to a delay time more than 1,000 times shorter. Thus the alpha cut-off frequency of the transistor is expected to increase from about 1 MHz by using the previous tunnel emitters to above 1 GHz by using the current Schottky emitter. THz operation is expected using a compact model of an ideal device. With further engineering, the vertical semiconductor-graphenesemiconductor transistor is promising for high-speed applications in future 3D monolithic integration because of the advantages of the atomic thickness and high carrier mobility of graphene, and the high feasibility of a Schottky emitter.

3.5.1.4 Structure and Electrochemical Properties of a Double Layer Formed at a Solid/Solid Electrode Interface

Understanding the electric double layer is essential to improve the electrochemical performance of related devices. Conventional solid/liquid interfacial electric double layer often suffers from a narrow voltage window and a serious self-discharge, which limits the energy density and efficiency achieved. We construct a high ionicconducting and nanometer solid/solid electrode interface by electrochemical coating with lithium difluoro (oxalate) borate, which widens the stable potential window. Through in-depth study on the formation and charge-transfer mechanism of this solid/solid interface, we propose a novel electric double-layer model and discuss its electrochemical performance.

The solid/solid electric double-layer is formed with desolvated ions. Compared with a solid/liquid electric double layer, due to the absence of solvent shell, there is a smaller separation distance and stronger interaction between the ions and surface. Therefore, the solid/solid electric doublelayer has an effect of capacitance enhancement. Through characterizing and analyzing the self-discharge behaviors of electrodes, we find that the self-discharge driven by ion concentration gradients and potential can be effectively restricted inside the solid/solid electric double-layers. A dual-graphene lithium ion capacitor was constructed by solid/solid interfacial electrode, which shows a high energy density and power density coupling with long cycle life and high energy efficiency. These studies will promote the understanding of electric double-layer mechanisms in organic systems and provide guidance for the design of high-performances cells.



Fig. 4: (a) Schematic of a traditional GLIC. (b) Schematic of a SS-GLIC. (c) Voltage drop and energy efficiency of a GLIC and SS-GLIC during self-discharge tests after charging to 4.3 V. (d) Relationship of energy density and power density for various electrochemical energy-storage systems. (e) Cycling stability of a SS-GLIC in the range of 0-4.3 V.

3.5.1.5 Homogenous Doping of Substitutional Nitrogen/Carbon in TiO₂ Plates for Visible Light Photocatalytic Water Oxidation

Doping can extend the light absorption range of widebandgap photocatalysts into the visible light region, which is significant in terms of fully harvesting and converting solar light. The desirable band-to-band redshift of the absorption edge of semiconducting binary metal oxides, such as a prototypical photocatalyst TiO₂, by doping is long targeted but remains a challenge, up to date. Besides the species of dopants, their spatially homogenous distribution in materials for the indispensable long-range interaction of the dopants with intrinsic bulk atoms is equally crucial in enabling the bandgap narrowing (a desirable band-toband visible light absorption spectrum is formed in this situation). Here, by taking the advantage of abundant 1D diffusion channels with rhombus-like cross-sections along the c-axis in the crystal structure of titanium oxalate hydrate to promote the entrance of nitrogen dopant species into the bulk and subsequent thermal topotactic transition in an atmosphere of gaseous ammonia, homogeneous doping of substitutional carbon/nitrogen for oxygen in the TiO₂ decahedral plates with a dominant anatase phase is obtained for the first time. The resultant $TiO_{2-x}(CN)_{y}$ with an unusual band-to-band visible light absorption spectrum and enhanced electron transport ability can induce photocatalytic water oxidation to release oxygen under visible light irradiation. This study (Adv. Funct. Mater. 29 (2019) 1901943) provides not only a promising visible light-responsive TiO, photocatalyst, but also an important strategy for developing other solar-driven photocatalysts.



Fig. 5: (a) UV–visible absorption spectra of three TiO_2 samples (the $\text{TiO}_{2-x}(\text{CN})_y$ with the homogeneous doping of nitrogen and carbon, the $\text{TiO}_{2-x}(\text{CN})_y$ with the nonhomogeneous doping of nitrogen and carbon (denoted as $\text{TiO}_{2-x}(\text{CN})_y$ -ref.) prepared by heating the $\text{TiO}_{2-x}(\text{CN})_y$ sample in air and the undoped TiO_2 sample prepared by the thermal topotactic transition of titanium oxalate hydrate in air). (b) I–V curves measured from a single particle of $\text{TiO}_{2-x}(\text{CN})_y$ or TiO_2 . The inset is the schematic of using two tungsten probes as electrodes to contact a particle to record its I–V curve, which was performed in a scanning electron microscope.



3.6 生物基材料与仿生构筑研究部

研究部主任: 张劲松

研究组负责人(5人)

张劲松(多糖纳米材料的非对称构筑) 杨振明(多孔材料仿生构筑与多孔场效应) 杨永进(复合材料的低成本跨尺度构筑) 矫义来(结构化催化材料) 张军旗(功能化高能金属)



3.6.1 研究工作简述

生物基材料与仿生构筑研究部主要研究领域包括:(1)多糖纳米材料的非对称构筑;(2)多孔材料仿 生构筑与多孔场效应;(3)复合材料的低成本跨尺度构筑;(4)结构化催化材料;(5)功能化高能金属。

本研究部在2019年度中,各PI方向的研究工作取得的进展如下:

自主开发了一种纤维素基元晶体(CECs)作为Pd催化剂的载体,将接近0价的Pd原子以低配位数原 位固定在特定的晶面上,获得了一种兼具高活性和高稳定性的Pd-CECs单原子催化剂。

引入"超材料"设计思路,结合电磁仿真,从微观到宏观尺度开展了不同基材的图案化电磁协同和 不同结构的梯度化阻抗匹配研究,研制了适于各种极端环境的多孔吸波材料,进一步拓展了吸波材料在 电磁控制领域的应用。

研制成功螺旋挤出式微波反应器。该连续式微波反应系统克服了釜式微波反应器微波有效穿透深度 不足的问题,微波能量可以被反应物料均匀有效地吸收利用,同时反应能够连续进行,并易于控制反应 参数,优化实验过程,满足连续化和自动控制的需求,具有良好的工业化应用前景。

以催化剂载体结构设计为突破口,通过在多孔碳化硅载体表面生长纳米碳化硅晶须提高其比表面 积;通过原位水热合成技术在碳化硅晶须表面生长纳米阵列过渡金属氧化物进一步提高催化剂利用率。 结果表明,泡沫碳化硅原位生长碳化硅晶须显著提高催化剂负载量,并暴露特征活性晶面,表现出良好 的催化活性和水热稳定性。

重点开展了含硼铝基贮氢复合燃烧剂(MgAlB系)的应用研制和外场试验测试。根据H、Mg、Al、 B梯级促燃的释能机制,在粉体制备过程中加入较高比例的无定形硼粉。实现了粉体理论能量水平的显著 提升,同时保障了铝、硼的高效燃烧,达到了实测能量水平大幅提升的目的。

3.6.1.1 耐极端环境、轻质、宽频多孔吸波材料

电磁波吸收材料(简称吸波材料)广泛应用 于电磁隐身、电磁屏蔽、电磁兼容等领域。为满足 实用化需求,吸波材料不仅要具有轻质、宽频吸波 特性,更要适应于高温、超低温、烧蚀、强振动等 极端环境。采用模板法和浆料发泡法研制了适于各 种极端环境的多孔吸波材料,并引入"超材料"设 计思路,结合电磁仿真,从微观到宏观尺度开展了 不同基材的图案化电磁协同和不同结构的梯度化阻 抗匹配研究。研制了介电损耗型和磁损耗型不同基 材的多孔双马树脂吸波材料,材料比重0.3g/cm³, 适用于-50℃~150℃的强振动环境。将不同电磁损 耗型多孔双马树脂材料进行多尺度图案化组合,实 现了500MHz-18GHz,即跨越厘米波和分米波波段 的超宽频带高效吸波。研制了开孔型和闭孔型不 同结构的多孔碳化硅吸波材料,材料比大约0.5g/ cm³,不同孔型结构多孔碳化硅材料适用不同环 境,均满足耐高温烧蚀(800℃~1500℃)性能要 求。通过表面开槽匹配设计,多孔碳化硅材料均可 实现1.5GHz-18GHz宽频带高效吸波。研制了多孔 碳泡沫吸波材料,材料比重大约0.45g/cm³,适用于 -190℃超低温环境,通过尖锥匹配结构设计,满足 暗室材料吸波要求。



图1(a)多孔双马树脂吸波材料及其性能;(b)多孔碳化硅材料及其吸波性能;(c)多孔碳吸波材料暗室箱吸波性能。



图2螺旋挤出连续式微波反应器。

3.6.1.2 螺旋挤出连续式微波反应系统

反应过程强化是化工过程强化的核心内容, 微 波强化技术是利用微波与反应体系中偶极子或者带 电粒子的交互作用以及微波对材料的选择性加热效 应,能够大幅度地提高反应速率,提高目标产物选 择性,显著减少污染,实现反应过程强化目标。针 对高黏度高腐蚀性反应液体存在的共性问题。

我们研制成功螺旋挤出式微波反应器。采用 矩形微波多模行波设计,反应器外侧为矩形屏蔽箱 体,反应器中心为透波立柱容器,立柱容器中内置 螺杆,反应物料在螺杆的螺旋槽中连续通过;电磁 场绕中心的立柱容器扩散展开,并被立柱容器内的 螺杆中通过的反应物料吸收,产生"内摩擦热"使 反应物料温度迅速升高,完成化学反应。建立包括 控制系统、螺旋挤出式微波反应器、进料器、螺杆 转动控制系统、原料罐和产品罐等主要部分的连续

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式微波反应系统。连续式微波反应系统克服了釜式 微波反应器微波有效穿透深度不足的问题, 微波能 量可以被反应物料均匀有效地吸收利用, 同时反应 能够连续进行, 并易于控制反应参数, 优化实验过 程, 满足连续化和自动控制的需求, 因此具有良好 的工业化应用前景。

3.6.1.3 纳米阵列结构化催化剂

结构化催化剂设计的初衷是通过催化剂载体材 料选择、结构设计和催化剂活性组分优化,实现催 化剂设计和反应器设计的结合,达到单位体积催化 剂最佳的催化效率。但基于宏观多孔催化剂载体和 涂覆方法制备的结构化催化剂存在流场不合理和催 化剂利用率低的问题,限制了其性能的发挥。

本工作通过在多孔碳化硅载体表面生长纳米碳 化硅晶须提高其比表面积;通过原位水热合成技术



图3 (a)纳米阵列钴锰氧化物结构化催化剂孔结构分布; (a1)、(a2)钴锰氧化物断面形貌; (a3) 纳米阵列钴锰氧化物结构化催 化剂实物图; (b)三种催化剂催化活性对比; (c) 纳米阵列钴锰氧化物结构化催化剂的水热稳定性。 在碳化硅晶须表面生长纳米阵列过渡金属氧化物, 进一步提高催化剂利用率;并以甲苯催化燃烧为探 针反应评价催化性能。结果表明,泡沫碳化硅原位 生长碳化硅晶须显著提高催化剂负载量,并暴露特 征活性晶面,表现出良好的催化活性和水热稳定 性。

3.6.1.4 水下配方用铝基贮氢复合燃烧剂的制备及 性能测试

在火炸药中添加铝粉等金属燃料是有效提高 能量水平的重要途径之一。由于固有属性限制,目 前广泛应用的铝粉难以满足进一步提高应用性能的 需求,必须寻求能量水平高、释能效率好、安全可 控、工艺性良好的新型金属燃烧剂。

我们所研制的铝基贮氢复合燃烧剂是利用机 械合金化的方法将铝与其他燃烧改进剂进行嵌合组 装,试验结果显示,可大幅减少燃烧过程中铝颗粒 的团聚问题,实现铝的细化燃烧,提高了铝的燃烧 释能效率,显著提高应用体系的能量水平。

本年度课题组针对某环境的释能特点,重点开 展了含硼铝基贮氢复合燃烧剂 (MgAIB系) 的应



图4含硼铝基贮氢复合燃烧剂 (MgAlB系) 扫描电镜照片。

用研制和试验测试。根据H、Mg、Al、B梯级促燃的释能机制,在粉体制备过程中加入较高比例的硼粉。实现了粉体理论能量水平的显著提升,同时保障了铝、硼的高效燃烧。

完成了MgAlB系复合高能燃烧剂的组成、性能 优化与应用性能验证试验,明确了关键工艺参数与 性能之间的关系,为进一步开展粉体制备技术研究 提供了可靠的数据支撑。

3.6 Biological Material and Biomimetic Architecture Division



DIVISION HEAD: ZHANG Jinsong

RESEARCH GROUP LEADERS: (5)

ZHANG Jinsong (Asymmeetric Architecting of Polysaccharide Nanomaterials) YANG Zhenming (Biomimetic Architecting of Porous Materials and Porous Field Effect) YANG Yongjin (Cost-effective Manufacturing of Architected Composite Materials in Multiscale) JIAO Yilai (Structured Catalytic Material) ZHANG Junqi (Functional High-energy Metals)



3.6.1 Summary of Scientific Activities

Developed cellulose element crystals (CECs) as the support for Pd catalysts. Pd atoms close to 0 valence are fixed in situ on a specific crystal plane with a low coordination number, and a kind of Pd-CECs monoatomic catalyst with high activity and high stability.

The porous electromagnetic absorbing metamaterials with excellent environmental adaptability and reliability are designed and fabricated. The porous absorbing materials as prepared have lightweight, broadband and adaptability to extreme-environment, which widens application of absorbing materials in electromagnetic field.

Developed spiral extrusion microwave reactor by adopting the rectangular microwave multi-mode traveling wave design. A continuous microwave reaction system including control system, screw extruder microwave reactor, feeder, screw rotation control system, raw material tank and product tank is established. The continuous microwave reaction system overcomes the problem of insufficient microwave effective penetration depth of the traditional reactor. The microwave energy can be absorbed and utilized uniformly and effectively by the reactants. At the same time, the reaction can be carried out continuously, and it is easy to control the reaction parameters, optimize the experimental process, which is very suitable for industry application.

Takes the structural design of catalyst support materials as a breakthrough, the specific surface area is increased by growing nano-silicon carbide whiskers on the surface of a porous silicon carbide support; the in-situ hydrothermal synthesis technology grows nano-array transition metal oxides on the surface of silicon carbide whiskers to further increase the catalyst. The results show that the in-situ growth of silicon carbide whiskers with foamed silicon carbide significantly increases the catalyst loading and exposes the characteristic active crystal plane, showing good catalytic activity and hydrothermal stability.

Develop the properity of MgAlB series of aluminum-based burners. Based on the energy release promoted from H to Mg, Al and B, a higher amount of amorphous B powder was added to the preparation process. The theoretical energy level of the burner powders is severely improved, and the energy releases of Al and B are promised. Thus, the energy level could greatly increased in the underwater application.

3.6.1.1 Extreme-environment-resistant, Lightweight and Broadband Porous Electromagnetic Wave Absorbing Material

In the civilian field, electromagnetic wave absorbing materials are widely used. And in some case, the absorbing materials require to work in an environment with high temperature, super-low temperature, ablation and strong jounce. It is necessary to devote to the research Extreme-environment-resistant, lightweight on and broadband electromagnetic wave absorbing materials. The porous materials are obtained by replica method and slurry foaming method, and have excellent environmental adaptability and reliability. The electromagnetic absorbing metamaterial bases on porous material and design of metamaterial. By simulation design of multi-scale structure and different materials, some kinds of electromagnetic absorbing metamaterial are prepared. The lightweight and

broadband microwave absorbing composites are prepared by adding dielectric loss materials, magnetic loss materials into bismaleimide porous as a matrix. The bismaleimide porous absorbing composites have a quite low bulk density below 0.3 g/cm³, and have excellent absorbing properties covering the frequency of 0.5 GHz~18 GHz. Furthermore, these absorbing composites could work in the environment with different temperature (-50°C~150°C) and strong jounce. The high-temperature-resistant (800°C~1500°C) and ablation-resistant absorbing material are developed by using open cell or closed cell SiC porous materials. The SiC porous materials have a low bulk density about 0.5 g/ cm³, and exhibit excellent absorbing properties from 1.5 GHz to 18 GHz with slotted design. The bulk density of the carbon porous absorbing material is about 0.45 g/cm³. This absorbing material is suitable for super-low temperature environment (-190°C).



Fig. 1: (a) The picture and absorption property of the bismaleimide porous absorbing material; (b) The picture and absorption property of the SiC porous material; (c) The picture and absorption property of microwave dark-room chest using the carbon porous material.

3.6.1.2 Continuous Screw Extrusion Microwave Reaction System

Reaction process strengthening is the core part of chemical process strengthening. Microwave strengthening technology can greatly improve the reaction rate, improve the selectivity of target products, significantly reduce pollution and achieve the goal of reaction process strengthening by using the interaction between microwave and dipole or charged particles in the reaction system and the selective heating effect of microwave on materials. Aiming at the common problems of reaction system with high viscosity and high corrosion reaction liquid, we successfully developed spiral extrusion microwave reactor by adopting the rectangular microwave multi-mode traveling wave design. The outer side of the reactor is a rectangular shielding box, and the center of the reactor is a wave permeable column container. A screw is installed in the column container, and the reactants pass through the screw's spiral groove continuously. The electromagnetic field spreads around the column container located in the center, and is absorbed by the reactants passing through the screw in the column container, generating "internal friction heat" and raise the temperature rapidly to complete the chemical reaction. A continuous microwave reaction system including control system, screw extruder





Fig. 2: Continuous Screw Extrusion Microwave Reaction System.





Fig. 3: (a) pore structure distribution of cobalt manganese oxides structured catalyst, (a1), (a2) cross-sectional morphology of cobalt manganese oxides, (a3) picture of cobalt manganese oxide structured catalysts, (b) Comparison of catalytic activity of the three catalysts, (c) Hydrothermal stability of nano-array cobalt-manganese oxide structured catalyst.

microwave reactor, feeder, screw rotation control system, raw material tank and product tank is established. The continuous microwave reaction system overcomes the problem of insufficient microwave effective penetration depth of the traditional reactor. The microwave energy can be absorbed and utilized uniformly and effectively by the reactants. At the same time, the reaction can be carried out continuously, and it is easy to control the reaction parameters, optimize the experimental process, and meet the needs of continuous and automatic control. Therefore, it has a good industrial application prospect.

3.6.1.3 Nano-array Structured Catalysts

The original intention of structured catalyst design is to achieve the best catalytic efficiency per unit volume of catalyst through the combination of catalyst design and reactor design through the selection of catalyst support materials, structural design and optimization of catalyst active components. However, the structured catalyst prepared based on the macroscopic porous catalyst carrier and coating method has the problems of irrational flow field and low catalyst utilization rate, which limits its performance.

This work increases the specific surface area by growing nano-silicon carbide whiskers on the surface of a porous silicon carbide support; the in-situ hydrothermal synthesis technology grows nano-array transition metal oxides on the surface of silicon carbide whiskers to further increase the catalyst utilization rate; VOCs combustion was used as a probe reaction to evaluate catalytic performance. The results show that the in-situ growth of silicon carbide whiskers with foamed silicon carbide significantly increases the catalyst loading and exposes the characteristic active crystal plane, showing good catalytic activity and hydrothermal stability.

3.6.1.4 Preparation and Application of Aluminumbased Hydrogen Storage Composite Burner

It is one of the important methods for the improvement of the energy level of applications by the addition of metal fuels such as aluminum powders and etc.. Due to the limitation of the inherent properties, the aluminum powder is difficult to meet the development of further improving the performance. It's necessary to find new metal burners with high energy level, efficiently energy release, safety and could be appropriate for application.

The aluminum-based hydrogen storage composite burner developed is assembled of aluminum and other composite such as MgH₂, B powder and etc., and could be used in AFE, TBA and propel etc. The experiment results show that the agglomeration of aluminum particles during



Fig. 4 : SEM image of Aluminum-based Hydrogen Storage Composite Burner (MgAlB series).

the combustion process could be greatly reduced, and the energy release efficiency of aluminum-based burner could be greatly improved due to the fine combustion of aluminum.

According to the characteristics of the energy release, we focused on the fabrication and test of MgAlB series of aluminum-based burners. Based on the energy release promoted from H to Mg, Al and B, a higher amount of amorphous B powder was added in the preparation process. The theoretical energy level of the burner powders is severely improved, and the energy releases of Al and B are promised.

Through the test, the composition and performance optimization of MgAlB burner were completed, and the relationship between the key process parameters and performance was explored, which could support the further research on the amplification preparation technology.



3.7 功能材料与器件研究部

研究部主任:张志东

研究组负责人(4人)

- 刘 伟 (功能薄膜中的交换耦合与磁电耦合)
- 王振华 (拓扑绝缘体纳米结构和器件)
- 李 昺 (磁性相变的中子散射研究)
- 胡卫进 (铁电薄膜与器件)

3.7.1 研究工作简述

本研究部的研究方向有功能薄膜中的交换耦合与磁电耦合、拓扑绝缘体纳米结构和器件、磁性相变 的中子散射研究、铁电薄膜与器件等。重点研究功能材料的基本物理性能(如电、磁、光、热、力等) 以及不同能量之间的转化,以及功能材料中不同类型的相变过程,包括结构相变、磁性相变、拓扑相变 等。探索新型拓扑磁性材料、磁电阻材料、电磁吸收材料、巨磁弹材料和固态制冷工质材料等。实现功 能薄膜材料和异质结构的生长,制备功能材料的微纳米结构和器件。研究功能材料的低维量子特性、纳 米复合效应等。实现纳米结构的量子输运调控、磁光电调控、界面调控、拓扑态调控等。

本年度在塑晶材料中发现庞压卡效应,有望在固态制冷领域得到应用。

本年度还在离子液体和铁电双门电压调控钴酸盐氧化物异质结的氧阀,多层薄膜中界面效应对自 旋轨道扭矩的影响以及自旋轨道扭矩对磁化强度翻转的调制作用,MnPdGa磁体中室温在低磁场下双斯 格明子的形成,拓扑晶体绝缘体薄膜Pb_{1-x}Sn_xTe (111)中拓扑相变以及可调的拓扑输运性质等方面取得研 究成果。此外还在用于热电材料的硫属化合物二维新相,磁性拓扑绝缘体和反铁磁绝缘体之间反铁磁 性界面耦合,在室温磁场控制关联Kagome磁体的拓扑电响应,LaMnO₃薄膜中应力诱导的团簇玻璃态, La_{0.7}Sr_{0.3}MnO₃:NiO纳米复合薄膜从面内到面外的交换偏置的转变等方面也取得了研究进展。

SYNL

2019年度,在国际学术刊物发表论文47篇。

3.7.1.1 基于界面效应调控自旋轨道扭矩

信息技术的快速发展对存储器的存储密度、 读写速度和稳定性等提出了更高的要求。为满足 这些苛刻要求,近年来人们开始研究自旋轨道扭 矩(SOT)。为了SOT相关器件得到实际应用,人 们需要考虑如自旋轨道耦合层的电流-自旋流转 换效率、磁性层的垂直磁各向异性、与半导体退



图1 样品Ta(5 nm)/CFB(1.2 nm)/MgO(2 nm)和样品Ta(5 nm)/ W(0.4 nm)/CFB(1.2 nm)/MgO(2 nm)的电流诱导磁化翻转。(a) 样品Ta/CFB在面内辅助外场Hx=+12 Oe和+300 Oe时电流诱 导磁化翻转的回线;(b)和(c)是对应的磁化翻转过程中的磁 畴形貌,磁畴形貌通过磁光科尔显微镜采集;(d)样品Ta/W/ CFB在面内辅助外场Hx=+12 Oe和+300 Oe时电流诱导磁化翻 转的回线;(e)和(f)是对应的磁化翻转过程中的磁畴形貌。

火工艺兼容性、隧道磁电阻等等诸多性能。在重 金属/铁磁/氧化物多层膜中有许多与界面相关的 效应,例如垂直磁各向异性、界面自旋通过率和 Dzyaloshinskii-Moriya (DM)相互作用等等,这些 效应都与SOT器件密切相关。

我们通过在 Ta/CoFeB界面中引入超薄W插 层、在Pt/CoFe界面中引入NiO插层,来研究界面 对自旋轨道扭矩翻转效率和磁畴翻转的动力学过程 的影响。实验表明两种插层通过提高界面自旋通过 率进而增强了各自体系自旋霍尔角,插层还降低了 电流诱导磁化翻转所需的辅助外磁场。通过磁光克 尔显微镜研究电流诱导磁化翻转的过程,证实了 DM相互作用场决定了SOT诱导磁化翻转的最小辅 助外场。此外,我们实现了利用SOT诱导双氧化物 自由层的磁化翻转,为SOT器件与当下高密度的磁 性隧道结的有效结合提供了实验基础。结果表明基 于界面效应调控SOT是有效可行的。相关工作发表 在Appl. Phys. Lett. 114 (2019) 082402和Appl. Phys. Lett. 114 (2019) 212404上。

3.7.1.2 拓扑晶体绝缘体Pb_{1-x}Sn_xTe(111)薄膜中的拓扑相变与高度可调的拓扑输运

拓扑晶体绝缘体是一种新型的拓扑材料,其 拓扑表面态受晶体对称性的保护。与拓扑绝缘体在 一个表面上只有一个狄拉克锥不同,拓扑晶体绝缘 体在一个表面上有多个狄拉克表面态,因此,其拓 扑表面态具有高度可调性。理论预测拓扑晶体绝缘



图2 (a-d) $Pb_{1-x}Sn_xTe(111)$ 薄膜在2K时磁电阻对磁场的关系曲线,锡的比例表示为x。红色的方框和黑色的圆圈分别代表了加 垂直磁场和平行磁场时, $Pb_{1-x}Sn_xTe(111)$ 薄膜平面内不同的磁电阻; (e) $Pb_{0.6}Sn_{0.4}Te薄膜磁电导的HLN拟合。$

体的拓扑表面态具有许多独特的量子现象,例如表面自旋滤波、应变诱导的狄拉克点位移和范霍夫奇点。为了获得这些新奇的物理特性,调控狄拉克能隙的打开和拓扑相变的发生对拓扑晶体绝缘体的应用具有重要意义。虽然角分辨光电子能谱(ARPES)已经揭示了拓扑表面态在Pb_{1-x}Sn_xTe(111)体系中的可调性,但在其拓扑相变和磁输运方面的研究尚未见报道。由于拓扑材料在未来电子器件中的实际应用最终取决于其输运行为,因此,我们期望通过输运特性来调控Pb_{1-x}Sn_xTe(111)薄膜系统中的拓扑相变。

在这项工作中,我们使用分子束外延(MBE)在 BaF₂(111)基片上生长单晶Pb_{1-x}Sn_xTe(111)薄膜,并 通过元素掺杂的方法研究了其拓扑相变和不同的输 运特性。我们的工作对于推动拓扑晶体绝缘体薄膜 体系在未来的量子计算和自旋电子学中的应用具有 重要意义。具体地说,在高质量的Pb_{1-x}Sn_xTe(111) 单晶薄膜中发现了由弱反局域化到弱局域化的转变 和可调的磁输运性质。如图2所示,在Pb1-xSnxTe(x > 0.4)薄膜的传输过程中出现了可能与拓扑表面态 有关的弱反局域化,而在Pb_{1-x}Sn_xTe(x < 0.4)薄膜中 出现了弱局域化。这种现象是由于拓扑晶体绝缘体 Pb1-xSnxTe中的拓扑相变打开了狄拉克能隙。通过铅 的掺杂,其本征的锡空位大大减少,改变了纯拓扑 晶体绝缘体SnTe中费米能级的位置,最终引起了新 的拓扑相变和可调控的磁输运性质。这些输运性质 的证据对基于拓扑晶体绝缘体Pb_{1-x}Sn_xTe的基础研究 具有重要意义,并将有助于可调的电子器件和自旋 电子器件的发展。相关工作发表在Nanotechnology 30 (2019) 275703

3.7.1.3 室温低磁场双斯格明子材料--MnPdGa

现代社会的信息爆炸式增长对信息存储提出 了更高的要求,具有拓扑保护的磁斯格明子有望实 现更小更快更强的信息存储。斯格明子材料主要集 中在手性磁体中,大部分只有在低温下才能形成斯 格明子,因此寻找新型的材料以实现室温斯格明子 十分重要。我们在这一工作中研究了中心对称的 MnPdGa磁体中的斯格明子的温度磁场行为。利用 电弧熔炼法制备了纯相的多晶样品,在洛伦兹透射 电镜(LTEM)中观察到了室温及低温下的斯格明子 演变过程,发现双斯格明子在室温小磁场下高密度 地稳定存在。测量了磁输运行为,发现样品具有明 显的拓扑霍尔电阻,其在室温附近具有较大值,与 LTEM中的高密度斯格明子相对应。通过交流磁化 率测试,确定了斯格明子存在的温度和磁场范围。 与其他室温斯格明子材料相比,MnPdGa体系中的



图3 室温低磁场下双斯格明子的LTEM观测及输运性质。

斯格明子具有密度高、所需外加磁场小的优点,为 斯格明子器件应用提供了良好的基础。相关工作发 表在Appl. Phys. Lett. 114 (2019) 142404 上。

3.7.1.4 利用离子液体和铁电双栅极形成原子级别 "氧阀"

宏观尺度上在流体系统中(气,液和固体)控 制流体的方向、压力和流量的阀门,作为一种重要 的传统零部件,在我们日常生活中扮演重要作用。 在半导体电子学领域,随着电子元器件的小型化和 低功耗的发展,在原子尺度上设计电压可控的阀门 至关重要。

我们利用反射式高能电子衍射辅助的脉冲激 光沉积制备了SrCoO₂₅/BaTiO₃的异质结薄膜。通过 在薄膜器件上滴加离子液体并施加电压对样品进 行调控,利用上海光源同步辐射X射线吸收谱,超 导量子干涉仪和输运测量系统来研究薄膜中的氧 空位, 磁电输运性能。研究发现, 通过离子液体 和超薄铁电层栅极的共同作用,可以在BaTiO3层覆 盖的SrCoO_{2.5}异质结构中,在室温下实现氧空位和 磁相变的远程调控,同时伴随着有趣的磁电耦合 效应。此外,由于垂直电子隧穿和铁电极化之间 的相互竞争作用,以及BaTiO3表面的氧迁移,超薄 BaTiO3层在负偏压下充当原子"氧阀"而对氧离子 传输是"半透明"的,进而导致新混合相的出现, 如图4所示。该工作首次构建并证明了基于离子液 体和铁电极化双栅极的"氧阀",为原子尺度下基 于"氧阀"功能来调控和设计微电子学器件奠定了 基础,相关工作发表于ACS Appl. Mater. & Inter. 11 (2019)19584上。



图4 (a)原始态SrCoO_{2.5}薄膜的倒易空间谱;(b)离子液体调控 后,SrCoO_{2.5}/BaTiO₃异质结薄膜的倒易空间谱;(c)离子液 体负电压下SrCoO_{2.5}/BaTiO₃异质结薄膜中的钴酸锶转变为 混合相的钴酸锶薄膜;(d)SrCoO_{2.5}/BaTiO₃异质结薄膜中离 子液体电调控机制;(e)电调控后薄膜中两相共存的直接观 察。



3.7 Functional Materials and Devices Division

DIVISION HEAD: ZHANG Zhidong

RESEARCH GROUP LEADERS: (4)

LIU Wei (Exchange Coupling and Magnetoelectric Coupling in Functional Films) WANG Zhenhua (Topological Insulators Nanostructures and Devices) LI Bing (Neutron Scattering Study of Magnetic Phase Transitions) HU Weijin (Ferroelectric Thin Films and Devices)
3.7.1 Summary of Scientific Activities

The research directions of our division are: Exchange coupling and magneto-electric coupling in functional films; Topological insulators nanostructures and devices; Neutron scattering study of magnetic phase transitions; Ferroelectric thin films and devices. The research interest is focused on physical (sych as magnetic, electronic, optical, thermal, etc.) properties of materials and the transfer between the different energies. We are also interested in studying different types of phase transitions in functional materials, for instance, structural phase transitions, magnetic phase transitions and topological phase transitions. The aim is to discover new topological magnetic materials, magnetoresistance materials, electromagnetic wave absorption materials, magneto-elastic materials and colossal barocaloric materials and so on. We realize the growth of functional materials thin films, heterostructures and nano-devices, in order to investigate lowdimensional quantum characters and nanocomposite coupling effects in functional materials and to realize the controllable quantum transports, controllable magneto-electro-optical properties, controllable interfacial effects and controllable topological states.

In 2019, a breakthrough is the discovery of colossal barocaloric effects in plastic crystals, which will have potential applications in solid refrigeration. There are some advances in oxygen-valve formed in cobaltite-based heterostructures by ionic liquid and ferroelectric dual-gating, interface effect of ultrathin W layer on spin-orbit torque in Ta/W/CoFeB multilayers, modulation of spin-orbit-torque-induced magnetization switching in Pt/CoFe through oxide interlayers, low-field formation of room-temperature biskyrmions in centrosymmetric MnPdGa magnet, topological phase transition and highly tunable topological transport in topological crystalline insulator $Pb_{1-x}Sn_xTe$ (111) thin films. There are also some progresses in the following topics: New two-dimensional phase of tin chalcogenides: candidates for high-performance thermoelectric materials, Observation of interfacial antiferromagnetic coupling between magnetic topological insulator and antiferromagnetic insulator, Magnetic-field control of topological electronic response near room temperature in correlated Kagome magnets, Strain-induced cluster glass state in LaMnO₃ films, Transition of the exchange bias effect from in-plane to out-of-plane in La_{0.7}Sr_{0.3}MnO₃:NiO nanocomposite thin films, and so on.

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In total, 47 papers have been published in international journals in 2019.

3.7.1.1 Modulation of Spin-orbit Torque Through Interface Effect

The rapid development of information technology puts higher demands on the storage density, read/write speed and stability of the memory. To meet these demanding requirements, the spin-orbit torque (SOT) has been studied in recent years. For the practical application of SOT related devices, one needs to consider the current-spin current conversion efficiency of the spin-orbit coupling layer, the perpendicular magnetic anisotropy of the magnetic layer, the compatibility with the semiconductor annealing process, the tunnel magnetoresistance and so on. There are many interface-related effects in heavy metal/ferromagnetic/ oxide multilayer films, such as perpendicular magnetic anisotropy, spin pass rate, Dzyaloshinskii-Moriya (DM) interaction, all of which are important for SOT devices.

We introduced ultra-thin W intercalation at the Ta /

CoFeB interface and NiO intercalation at the Pt / CoFe interface to study the influence of the interface on the spin-orbit torque efficiency and the process of magnetic domain inversion. It is clear that each interlayer enhances the spin hall angle of the respective systems by increasing the interface spin pass rate, and each interlayer also reduces the external magnetic field required for currentinduced magnetization inversion. The magneto-optic Kerr microscope is used to study the process of current-induced magnetization reversal, and it is confirmed that the DM interaction field determines the minimum external field of SOT-induced magnetization reversal. In addition, we have realized the magnetization inversion of the double oxide free layer by using SOT, which provides an experimental basis for the effective combination of SOT devices and the current high-density magnetic tunnel junctions. The results show that modulating SOT based on interface effects is feasible and effective. Related works are published in



Fig. 1: Current-induced switching for Pt(5 nm)/CoFe(1 nm)/ MgO(2 nm) (sample Pt), Pt(5 nm)/MgO (1 nm)/CoFe(1 nm)/ MgO(2 nm) (sample MgO) and Pt(5 nm)/NiO(1nm)/CoFe(1 nm)/MgO(2 nm) (sample NiO). Current-induced switching for various in-plane field H_x for sample Pt (a), sample MgO (b) and sample NiO (c). Kerr images after various current pulses during the switching process at $H_x = \pm 2000$ Oe (d), ± 100 Oe (e) and 0 Oe (f) for sample Pt, at $H_x = \pm 25$ Oe for sample MgO (g) and sample NiO (h).

Appl. Phys. Lett. 114 (2019) 082402 and *Appl. Phys.* Lett. 114 (2019) 212404.

3.7.1.2 Topological Phase Transition and Highly Tunable Topological Transport in Topological Crystalline Insulator Pb_{1,x}Sn_xTe (111) Thin Films

Topological crystalline insulators (TCIs) are a type of novel topological material whose topological surface states (TSSs) are protected by the crystalline mirror symmetries. Different from topological insulators (TIs) with one Dirac cone on one surface, the TCIs have multiply Dirac surface states on one surface, thus, giving rise to the highly tunability of the TSSs. Theoretically, TCI's TSSs are predicted to have many unique quantum phenomena, such as surface spin filtering, strain-induced Dirac point shift and Van-Hove singularity. To achieve the exotic properties, controlling the Dirac gap open and topological phase transition is of great importance to the application of TCIs. Although the tunability of the TSSs in Pb₁. _xSn_xTe (111) system was revealed by the angle-resolved photoemission spectroscopy (ARPES), the transport study for its topological phase transition and magnetotransport behavior has not been reported in the transport studies. The modulation of topological phase transition in $Pb_{1,x}Sn_xTe$ (111) film system through transport characterization is expected to be explored, because the real application of topological materials in future electronic device is finally decided by its transport behavior.

3.7.1.3 Low-field Formation of Room-Temperature Biskyrmions in MnPdGa Magnet

Explosive increase of information in our modern society makes the urge need of new information storage technology. Magnetic skyrmions, a kind of localized spin textures topologically protected in magnetic materials, are highlighted as potential information carriers for highdensity magnetic storage devices. Usually the skyrmions were found in chiral magnets which host skyrmions in low temperature. For technological applications, the stabilization of skyrmions in a temperature range around room temperature is essential. Here, we demonstrate the formation of magnetic biskyrmions in a low magnetic field at room temperature in centrosymmetric hexagonal MnPdGa magnet via Lorentz transmission electron microscopy in combination with transport and magnetic



Fig. 2: The magnetic field dependence of Hall resistance R_{xy} (B) for $Pb_{1-x}Sn_xTe$ thin films (x=0.2, 0.4, 0.7 and 1.0) at 2K. (b) The carrier (holes) density and mobility of $Pb_{1-x}Sn_xTe$ (111) (x=0.2, 0.4, 0.7 and 1.0) at 2K. (c) The schematic diagram on the change of band structure and E F with the Sn content.



Fig. 3: Magnetic phase diagram of bulk polycrystalline MnPdGa. (a) Temperature dependence of the normalized AC susceptibility on applied magnetic field (shifted vertically by a step of 0.1 for clarity). The dotted lines indicate the three critical fields shown in panel (b). As shown in the inset, the first derivative of the susceptibility shows three kinks, indicating the transformation of magnetic states: helical (H) or spin-canted (C), biskyrmion lattice (SkX) and field-induced spin-collinear ferromagnetic (FM). (b) Field-temperature phase diagram based on the topological Hall resistivity and the AC susceptibility.

measurements. High-density biskyrmions are generated at 300 K in a magnetic field of 0.15 T. A large topological Hall resistivity is observed near room temperature under low field. Furthermore, a wide temperature and magnetic-field window for biskyrmions is deduced from transport and AC magnetic susceptibility results. The simultaneous features of high density and low magnetic field near room temperature in a single-component material make MnPdGa a promising candidate for future skyrmion-based topological spintronics applications.

3.7.1.4 Oxygen-Valve Formed in Cobaltite-Based Heterostructures by Ionic Liquid and Ferroelectric Dual-Gating

Conventional valves, which control the direction, pressure, and flow of a fluid (liquid, gas, powder) in a fluid system in macroscale, provide a fundamental role in our daily life. Nevertheless, with the urgent requirement for miniaturization and low power consumption of the devices in semiconductor industry, designing the voltage-



Fig. 4: Magnetic and electrical transport properties of three heterostructures. (a) In-plane magnetic hysteresis loops at 10 K for B-SCO (18 nm), STO (4 nm)/P-SCO (18 nm) and BTO (4 nm)/M-SCO (18 nm) heterostructures. (b) Temperature dependent magnetization curves with field cooling, at a magnetic field strength of 1 kOe for three SCO-based heterostructures. (c) Temperature dependence of electrical resistance of three SCO-based heterostructures. (d) Strongly coupled magnetoelectric effect in multivalent strontium cobaltites films under different temperature regions and resistance values. Red and light green arrows represent negative and positive gate voltages, respectively. The proton of oxygen ion is marked side of arrows. The ionic valences of Co ions and the compositions of strontium cobaltites films are also involved inside the figure. PM, FM, and AFM represent paramagnetism, ferromagnetism, and antiferromagnetism, respectively.

actuated valve for controlling charge flow and electrical behavior on atomic scale is quite important nowadays. Here we report that via a combination of ionic liquid and ferroelectric gating, the remote control of oxygen vacancies and magnetic phase transition at room temperature can be achieved in $SrCoO_{2.5}$ films capped with an ultrathin ferroelectric BaTiO₃ layer. The ultrathin BaTiO₃ layer acts as an atomic oxygen valve and is semitransparent to oxygen ions transport due to the competing interaction between vertical electron tunneling and ferroelectric

polarization plus surface electrochemical changes in itself, thus resulting in the striking emergence of new $SrCoO_x$ mixed-phase. The lateral coexistence of brownmillerite phase $SrCoO_{2.5}$ and perovskite phase $SrCoO_{3-\delta}$ was directly observed by transmission electron microscopy. Besides the fundamental significance of long-range interaction in ionic liquid gating, the ability to control the flow of oxygen ions across the heterointerface by the oxygen-valve provides a new approach on the atomic scale for designing multi-state memories, sensors, and solid-oxide fuel cells.

3.8 先进钢铁材料研究部

研究部主任: 李殿中

研究组负责人(4人)

王 培 (特殊钢) 傅排先 (大型特殊钢构件) 陆善平 (特种焊材) 李殿中 (素钢材料设计)



3.8.1 研究工作简述

先进钢铁材料研究部主要研究领域包括:特殊钢、大型特殊钢构件、特种焊材以及素钢材料设计等。

2019年度,研究部围绕我国重点领域特殊钢材料及其构件生产制造过程中的重大技术难题和发展需求,开展了核电大构件碳偏析追踪、某重大装备关键构件特殊钢研发与制造、稀土耐热钢研发、核废料 处置容器和海工钢焊接材料研制与接头性能等的研究与应用工作,同时继续在稀土轴承钢与高端轴承制 造、大型金属构件构筑成形等技术推广上取得突破。主要研究成果如下:

揭示了双低氧稀土处理提升轴承钢疲劳性能的微观机制,发现稀土对夹杂物的变质处理,延长了疲劳裂纹扩展过程中的FGA区的形成过程,大幅提升轴承钢的超高周疲劳寿命,为高端轴承自主可控制备 奠定材料基础。研究成果在轴承行业获得广泛应用,并获得科学院战略先导专项支持。

开发了低成本、长寿命低镍稀土耐热钢,初步实现了钢的素化,已小批量用于轧钢生产线的炉底 辊、辐射管考核。

继续推进金属构筑成形技术在关键构件制造领域的应用,成功制造出世界最大的直径15.6米,重150 吨的核电用不锈钢环等多个超大构件,被多家权威媒体报道。

通过多尺度原位实验和基于位错密度的多晶晶体塑性有限元相结合,揭示了多相材料中微观应力应 变分配影响宏观性能的机制,指导设计某系统全部核心承力部件用高强高韧特殊钢强化特征,解决了高 强不锈钢强韧性匹配难题,进行了产品生产。

系统开展了奧氏体基不锈钢焊缝金属高温断裂行为和高温铁素体对接头组织性能的影响研究,初步 探索了高强海工钢焊接接头组织与性能关系。研制的钠冷快堆用不锈钢氩弧焊材获得工业批量应用。

3.8.1.1 双相不锈钢中应力应变分配的多尺度原位 研究

通过原位高能同步辐射x射线衍射、微观数字 相关法、EBSD和TEM多种方法相结合,从宏观、 介观和微观尺度研究了双相不锈钢中非均匀变形行 为。在宏观尺度上,奥氏体和铁素体的不同的屈 服强度引发材料中非均匀变形行为。在介观尺度 上,由于晶粒尺度上的变形梯度的出现,奥氏体和 铁素体屈服行为在晶粒层面上都呈现出非同步性。 靠近晶界的部位先发生屈服,这是因为晶界对位错 移动的作用导致晶界附近应变集中。这种晶粒尺度 上的不均匀变形导致晶粒内部的晶格旋转等现象的 发生。进一步研究发现,通过合理调控双相不锈钢 显微组织组成和界面,改变其微观应力应变分配规 律,可以实现对其宏观强度-塑性匹配的优化。通



图1 不同变形阶段样品的相分布图、反极图及局部取向差图。



过调控微观应力应变的分配,可以使初始状态下为 软相的奥氏体相在变形过程中逐渐转变为硬相,从 而使其与铁素体之间的应力应变分配发生动态调 整。当这种相对硬度"反转"发生在均匀变形阶段 时,可以有效消除材料内部微观尺度上的不均性, 从而同时提高材料的强度和塑性。该研究提供了一 个新的方法探索材料内部的变形机制,给人们通过 调控微观尺度非均匀变形提升材料宏观性能提供了 新思路。

3.8.1.2 奥氏体不锈钢焊缝金属高温断裂行为研究

Fe-25Cr-20Ni型奥氏体不锈钢焊接材料,因其 具有良好的抗高温氧化和蠕变性能以及优异的耐腐 蚀性、被选为高放核废料玻璃固化体产品容器的候 选焊材。产品容器壁厚较薄、玻璃化浇注过程中、 产品容器需承受1100℃高温玻璃体冲击,这对焊缝 金属的高温力学性能提出了很大的挑战。奥氏体材 料随温度升高过程中,会出现强度与塑性同时缺失 的现象。这将直接影响到产品容器的稳定服役以及 核废料的安全保障。研究结果表明, Fe-25Cr-20Ni 焊缝金属在700℃~1000℃会出现强度与塑性快速 下降。这与焊缝金属在温度升高过程中变形行为的 转变有关。高温时沿晶脆断的发生引起了焊缝塑性 快速下降。通过添加强碳化物元素Nb到焊缝金属 中,可以促使一次共晶Nb(C,N)在焊缝凝固过程中 析出,进而钉扎晶界,促进晶界弯曲,使得焊缝金 属高温阶段由沿晶脆断转变为穿晶韧断、从而显 著提高焊缝金属的高温塑性。同时由于固溶Nb与 Nb(C, N)带来的强化作用,焊缝金属在1000℃时强 度可提高约50%。

3.8.1.3 核电大锻件碳偏析预测、追踪与控制

碳偏析是核电领域钢铁大铸坯制备中面临的 世界性难题。近年来,法国、美国和中国核电站大 锻件均检测到了严重的碳偏析缺陷。由于坯料尺寸 大,凝固时间长,严重的成分不均匀问题导致目前 百吨级大钢锭材料利用率不足60%,甚至整支钢锭 直接报废。因此,发展基于计算机模拟技术的全流 程碳偏析预测、追踪与控制意义重大。

我们自主开发了多包合浇、凝固、锻造全流程 的数据传递和模拟技术,能够实时追踪每个工序碳 偏析演化过程,并基于全流程偏析追踪制订了关键 锻造工艺,保证了锻件的成分一致性要求,实现了 核级筒节均质大锻件(钢锭重量480吨)成功制备

(Fig.4a)。利用欧拉-拉格朗日多相流偏析模型系 统研究了核电大锻件碳偏析形成机制及影响因素, 首次提出了均质钢制备的临界氧判据,发现了法国 电力集团阿海珐公司制备的在役蒸汽发生器封头出 现严重碳偏析的根源,成功为其提供了解决方案。 研究发现,核电大锻件主要存在两种严重的偏析类 型,顶部正偏析和两侧A形通道偏析。正偏析主要 与凝固过程中的热传输密切相关,不合理的冒口设 计将大大改变温度场分布规律,比如冒口高度不足 所引起的不合理温度场分布将使得碳偏析成倍增加 (Fig.4 (b))。不同于正偏析,A形通道偏析受纯

净度影响极大。比如,当氧含量较高时,由此导致 的夹杂物团簇在漂浮过程中会扰动局部流场和凝固 路径,使得糊状区失稳。这一研究揭示了钢铁大铸 坯纯净度与均质化之间的内在关联,相关偏析机制 与新模型的建立使得对百吨级核电大钢锭的通道偏 析预测首次成为了可能(Fig.4(c)、Fig.4(d))。



图2 Fe-25Cr-20Ni焊接填充金属强度和韧性随温度变化曲线。



图3铸锻一体化全流程偏析模拟技术工业应用。



3.8 Advanced Steel Materials Division

DIVISION HEAD: LI Dianzhong

RESEARCH GROUP LEADERS: (4)

WANG Pei (Special Steels)

FU Paixian (Heavy Special Steels Castings and Forgings)

LU Shanping (Special Welding Materials)

LI Dianzhong (Material Design of the Lower Cost Steel with Light and Micro-alloying Elements)



3.8.1 Summary of Scientific Activities

The current focus of our dvision includes special steels, heavy special steels castings and forgings, special welding materials, and material design of the lower cost steel with light and micro-alloying elements.

In the past year of 2019, the main work focuses on the development of new special steels and key technologies encountered in the manufacture of special steel components. We have carried out the investigation on tracking of carbon segregation in heavy nuclear forgings, designing new special steel and manufacturing technologies for an important equipment, developing RE-added heat resistant steel, and special welding materials and mechanical properties of welded joint, at the same time, we have continue the research and industry application of RE-added bearing steel and additive forging technology.

We clarified the mechanism behind the excellent fatigue properties of RE-added bearing steel. It is found that the modification of inclusions by RE delays the formation of FGA zone in fatigue testing, which extends the fatigue life of bearing steel. The prolonged fatigue life of RE-added bearing steel provides a substantial support to the manufacture of high-performance bearings. The RE-added steels have been widely used in China, and promotes a Strategic Priority Research Program of CAS.

The heat resistant steels containing small content of the nickel with lower cost and long service life, named CNRE, are developed by microalloying the RE element with carbon and nitrogen. And a great number of heart rollers and radiant tubes made of these CNRE steels have been serving up to 1150°C for long term in industrial furnaces.

Using our novel additive forging technology, an austenitic stainless steel supporting ring with the world's largest diameter (15.6 meters) and the largest weight (150 tons) was successfully manufactured in 2019. The research results were widely reported and highly praised in the industry.

By combining the multiscale in-situ experiments and crystal plasticity simulations using models based on dislocation density evolution, we clarify the influence of microscale stress/strain partitioning on the macroscale mechanical properties, and design a new martensitic steel with high strength and high ductility simultaneously used in an important component.

We carried out the investigation on the elevated temperature fracture behavior and the delta ferrite affection on the microstructure and mechanical properties of austenitic steel weld metal, as well as the relationship between the microstructure and mechanical properties of the weld joint of high strength marine steel. And we designed some kinds of special weld materials used in SFR reactor, container of high-level nuclear waste glass, and high strength marine steel. All of them are used in industrial application.

3.8.1.1 A Multi-scale Study on the Heterogeneous Deformation Behavior in a Duplex Stainless Steel

The heterogeneous deformation behavior in a 2205 duplex stainless steel has been multi-scaled studied via the combination of in situ high energy X-ray diffraction, microscopic digital image correlation, electron backscatter diffraction, and transmission electron microscope observation. On the macroscopic level, the difference in the yielding behaviors of between austenite and ferrite causes

the heterogeneous deformation behavior in the material. By further analyses on the mesoscopic scale, the yield behaviors of austenite and ferrite are asynchronous within each grain. The areas near the boundaries are the first part to deform plastically. This can, furthermore, cause the deformation gradient in the microstructure. The former phenomenon can be explained by the various dislocation behaviors between the phases and the impeded effect of boundaries on the dislocations on the microscopic scale. The heterogeneous deformation behavior causes lattice rotation during the deformation process. More important, when we optimize the volume fraction of constituent phase properly, the initial softer phase, austenite, becomes the harder phase during deformation, which causes dynamic strain and stress partitioning between the austenite and ferrite at different deformation stages. Strain and stress partitioning between the constituent phases change

during the uniform deformation stage, which can lead to homogeneous deformation and simultaneously enhance the elongation and tensile strength. This research provides a new idea on the method of the deformation mechanism study as well as a more detailed explanation of the heterogeneous deformation behaviors in a duplex stainless steel.



Fig. 1: The lattice strain of different planes of austenite and ferrite as a function of the applied stress.

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Fracture Behaviors of Fe-25Cr-20Ni Austenitic in the weld metal, which can hinder the motion of the Steel Weld Metal for the Container of High-level grain boundaries during the solidification process of **Nuclear Waste Glass**

material is regarded as a competitive candidate alloy for the container of high-level nuclear waste glass owing to its intragranular ductile fracture instead of an intergranular outstanding resistance to elevated temperature oxidation, creep and corrosion. The container with a thin wall will experience hot impact up to 1100°C during the process of filled with high-level nuclear waste glass, which gives a huge challenge to the performance of the Fe-25Cr-20Ni weld metal. Austenitic alloys generally suffer from a reduction both in strength and plasticity with the increase of temperature, which is detrimental to the service of the container and the security of nuclear waste. The elevated temperature properties of the candidate welding materials have been investigated and the results indicate that the strength and elongation of the Fe-25Cr-20Ni weld metal experience a rapid decline at the temperature range from 700°C to 1000°C. The phenomenon is attributed to the transformation of the deformation behaviors of weld metal at elevated temperature. The occurrence of the intergranular brittle fracture promotes the premature fracture of weld metal. Moreover, the addition of the stabilizing elemental

3.8.1.2 Investigation on the Elevated Temperature Nb can cause the precipitation of the eutectic Nb(C, N) weld metal and then make the grain boundaries become tortuous. Compared with the straight grain boundaries, the Heat resisting Fe-25Cr-20Ni austenitic steel weld tortuous grain boundaries have more excellent resistance to sliding. The Nb-bearing weld metal will fracture by an brittle fracture and then possess a higher plasticity at elevated temperature. Meanwhile, compared with that of Nb-free weld metal, the strength of the Nb-bearing Fe-25Cr-20Ni weld metal is increased approximately 50% at



Fig. 2: Morphologies of the grain boundary in (a) Nb-free and (b) Nb-bearing weld metals, tensile fracture surfaces of (c) Nb-free and (d) Nb-bearing weld metals at 900 °C.

 1000° C because of the strengthening effect of the solution Nb and eutectic Nb(C, N).

3.8.1.3 The Prediction, Tracking and Controlling of Carbon Segregation of Heavy Nuclear Forging via Numerical Simulation Technique

Carbon segregation is the most typical defect of heavy steel ingots in the field of nuclear power worldwide. Recently, it has been widely detected in the forging used in the nuclear island equipment during the maintenance period in France, USA and China. Due to the large size of steel ingot and its long solidification time, the material utilization is less than 60 percent currently, caused mainly by the severe chemical heterogeneity, and even the whole ingot is scrapped. Hence, it is critically significant to carry out the track, prediction and control of carbon segregation of heavy forgings based on the numerical simulation technique.

We have accomplished the data transfer and carbon segregation prediction of heavy steel forging during the entire process from multi-ladle pouring, solidification to forging. By tracking the segregation evolution, the key forging parameters such as punching dimension was accurately calculated and, the simulation solution successfully guaranteed the uniform carbon distribution (± 0.015 wt%) of 480-ton heavy ingots to produce the highquality nuclear-level forgings. Besides the application in the fabrication of the above heavy forgings domestically, our self-developed Euler-Lagrange segregation model and procedure has been applied to distinguish the origin of carbon segregation determined in the nuclear forgings in serve in France. Its formation mechanism and factors in the heavy steel ingots has been elucidated in detail, accordingly the critical oxygen content to produce the homogenized steels is surprisingly found for the first time. Meanwhile, the solution to control the carbon segregation is also provided based on the numerous simulations. It shows that, there are two typical segregation types in the heavy steel forgings, the top positive segregation and the A-type channel segregation distributed at two sides of ingot body. The positive segregation is mainly caused by the temperature transport, and the poor riser design can induce the unreasonable distribution of temperature field. For instance, the carbon segregation severity will become two times larger when the pouring height in the top is insufficient. Yet, the root cause of channel segregation is totally different from the positive segregation, and it is ascribed to the high impurities such as oxygen. When oxygen content is very high, the forming oxide cluster disturbs the local flow and destabilizes the mushy zone, consequently triggering the onset of channel segregation. Excitingly, this study extensively bridges the cleanliness and homogenization of steels. The novel mechanism and segregation model makes it possible, for the first time, to reproduce the channel segregation in heavy steel ingots above one hundred ton.



Fig. 3: The application of segregation simulation technique covering the entire process from multi-ladle pouring, solidification to forging.



3.9 材料设计与计算研究部

研究部主任: 陈星秋

研究组负责人(1人)

陈星秋 (合金计算设计与方法)



3.9.1 研究工作简述

材料设计与计算研究部结合多尺度、高通量计算与模拟、大数据、机器学习和智能设计,利用计算 和数据驱动解析材料成分-结构-性能关系,高效低耗地探索和发现高性能结构和新兴量子材料,强调计算 向导的实验验证。目标瞄准计算材料学的学科前沿,解决多组元合金的多尺度的计算关键科学问题,推 动学科发展。

本年度工作有:发现了金属铍中拓扑狄拉克节线量子态引发的巨大表面电声耦合的机理,以及钨中 的有质量狄拉克点拓扑量子态。此外,我们还在拓扑声子材料的设计工作中取得了一系列成果,包括碳 化钨结构TiS家族化合物中的外尔声子,超导材料MgB2的拓扑声子态和石墨烯中的拓扑声子,并且开发出 了拓扑声子材料高通量搜索计算设计的软件。

利用前期提出的金属电化学腐蚀中阳极溶解第一性原理计算模型研究了镁合金中常见的孪晶界对其 电化学腐蚀的影响机制,揭示了实验上观测到的变形孪晶加速镁合金腐蚀现象的本质原因。继续发展了 电化学腐蚀中典型的阴极析氢反应的第一性原理计算模型,完善了金属和合金电化学腐蚀计算模型,并 利用该模型计算得到的不同金属表面的析氢反应的交换电流密度值与实验上已经观测到的结果符合的很 好。

采用第一性原理分子动力学研究了U-Nb/Ti液态合金的动力学性能,获得了U-Nb/Ti液态合金的动力学 与热力学数据,并研究揭示了两种液态合金的局域结构演化规律;采用第一性原理研究了Fe₂V_{0.8}W_{0.2}Al无 序BCC固溶合金的能带结构,通过与维也纳技术大学实验合作,揭示其复杂能带结构,潜在地有利于其 热电增强;对U-O-Fe-Zr四元体系的结构-组成-性质进行第一性原理研究,发现了新结构,并计算了新结 构的热力学、力学以及电子结构等性质;采用第一原理与集团展开和模特卡洛模拟相结合的方法研究了 镍基合金中的相稳定性和相分离过程,发现Ni-Al在0K下存在的稳定结构,计算获得Ni-Al合金相图。

围绕凝固组织演化和偏析问题开展了介观尺度相关计算方法开发、模型构建和机理研究。基于所开发的高效率凝固相场模型及2D和3D自适应有限元并行计算方法,并澄清了流动作用下的2D和3D相场模拟的枝晶生长定量差别;建立了考虑异质颗粒运动和自然对流作用的多场耦合凝固相场模型,揭示了碳钢中氧化夹杂物与枝晶生长、液体流动之间的多种作用模式;基于定量相场模拟和原位观察实验发现了晶粒早期反常生长动力学。

3.9.1.1 发现金属铍中拓扑狄拉克节线量子态诱发 表面电声耦合反常增强现象

电声耦合效应作为材料中的一种普遍存在的物 理现象,对材料在有限温度下的电子结构及输运性 质都具有着重要的影响,一直是凝聚态物理和材料 学研究的最为关注的课题之一。上世纪90年代,有 学者在金属铍表面观测到了反常巨大的电声耦合效 应,高达0.85-1.25,比起体相电声耦合效应高出了 5倍。这一发现引起广泛的关注和研究但对其机理 未明,并引起了广泛的争论,成为了一个悬而未决 的谜题。

为了解决这一问题,在我们以前率先发现拓扑 狄拉克节线量子态的基础上,通过高精度的第一原 理计算方法,修正了之前研究中的伊利艾伯格函数 计算误差。为了进一步突破之前的研究结果,我们 还发展了算法,将该函数的分布与积分变换到动量 空间中,以观测每个电子及声子动量对电声耦合的 影响,探索这一现象的根本原因。结合电子拓扑量 子态在表面的分布情况,揭示了拓扑量子态对其表 面电声耦合的贡献占比超过了80%。这表明这一现 象是由体材料中的拓扑狄拉克节线量子态引起的。 其物理根源在于通过拓扑节线量子态形成的鼓膜状 表面态在费米能级处局域,产生了很高的电子态密 度,进而诱发了巨大的表面电声耦合效应增强。

这一发现澄清了长期以来广受争议的金属铍 表面电声耦合反常增强的机理,同时也揭示了其它 拓扑材料中存在相似的效应。审稿专家评价该工作 的意义认为:"这些研究者正在刷新寻找改进量子 计算和模拟并具有量子相干性的材料的科学(包括 物理)"和"我认为这些新结果难以置信的引人入 胜"。

相关成果在线发表于Phys. Rev. Lett. 123 (2019) 136802 并入选亮点文章在PRL网站推荐。



图1 金属Be (0001) 表面上拓扑非平庸表面态引发的各向异性反常电声耦合局域增强峰。





3.9 Computational Materials Design Division

DIVISION HEAD: CHEN Xingqiu

RESEARCH GROUP LEADER (1)

CHEN Xingqiu (Computational Alloying Design and Methodologies Initiative)

3.9.1 Summary of Scientific Activities

Studies mainly focus on effective and economical computation- and data-driven tools, discoveries and compositionstructure-property elaborations of high-performance structural alloys and novel quantum materials in combination with advanced tools of high-throughput computation, big data, and machine learning as well as artificial intelligence. In particular, we emphasize the computation-guided experimental verifications. The mission is to solve the crucial issues of multiscale computational design of high-performance materials and to advance the frontier of Computational Materials Science.

In 2019, based on our previous work, we have further made lots of new progresses in several aspects: We have demonstrated that the underlying Dirac nodal line triggers the anomalously large electron-phonon coupling enhancement of Be (0001), the presence of massive Dirac points in β -W, and a series of important progresses of topological phonon materials, including the WC-type TiS family Weyl phonon compound and the topological phonon nodal lines in MgB₂ as well as topological phonons in graphene. In addition, we have developed a software to design and calculate topological materials with high throughput manner.

We have developed the studies of the first-principles modelling of electrochemical corrosion. Firstly, the mechanism of the influence of common twin boundaries in magnesium alloys on its electrochemical corrosion was first studied by using the first-principles calculation model of anode dissolution in metal electrochemical corrosion proposed earlier. Then we continued to develop the first-principles calculation modelling of the typical cathodic hydrogen evolution reaction, so as to complete the calculation model of the electrochemical corrosion of metals and alloys. The exchange current density values of the hydrogen evolution reactions on different metal surfaces calculated using this model are in good agreement with the experimental results, which proves the reliability of the model. Combining both the calculation modellings of anodic dissolution and hydrogen evolution reaction, we further studied the electrochemical corrosion behavior of different crystal planes of pure magnesium and the influence of different alloy elements on the corrosion of magnesium alloys.

Through liquid and disordered alloys, we have studies four aspects: (i) We have simulated the local structural dynamics of the U-Nb and U-Ti liquid alloys, the thermodynamic and dynamical data of the U-Nb and U-Ti liquid alloys, and the local structural evolution of both the alloys was revealed, respectively. (ii) We studied the electronic band structures of a metastable fully disordered BCC-type Fe2V0.8W0.2A1 alloy and revealed the presence of disordered structure and possible Weyl fermions to be beneficial to its thermoelectric performance. (iii) The structure searching on the U-O-Fe-Zr system has been performed through first-principles calculations and some novel phases were found. Furthermore, their thermodynamic properties, mechanical properties and electronic properties have been discussed in details. (iv) Using first-principles combined with Cluster-Expansion method and Monte-Carlo technique, the phase stability and segregations of Ni-Al alloys at 0 K, and derived the phase diagram of Ni-Al binary alloy.

In the mesoscale, studies are oriented on the development of the numerical models and computing methods to simulate the evolution of polycrystalline growth and microsegregation during solidification. Based on the established high efficient phase-field model with nonlinear precondition treatment and the elaborated parallel computing program of the adaptive finite element method in 2D and 3D, the quantitative difference of dendritic growth in 2D and 3D phase-field simulations with coupling of melt flow has been clarified in depth. A multiphysics phase-field model incorporation with liquid flowand foreign particles has been established. And then the motion of solid inclusions in steel melt and their interactions with liquid flow and dendritic growth are revealed through numerical simulations, which primarily illustrates the initiation mechanism of channel segregation in steel ingots. Besides, an anomalous initial crystal growth kinetic whose behavior goes far beyond the concept described by classical crystal growth theory is found in terms of the quantitative phase-field simulations and real-time observations of Al-Cu alloys.

3.9.1.1 Topological Dirac nodal line triggers the anomalously large electron-phonon coupling strength on a Be (0001) surface

The electron-phonon coupling (EPC) is a fundamental phenomenon in materials and it plays an important role on the finite-temperature-dependent electronic band structures and transport properties. In 1990s, the anomalously large EPC strength on Be (0001) surface was reported to be as high as 0.85 to 1.25, attracting extensive attentions. However, to date its physical mechanism of such phenomenon still remains unclear.

On basis of our previous discovery on topological Dirac nodal lines in Beryllium (*Phy. Rev. Lett.* 117 (2016) 094401), we have further developed a high-precision first-principles calculations on the EPC. Significantly, we have corrected the computational errors of the crucial Eliashberg coupling function (ECF) in the early studies. Furthermore, we have decomposed the ECF as a function of each electron momentum, each phonon momentum, and each phonon vibration mode to illustrate the contribution of each electron and each phonon on the surface EPC of the Be (0001) surface. In combination with the distribution of

topological states at the electronic momentum of lattice, we have clarified that the topological states coupling with phonon states significantly contribute over 80% of the total EPC strength on Be (0001). The results reveal the strong EPC of the Be (0001) surface is mainly induced by the topological Dirac-nodal-line induced drumhead-like nontrivial surface states. The presence of the drumhead-like surface states at the Fermi level results in a highly localized and high electronic states, which triggers a large EPC.

Twin boundaries play a critical role in controlling mechanical properties of Mg alloys. Thus, it is essential to have in-depth understandings of their structure and chemical compositions. Periodic segregation of solute atoms in twin boundaries has been reported, and many studies have revealed, by both experimental observation and computational simulation, that such segregation can retard the motion of twin boundaries and thus strengthen the alloys. However, these existing studies on such segregation behavior mainly focused on binary Mg alloys, where the only one alloying element can be readily determined by HAADF-STEM images. But many commercial Mg alloys usually have a combination of several alloying elements. The segregation behavior in twin boundaries in such.



Fig. 1: ECF and EPC strength at the \overline{K} point. (a) shows the total EPC strength of each phonon band and the EPC strength contributed by the Dirac node line induced surface state (DNSS) at the \overline{K} point. The red point is the total EPC strength, and the blue point is the DNSS contributed EPC strength; (b) is the 3D picture of the ECF on first phonon band in BZ, at the \overline{K} point. The anisotropy of EPC can be observed; (c) shows the EPC strength along different directions; (d) is the Fermi surface of the 16-atom layer film; (e) to (m) show the ECF in BZ of several phonon bands.



3.10 轻金属材料研究部

研究部主任: 黄晓旭

研究组负责人(4人)

黄晓旭(力学行为与强韧化机理) 刘 庆(形变机理与组织调控) 王敬丰(先进轻金属材料与应用) JUUL JENSEN Dorte(先进表征技术)



3.10.1 研究工作简述

本研究部主要开展轻金属材料的前瞻性、战略性、前沿性基础研究,瞄准轻金属的关键基础问题, 不断产出具有国际影响力的原创成果,引领领域发展、推动技术进步。瞄准国家重大需求,凝练和解决 轻金属材料技术领域的重大共性学科问题,支撑国防建设和国民经济发展。研究方向包括相变机理与合 金设计、形变机理与组织调控、力学行为与强韧化机理、先进轻金属材料与应用和先进表征技术。2019 年度,本研究部的重要进展有

(1)开发了适用于轻合金研究的原子尺度元素面分析技术,并利用该技术首次确定了QE22合金中一种新的溶质原子孪晶界偏聚现象,即Nd和Ag原子分别占据孪晶界上的受拉和受压位置。本研究工作展示了原子尺度元素面分析技术可以提供原子尺度的结构和化学信息,从而大大推动轻合金和其他工程材料的发展。

(2)采用累积叠轧(ARB)工艺制备了纳米结构Mg-3Gd合金板材,并系统研究了Mg-3Gd合金在 ARB及退火过程中微观结构的演化、微观结构和晶粒尺寸对Mg-3Gd合金力学行为和变形机制的影响。在 微观结构参数定量化的基础上,揭示了Mg-3Gd合金的强韧化机理,提出强度与微观结构的定量化模型。

(3) Hall-Petch关系可以定量描述细晶强化效果,但已有的Hall-Petch斜率计算方程无法预测密排六 方结构金属Hall-Petch斜率的晶体学取向相关性。本研究通过建立可准确描述晶体学取向影响细晶强化效 果的模型和参数,在此基础上,将上述模型在Hall-Petch斜率计算方程中准确表达,建立了可准确预测密 排六方结构金属Hall-Petch斜率取向相关性的新计算方程,推动了细晶强化理论的发展。

(4) 针对超级电容器用三维组装纳米多孔石墨烯进行了由宏观到微观组织变形机理的原位力学研究,发现三维组装纳米多孔石墨烯的组织可因热处理而改变,由柔性网络转变成刚性网络,相应的变形能力亦由塑性变形转变为伪弹性变形。

(5) 提出一种新的复合施密特因子的概念,可以将外应力和局部剪切应力结合在一起,更好地解释晶界处的孪晶-孪晶,以及孪晶-滑移的应力或应变传递现象,为发展适用于六方结构金属的晶界强度模型提供了一种新思路。

3.10.1.1 多元镁合金中共偏聚原子的直接观察及 其影响

现孪晶界对镁合金的性能起着决定性的影响。 因此,对镁合金中孪晶界面的结构及成分进行研究 具有非常重要的意义。文献已经报道了镁合金中溶 质原子在共格孪晶界的周期性偏聚,而且从实验 和计算方面证实了溶质原子的周期性偏聚可以钉 扎孪晶界面,从而提高镁合金的强度。目前的研究 工作主要集中在二元镁合金体系,利用原子分辨的 HAADF-STEM技术可以准确确定溶质原子的偏聚 位置。然而,工程中实际使用的镁合金通常含有多 种合金元素,而在多元镁合金中合金元素在孪晶界 面的偏聚行为尚不清楚。要确定多元镁合金中共格 孪晶界偏聚的溶质原子的类型需要采用原子分辨的 元素面分布技术,但是由于电子束对镁合金样品的 辐照损伤该技术一直很难实现。

本研究首次获得了商业QE22合金中孪晶界偏 聚原子的原子尺度元素面分布图。利用该技术发现 并确定了QE22合金孪晶界上一种新的元素共偏聚 现象,即Nd和Ag原子交替占据孪晶界上的受拉和 受压位置。研究发现双原子孪晶界偏聚能改变孪晶 界的迁移机制,其钉扎孪晶界的能力是没有偏聚的 大约33倍。本研究工作展示了原子尺度元素面分析 技术可以提供原子尺度的结构和化学信息,从而大 大推动轻合金和其他工程材料的发展。该工作详见 Nat. Commun. 10 (2019) 3243。

3.10.1.2 Mg-3Gd变形行为与力学性能的晶粒尺 寸效应

本研究选用Mg-3Gd (wt.%) 合金为研究对 象,采用累积叠轧 (ARB) 及后续不同工艺退火, 制备了三种不同微观结构和晶粒尺寸的样品。系统 研究了Mg-3Gd合金在ARB及退火过程中微观结构 的演化、微观结构和晶粒尺寸对Mg-3Gd合金力学 行为和变形机制的影响;在微观结构参数定量化的 基础上,揭示了Mg-3Gd合金的强韧化机理,提出 强度与微观结构的定量化模型。主要研究结果如 下:



图1 (1012)共格孪晶界上交替分布的Nd、Ag原子柱: (a) 原子分辨率的HAADF-STEM图,入射电子束方向平行镁基体 [1210]; (b)为(a)中部分区域的放大图像; (c-e) 原子分辨率的EDS图,对应的元素分别是(c) Nd, (d) Ag 和(e) (Nd + Ag); (be) 中的虚线圆表示受拉位置; (f) 原子分辨率的HAADF-STEM图,入射电子束方向平行镁基体[1011]; (g)为(f中部分区域的 放大图像; (h-j) 原子分辨率的EDS图,对应的元素分别是(h) Nd, (i) Ag 和(j) (Nd + Ag); (k) (1012)孪晶界Nd和Ag原子排列 示意图,蓝色和红色的箭头分别表示[1210]和[1011]方向; (1,m)分别沿[1210]和[1011]方向观察的孪晶界偏聚的示意图; (n, o)分别为[1210]和[1011]方向的HAADF-STEM模拟图像,(n)和(o)中实线框中的部分为实验像。

采用ARB工艺制备了纳米结构Mg-3Gd合金板 材、样品的结构由纳米尺度的孪晶结构、位错结构 和纳米晶结构组成。样品经不同温度退火后,样品 的微观结构可分为三类:纳米结构、微纳层状异 构、微米尺度的再结晶组织。纳米结构形变样品的 强度高、塑性差;退火中表现出明显的硬化现象, Gd元素退火后在晶界、孪晶界、层错和位错等缺 陷处偏聚是硬化现象的主要原因。此外,纳米结构 退火样品的强度和延伸率较形变样品都增加,这与 非基面位错开动并与Gd原子对位错的钉扎有关。 微纳层状异构结构样品表现出良好的强塑性匹配, 其强度与形变样品相当,延伸率大于原始粗晶样 品。微米结构样品随着晶粒尺寸的减小、表现出力 学行为和变形机制的双重转变: (1) 力学行为的 转变,从连续流变应力向不连续流变应力(即出现 屈服点现象)的转变; (2) 变形机制的转变, 从 孪晶和<a>滑移为主导向<a>和<c+a>滑移为主导的 转变。该项工作详见Acta Mater. 183 (2020) 398。

3.10.1.3 织构影响镁合金Hall-Petch斜率的定量 研究

现细晶强化是金属材料最重要的强化方式之一,其强化效果可以用经典的Hall-Petch关系描述。已有的关于Hall-Petch斜率计算公式 $\sigma_y = \sigma_0 + k d^{1/2}$ 对于fcc和bcc结构金属比较适用,但是其在预测六



Engineering strain (%)

图2 (a) ARB处理后Mg-3Gd合金的显微组织; (b) ARB处理 前的初始试样以及在不同条件下进行ARB处理和退火后得 到不同晶粒尺寸的试样的工程应力应变曲线。



图3 (a) 定量描述细晶强化作用取向相关性的模型及参数描述外应力对k值影响示意图,其中m₁和m₂表示施密特因子,其中X₁和X₂是滑移方向;(b)发展的不同织构Hall-Petch斜率k的新计算方程与原有方程预测效果对比。

方结构镁合金霍尔派奇斜率时几乎失效。

本研究通过将织构对霍尔派奇斜率影响分成内 应力和外应力作用,将两种作用在位错塞积模型中 准确描述,获得新的计算方程k=2σ_dm⁻¹r^{1/2}可以准 确预测不同织构下的Hall-Petch斜率k。上述方程已 被用以有效揭示已报道的多种织构影响Hall-Petch 斜率的机制。该项工作详见Acta Mater. 173 (2019) 142。

3.10.1.4 三维组装纳米多孔石墨烯的力学性能原 位研究

目前已取得大量进展,相比而言,功能材料的结构 稳定性等则研究较少。本研究针对超级电容器用三 维组装纳米多孔石墨烯进行了由宏观到微观组织变 形机理的原位力学研究。三维组装纳米多孔石墨烯 的组织可因热处理而改变,由柔性网络转变成刚性 网络,相应的变形能力亦由塑性变形转变为伪弹性 变形。由下图可以实时观察到室温下高密度多孔石 墨烯 (HPGM-RT) 样品在加载过程中出现塑性变 形,而1600℃热处理的HPGM-1600样品在80mN的 加载条件下仍然以弹性变形为。卸载后在样品表面 留下变形的痕迹可能与微观组织的变形有关。该项 工作详见 Acta Mater. 29 (2019) 1900311。



图4 HPGM-RT (a-c)及1600℃ 热处理样品 (d-f)在SEM中的原位力学表征; (a) (d)纳米压痕前; (b) (e)纳米压痕后; (c) (f)原位 加载力学曲线。

利用原位手段研究结构材料的组织与性能关系

3.10.1.5. Mg塑性变形中的复合斯密特因子 新模型

孪生作为密排六方结构金属最重要的塑性变形 机理之一,其启动条件和活度与基于晶体取向的施 密特因子(Schmid factor, SF)和晶界处的应变协调密 切相关。大量实验观察证实,SF和应变协调因子 (m')是预测孪生启动和变体选择的重要几何参数, 通过严格的理论推导将SF和m'结合在一起,提出一 个复合施密特因子(Composite Schmid factor,CSF) ,很好地解释了镁合金在塑性变形过程普遍存在的 穿越晶界的现象及其变体选择行为。晶体塑性模 拟证实,在小变形量下CSF可以很好的反应晶界处 孪生/滑移系统所承受的局部分解切应力 (Resolved shear stress, RSS)。从应变协调的角度来看,CSF 代表了对施加应变以及局部剪切应变的整体协调能 力。沿挤压方向对AZ31挤压镁合金分别施加1.2% 和5%的应变,并对晶间孪晶对进行统计分析。结 果表明,两种不同塑性应变下SF值分布变化不明 显,而CSF值随着应变量的增加明显降低,表明大 载荷下CSF值较低的孪晶也可以激活。与SF相比, CSF是一种新的基于晶界的取向因子,可以更有效 地预测晶间孪晶对的启动与变体选择行为,且在小 应变条件下更为明显。综上所示,论文提出一种新 的复合施密特因子的概念,可以将外应力和局部剪 切应力结合在一起,更好地解释晶界处的孪晶-孪 晶,以及孪晶-滑移的应力或应变传递现象,为发 展适用于六方结构金属的晶界强度理论模型提供了 一种新思路。该工作详见Int. J. Plasticity. 123 (2019) 208。



图5 (a) 晶界(GB)上可能出现的应变协调模式: 孪晶(T1)-孪晶(T2)与孪晶(T1)-滑移(S2); (b)由孪晶T1产生的局部剪切作用到 孪晶T2 系统上的示意图。



3.10 Light Metal Materials Division

DIVISION HEAD: HUANG Xiaoxu

RESEARCH GROUP LEADERS: (4)

HUANG Xiaoxu (Strengthening and Toughening Mechanism) LIU Qing (Deformation Mechanism and Microstructure Control) WANG Jingfeng (Advanced Light Metals and Applications)

3.10.1 Summary of Scientific Activities

This division aims at proposing and solving important scientific problems in the field of light metal material technology, for supporting the national defense and economy development. We focus on phase transformation mechanism and alloy design, deformation mechanism and microstructure control, mechanical behavior and toughening mechanism, advanced light metal materials and applications, and development of advanced characterization technologies. The main achievements of this division in 2019 are as following:

(1) Atomic-resolution EDS maps of segregated solute atoms in twin boundaries in a commercial QE22 alloy were successfully acquired. A new pattern of solute segregation in twin boundaries was observed. The segregation of specific solutes switches the migration mechanism of the twin boundary from the commonly accepted mode to a new one.. This work demonstrates that the atomic-scale analysis of the distribution of alloying element atoms is now possible by using atomic-resolution EDS, which will greatly promote the development of light alloys and other engineering materials.

(2) Samples of Mg-3Gd (wt. %) were prepared by accumulative roll-bonding (ARB) followed by annealing at different temperatures to produce samples with different grain sizes. The microstructure evolution of Mg-3Gd alloy during ARB and annealing were investigated, and the effects of grain size on mechanical behavior and deformation mechanism were systematically studied. With microstructure parameters quantified, the strengthening and toughening mechanism of Mg-3Gd alloy was revealed, and a quantitative model of strength and microstructure was proposed.

(3) The models and parameters to describe the crystallographic orientation effect on grain-boundary strengthening are built and incorporated into the equation to calculate Hall-Petch slope. A new equation which can predict well the texture effect on grain-boundary strengthening of hcp metals is developed. The results make a substantial advance in Hall-Petch theory.

(4) The deformation mechanism of self-assembled three-dimensional nanoporous graphene for supercapacitor was in situ studied. It was found that the microstructure of self-assembled three-dimensional nanoporous graphene could be changed by heat treatment, from flexible network to rigid network. Correspondingly, it could also be changed from plastic deformation to pseudoelastic deformation.

(5) A composite Schmid factor (CSF), which incorporates the external stress and the local shear stress, is proposed to better explain the stress or strain transfer of twin-twin and twin-slip. This work provides a new way to develop the grain-boundary strengthening model for hexagonal metals.

SYNL

3.10.1.1 Direct Observation and Impact of Cosegregated Atoms in Magnesium Having Multiple Alloying Elements

Twin boundaries play a critical role in controlling mechanical properties of Mg alloys. Thus, it is essential to have in-depth understandings of their structure and chemical compositions. Periodic segregation of solute atoms in twin boundaries has been reported, and many studies have revealed, by both experimental observation and computational simulation, that such segregation can retard the motion of twin boundaries and thus strengthen the alloys. However, these existing studies on such segregation behavior mainly focused on binary Mg alloys, where the only one alloying element can be readily determined by HAADF-STEM images. But many commercial Mg alloys usually have a combination of several alloying elements. The segregation behavior in twin boundaries in such Mg alloys with multiple alloying elements has not been well established. Direct observation and identification of multiple alloying elements segregated at twin boundaries need atomic-resolution EDS maps, which are previously thought experimentally challenging to be obtained in Mg alloys due to the severe beam damage. In this work, atomicresolution EDS maps of segregated solute atoms in twin boundaries in a commercial QE22 alloy are successfully acquired at much lower electron voltage. A new pattern of solute segregation in twin boundaries is observed, i.e.



Fig. 1: Alternating distribution of Nd and Ag columns in a coherent $(10\overline{1}2)$ twin boundary. (a) Atomic-resolution $[\overline{1}2\overline{1}0]$ HAADF-STEM image. (b) Enlargement of a region in (a). (c-e) Corresponding atomic-resolution EDS maps showing atomic columns rich in (c) Nd, (d) Ag and (e) (Nd + Ag). Dashed circles in (b-e) indicate extension sites. (f) Atomic-resolution $[\overline{1}011]$ HAADF-STEM image. (g) Enlarged image of a boundary segment in (b). (h-j) Corresponding atomic-resolution EDS maps showing atomic columns rich in (h) Nd, (i) Ag and (j) (Nd + Ag). (k) Schematic diagram showing arrangement of Nd and Ag atoms within a (10\overline{1}2) twin boundary. Blue and red arrows indicate $[\overline{1}2\overline{1}0]$ and $[\overline{1}011]$ directions, respectively. (1, m) Segregation layer viewed along (l) $[\overline{1}2\overline{1}0]$ and (m) $[\overline{1}011]$. (n, o) Simulated $[\overline{1}2\overline{1}0]$ and $[\overline{1}011]$ HAADF-STEM images respectively. Insets in (n) and (o) are experimental images.

alternating Nd and Ag atoms fully occupied the extension and compression sites in the twin boundaries, respectively. The segregation of specific solutes switches the migration mechanism of the twin boundary from the commonly accepted mode to a new one, and which increases the boundary pinning effect by more than 33 times. This work demonstrates that the atomic-scale analysis of the distribution of alloying element atoms is now possible by using atomic-resolution EDS, which will greatly promote the development of light alloys and other engineering materials. More detailed description can be found in *Nat Commun.* 10 (2019) 3243.

3.10.1.2 Grain Size Effects of the Deformation Behavior and Mechanical Properties in Mg-3Gd Alloys

Samples of Mg-3Gd (wt. %) were prepared by accumulative roll-bonding (ARB) followed by annealing at different temperatures to produce samples with different microstructures and grain sizes. The microstructure evolution of these samples were systematically investigated, and the effects of grain size on their mechanical behaviors and deformation mechanism were studied. With microstructure parameters quantified, the strengthening and toughening mechanism of Mg-3Gd



Fig. 2: (a)The microstructure of Mg-3Gd alloy after ARB-processing. (b) Engineering stress-strain curves of the initial sample before ARB and for samples of different average grain sizes obtained by ARB-processing and annealing under different conditions.

alloy was revealed, and a quantitative model of strength and microstructure was proposed. The main results are as follow:

Nanostructured Mg-3Gd alloy plates were prepared by ARB process. The samples present three different microstructures, i. e. nanostructure, micro-nano lavered heterostructure, and micro-scale recrystallized structure, after annealed at different temperatures. First, the nanostructured deformed samples have high strength and poor plasticity. Notable hardening during annealing is observed, and the segregation of Gd elements at grain boundaries, twin boundaries, stacking faults and dislocations is thought to be the primary cause. In addition, both the strength and elongation of annealed nanostructured samples are increased compared with the deformed samples, which is owning to the activation of non-basal plane dislocations and the pinning of dislocations by Gd atoms. Second, the samples with micro-nano layered heterostructures show good strength and plasticity. The strength was equivalent to that of the deformed samples, and the elongation was larger than that of the original coarse-grained samples. Third, samples with micro-scale recrystallized structures demonstrated changes of both mechanical behavior and deformation mechanism with the decrease of the grain size: (i) a transition in the mechanical behavior from continuous flow to discontinuous flow associated with a yield point phenomenon, and (ii) a transition in the deformation mechanisms from <a> slip and twinning to $\langle a \rangle$ and $\langle c+a \rangle$ slip. More detailed information can be found in Acta Mater. 183 (2020) 398.

3.10.1.3 Quantitative Study on the Texture Dependence of Grain-boundary Strengthening for Hcp Metals

The high texture dependence of a Hall-Petch slope (k) for Mg alloys has been frequently reported. Several important equations used to calculate k have been previously developed, and although they seem to work well for fcc and bcc materials, they often fail to predict the highly texture-dependent k in Mg alloys. A new equation based on the dislocation pileup model was developed in this study. The validity of this new equation was tested through a comparison of the predicted k values with the experimental values as well as the calculations from older equations. The results indicate that the new equation can achieve an accurate prediction for several previously reported texture effects on k, whereas the k values predicted by the older equations often exhibit a clear deviation. The reasons for this were analyzed and discussed. The strong deformation anisotropy for Mg alloys leads to a complex texture effect on k, including the effects from both external and internal stresses. Both effects are well expressed in the new equation. In contrast, the old equations consider the external stress effect, but do not express well the internal stress effect. In addition, the old equations consider only the predominant deformation mode. However, our results indicate that the activation of a portion of another deformation mode other than the predominant one plays an important role in the k value. In the new equation, all possible deformation modes and their fractions are considered in the calculation. Using the



Fig. 3: (a) Schematic diagrams showing models and parameters to describe the effects of crystallographic orientation on grainboundary strengthening, where m_1 and m_2 are Schmid factors, X_1 and X_2 are slip directions; (b) a comparison of the predicted k values between the new and old equations.

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important parameters of the new equation, the mechanisms for several texture effects on k as previously reported were discussed and new understandings were obtained. More detailed information can be found in *Acta Materi*. 173 (2019) 142.

3.10.1.4. In situ study on mechanical properties of self-assembled three-dimensional nanoporous graphene

A lot of progress has been made at present in the insitu study of the relationship between the structures and properties of structural materials, but few research has been made on the structural stability of functional materials. In this work, the deformation mechanism of self-assembled three-dimensional nanoporous graphene for supercapacitor was in situ investigated from all scales. It was found that the microstructure of the nanoporous graphene can be changed from flexible network to rigid network by heat treatment. Correspondingly, it could also be changed from plastic deformation to pseudo elastic deformation. We can see from Fig. 4 that the highly dense-yet-porous graphene monolith treated at room temperature (HPGM-RT) sample has plastic deformation during loading, while the HPGM-1600 sample still has elastic deformation under a load of 80 mN. After unloading, some slight traces on the sample surface might be related to the microstructure deformation.

More detailed information can be found in *Adv. Funct. Mater.* 29 (2019) 1900311.

3.10.1.5. Understanding Common Grain Boundary Twins in Mg Alloys by a Composite Schmid Factor

It is well known that twinning likely nucleates and forms pairs at grain boundaries (GBs) during the deformation of Mg alloys. Therefore, the crystallography of GBs plays an important role in selecting twin variants. In this regard, the Schmid factor (SF) cannot predict from which GBs twinning prefers to nucleate. To solve this problem, a composite Schmid factor (CSF) is proposed in this paper that incorporates both the SF and a geometric compatibility factor (m'). First, the link of the CSF with the SF and m' is defined and discussed based on theoretical derivations. Then, experiments were carried out to investigate the effects of this parameter in predicting {10-12} extension twins in AZ31 Mg alloys. A CSF threshold for the activation of common-boundary twins was noticed and it decreases with the applied strain. By contrast, the SF threshold and its dependence with strain is not obvious. Moreover, the CSF is more effective in predicting the variants of common-boundary twins especially for small strain. More detailed information can be found in Int. J. Plasticity 123 (2019) 208-233.



Fig. 4: Mechanical characterizations of bulk HPGM by in situ SEM nanoindentation. (a-b) SEM images of HPGM-RT before and after nanoindentation under a load of 10 mN; (c) Load-displacement curves of HPGM-RT with the loads limited at 10, 20, and 30 mN, revealing a plastic deformation; (d-e) SEM images of HPGM-HT before and after nanoindentation under a load of 30 mN; (f) Load-displacement curves of HPGM-HT with the loads limited at 20, 40, and 80 mN, characterized by the elastic recovery.



Fig. 5: Illustration of two kinds of strain accommodation modes at grain boundary (GB): a twin pair T1-T2 and twin-slip pair T1-S2; (b) Illustration of the basis of T1 and T2, and the shear stress of T1 resolved on T2.





3.11 大湾区研究部

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黄明欣 (纳米结构钢与超高强度钢)

陈 弦 (相变金属的低滞后和高变形性)

3.11.1 研究工作简述

利用前期积累的表面纳米化技术 (SMAT)、材料纳米力学分析技术、结构材料残余应力优化技术 等,积极推进新金属及纳米结构材料在贵金属首饰业、钢铁行业、微机系统、汽车行业、航空航天工 业、生物医学行业和大型核电设备的应用及产业化。具体研究方向包括:新型结构材料设计与集成;表 面与预应力工程与先进设;新型多稳态板壳 ("变形金刚")研究及应用;增材制造材料与工艺;超纳 材料与集成。本研究部年度工作综述如下:

1. 开始搭建纳米材料制备、增材制造、并行工程设计平台;

2. 开展了制备样品的技术方法和理论研究,并初步完成样品制备;

3. 研究了高性能纳米金属材料的成份及工艺:

(1)开发了一种由纳米金属玻璃(MG)壳层包裹铝纳米颗粒构成的分级纳米结构铝合金。实现了 超高的屈服强度(拉伸1.2 GPa,压缩1.7 GPa)、15%的拉伸塑性和超过70%的压缩塑性。这种塑性变形机 制也是铝等低熔点金属将晶粒尺寸降至10nm以下的有效方法,从而使得这种结构设计成为强度-塑性平衡 的一种解决方案。

(2)将原位拉伸试验与基于位错的理论模型和分子动力学模拟相结合,建立了奥氏体不锈钢中纳米 孪晶的清晰变形模式。揭示了部分位错滑移所引起的内部过渡机制。

(3)研究了不同碳含量下孪晶诱发塑性(TWIP)钢随温度及应变速率敏感的屈服现象,获得了材料屈服时位错克服障碍运动所需的激活能和激活体积。提出了含碳TWIP钢在发生屈服时位错的动力学模型,首次定量建立了TWIP钢发生屈服时激活能和激活体积随碳含量的函数关系,并由此能够预测出不同碳含量TWIP钢的屈服强度随温度和应变速率的变化关系。

(4)研究了一种低碳低成本可焊高强度低合金HSLA钢的增强增韧机制。在640℃热处理下,其屈服 强度(YS)和极限抗拉强度(UTS)分别超过1000和1100MPa,拉伸塑性>10%(断面收缩率>60%)。 通过调控,还能获得良好的低温冲击性能、高YS以及高UTS。此外,在640℃下长期时效,能够得到有益 于钢铁制造的相对较低的YS(近800 MPa)和UTS(近900 MPa)。

4. 提出了一种新的表面形变梯度的光学微分测量方法。将微分相差成功的应用于测量马氏体相变微观结构的相变形变梯度及其晶格对称变体。还提出了三维全场相变应变场的重建算法,成功地呈现了马氏体的三维微观结构和全场形变梯度。

3.11.1.1 高强高延性纳米结构铝合金

高强高延性通常是结构金属的互斥特性,这点 对于广泛应用于商业的铝基合金尤其重要。为了克 服这种强度-延性的权衡,我们开发了一种由纳米 金属玻璃(MG)壳层包裹铝纳米颗粒构成的分级纳 米结构铝合金。实现了超高的屈服强度,拉伸1.2 GPa(压缩1.7 GPa)、拉伸15%塑性(压缩超过 70%)。

以往的研究指出由于热激活的晶界迁移,通过 应变使低熔点金属晶粒细化极为困难。我们的研究 中获得了~8nm的晶粒尺寸。纳米MG相有效地阻碍 了晶界的迁移,从而阻止了软化机制(如晶粒生长) 的发生,实现了合金的超高强度。

纳米MG相中塑性流动均匀性显著。且在塑性 流动过程中,纳米MG相的流动应力可能到达理论 强度。这说明纳米MG相在塑性变形过程中仍然具 有较强的韧性,能够阻止纳米晶粒的软化机制,如 传统纳米晶材料中的GB迁移。此外,其均匀的流 动行为适应了纳米颗粒的大塑性变形,阻止了应力 局部化等剪切变形机制。

同时,MG相边缘的移动原子在遇到位错时可以作为理想的汇。结果导致这些位错在界面处消失,而玻璃/晶体界面附近的晶粒区域恢复到准无位错状态。过渡位错的连续产生-移动-湮灭导致了分级纳米Al合金的均匀变形。

这种塑性变形机制也是铝等低熔点金属将晶粒 尺寸降至10nm以下的有效方法,从而使得这种结 构设计成为强度-塑性平衡的一种解决方案。我们 的研究结果阐明了在材料工程中采用分级纳米结构 的方法,不仅有助于韧性轻量合金的开发,而且有 助于微机电系统(MEMS)柔性可穿戴设备的应用。

该工作发表于Nat. Commun. 10 (2019) 5099.



图1 分层纳米铝合金的塑性变形机理: (a) 压缩后直径1 µm微柱的横截面TEM图; (b) (a)中白色虚线矩形框的放大TEM图. (c) 纳米薄层颗粒G1, G2, 和 G3附近的HRTEM图; (d) 纳米薄层颗粒G4, G5, 和G6附近的HRTEM 图. 纳米尺度的MG相显示 为浅黄色. 右下角的插图是虚线正方形区域的IFT图像; (e) 位错的活动与纳米MG相的相互作用。



3.11 Greater Bay Division

DIVISION HEAD: LU Jian

RESEARCH GROUP LEADERS: (5)

LU Jian (Structural Nanomaterials and Prestressed Engineering; 4D Printing)

LIU Chain-Tsuan (Physical Metallurgy and Mechanical Behaviour of Metals, Alloys, Nanostructure Materials, Intermetallic Compounds and Bulk Morphous Alloys)

SROLOVITZ David Joseph (Computational and Theoretical Materials Science; Defects; Growth; Evolution; Deformation of Material)

HUANG Mingxin (Nanosteel and Ultra Strength Steel)

CHEN Xian (Low Hysteresis and High Transformability of Phase-changing Metals)

3.11.1 Summary of Scientific Activities

Summary of the work of 2019:

1. Started building the platform for nanomaterial preparation, additive manufacturing and concurrent engineering design.

2. Sample preparation in theory and technology, with the initial sample preparation completed.

3. Investigated the components and technology of high performance nano metallic materials:

(1) We developed a hierarchical nanostructured Al alloy with a structure of Al nanograins surrounded by nano-sized metallic glass (MG) shells. It achieves an ultrahigh yield strength of 1.2 GPa in tension (1.7 GPa in compression) along with 15% plasticity in tension (over 70% in compression). This plastic deformation mechanism is also an efficient way to decrease grain size to sub-10 nm size for low melting temperature metals like Al, making this structural design one solution to the strength-plasticity trade-off.

(2) We constructed a clear deformation pattern of natotwins (NTs) in austenitic stainless steel by combining in situ tensile tests with a dislocation-based theoretical model and molecular dynamics simulations. The simulation results are highly consistent with the observed strong lambda-effect, and reveal the intrinsic transition mechanisms induced by partial dislocation slip.

(3) The temperature- and rate-dependent yielding of twinning-induced plasticity (TWIP) steels containing various carbon contents were investigated. The activation volume and the activation energy have been determined. A constitutive model, which rationalizes yielding as the thermally assisted bowing out of dislocations under the pinning effect of carbon solutes, is proposed, and for the first time quantitatively predicts the thermal activation parameters of TWIP steels as a function of carbon content. Based on the modeling results of thermal activation parameters, the overall temperature- and rate-dependent yield stresses of TWIP steels containing various carbon contents are predicted, showing good agreements with experimental results.

(4) The strengthening mechanisms as well as the toughening of a low cost weldable HSLA steel with a low content of carbon were carefully investigated. The low-C-Ni-Cu HSLA steel can achieve a yield strength (YS) and ultimate tensile strength (UTS) over 1000 and 1100 MPa, respectively, with tensile ductility >10% at a heat-treat temperature of 640°C through multiple strengthening mechanisms. Besides, a good low-temperature (similar to 40°C) impact performance (similar to 200 J) with high YS (similar to 900 MPa) and UTS (similar to 1000 MPa) can be obtained. Moreover, a relatively lower YS (similar to 800 MPa) and UTS (similar to 900 MPa) useful for steel manufacturing can be attained by a prolonged aging at 640 °C.

4. We theorize a mathematical model by which the topography and the full-field deformation of martensitic microstructure are quantitatively determined by the reflected light differential interference contrast microscopy technique. This work underlies a new approach for quantitative surface topography determination with wide applications in experimental mechanics.

3.11.1.1 Hierarchical Nanostructured Aluminum Alloy with Ultrahigh Strength and Large Plasticity

High strength and high ductility are often mutually exclusive properties for structural metallic materials. This is particularly important for aluminum (Al)-based alloys which are widely commercially employed. In order to overcome this strength-ductility trade-off, we developed a hierarchical nanostructured Al alloy with a structure of Al nanograins surrounded by nano-sized metallic glass (MG) shells.It achieves an ultrahigh yield strength of 1.2 GPa in tension (1.7 GPa in compression) along with 15% plasticity in tension (over 70% in compression). The nano-sized MG phase facilitates such ultrahigh strength by impeding dislocation gliding from one nanograin to another, while continuous generation-movement-annihilation of dislocations in the Al nanograins and the flow behavior of the nano-sized MG phase result in increased plasticity.

Previous investigations pointed out that due to thermally activated GB migration, grain refinement of low melting temperature metals by straining is extremely difficult. n our study, ~8 nm grain size was achieved. In other words, the nano-sized MG phase effectively impedes GB migration , which prevents softening mechanisms (such as grain growth) from taking place, contributing to the alloy's ultrahigh strength.

The homogeneous plastic flow in the nano-sized MG phase is notable, and the flow stress of the nano-sized MG phase may reach to theoretical strength during plastic flow. This indicates that the nano-sized MG phase is still strong during plastic deformation and is able to prevent the softening mechanism of the nanograins, such as GB migration in the conventional nanocrystalline materials. Moreover, its homogeneous flow behavior accommodates the large plastic deformation of the nanograins, which prevents shear deformation mechanism, such as stress

localization, indicating a high toughness of the alloy.

Because the nano-sized MG phase can flow at such high stress level, the mobile atoms on the edge of the MG phase are able to act as the ideal sink for dislocations when they are encountered. As a consequence, these dislocations disappear at the interfaces and the grain regions near the glass/crystal interfaces return to quasi-dislocation free. The continuous generation-movement-annihilation of transitory-dislocations contributes to the homogenous deformation of the hierarchical nanostructured Al alloy.

This plastic deformation mechanism is also an efficient way to decrease grain size to sub-10 nm size for low melting temperature metals like Al, making this structural design one solution to the strength-plasticity trade-off. Our results illustrate a hierarchical nanostructure approach in material engineering and may contribute to not only the development of tough lightweight alloys but also the applications of microelectromechanical systems (MEMS) flexible wearable devices.

This work was published in *Nat. Commun.* 10 (2019) 5099.



Fig.1: Plastic deformation mechanism of the hierarchical nanostructured Al alloy. (a) Cross-sectional TEM image of a 1 µmdiameter pillar after compression. (b) Enlarged TEM image from white dashed rectangle area in (a). The red arrows indicate the positions of some dark regions. (c) HRTEM image near nanolamellar grains G1, G2, and G3, clearly demonstrates the existence of the amorphous phase (glass layer) after deformation. (d) HRTEM image near nanolamellar grains G4, G5, and G6. The nano-sized MG phase is colored by light yellow. The lower right inset is inverse Fourier transformation (IFT) image of the dashed square area in the main image, showing some of the dislocations ' $^{\perp}$ '. (e) Illustration of dislocations' activities interacted with the nano-sized MG phase. A dislocation (' $^{\perp}$ ') is generated on the glass-grain 2 interface and then moves inside grain 2. Another dislocation (' $^{\perp}$ ') moves inside grain 1 and then is absorbed by the atoms on the edge of the nano-sized MG phase (dislocation annihilation). The red and blue spheres represent mobile and less mobile atoms respectively. The dashed circles represent the original positions of the mobile atoms. The black arrows denote the motion directions of the dislocations



3.12 联合研究部

研究部主任: 卢 柯

研究组负责人(8人)

金海军(纳米多孔金属)
姜 辛(薄膜材料与界面)
齐 伟(能源催化材料)
李 琦(环境与可持续发展材料)
郃凯平(热电材料与器件)
韩 拯(量子材料与量子调控)
苏国跃(特殊型材料工艺及可靠性)
尚建库(净水材料)
3.12.1 研究工作简述

联合研究部瞄准多种结构材料与功能材料中的基础科学问题与难题,在新材料设计与制备、结构-性能关系、功能性器件开发以及特种型材加工等方面开展系统研究,目标是探索新材料、新功能、新原理及新工艺,深入理解其机理机制,发展性能优异新型结构材料及功能材料与器件,并力图解决工程材料制造加工及服役过程中的重大问题。发表SCI论文91篇,申请专利37项,获授权专利28项。

本年度取得的重要进展有:

(1)首次制备出具有高度有序显微特征的金属硫族化合物/碳纳米管柔性热电薄膜材料,该材料在柔性半导体和器件领域具有广泛应用前景;

(2)成功构建了具有优异存储器性能的各向异性二维碲化镓浮栅存储器件,为实现新型的逻辑运算 及存储单元提供了新思路;

(3)首次在人类头发基底上构建了氧化锌的异质结构柔性光电子器件,为高性能柔性光电子器件的 制备提供了新设计思路和可行性工艺;

(4)证明适当反应条件是展现掺杂纳米碳材料高催化活性的关键,首次揭示了杂原子修饰的纳米碳 材料在烷烃氧化脱氢反应中的构效关系规律;

(5)在内部构造三维微流体通道并注入液态金属制备出金属三维太赫兹波光子晶体,简化了相关器件的制备工艺,降低了成本,并解决了实时调整以及水分对太赫兹波的吸收等问题;

(6)制备了微米多孔铁-铬材料,表明其强度和弹性模量之间符合指数为3/4的指数关系,对完善脱合金制备多孔结构的力学模型具有重要意义;

(7) 首次在国内成功挤压出直径1.2米的大尺寸耐蚀合金无缝管,突破了坯锭控温、挤压润滑等相关 技术,实现该类管材的国产化,为相关化工、发电、海工装备的自主可控提供保障。

3.12.1.1 二维极限下巨各向异性电阻效应及其调 控

"横看成岭侧成峰",这是著名诗人苏东坡在 描述庐山景观的各向异性。

SYNL的研究团队与国内外合作者共同研究发现,在二维世界里,电子在晶格中的传输也可以用 类似的语言来描述这种物理现象。不过,物理世界 的"远近高低各不同",指的不是山水风景,而是 导电特性,即导电特性沿着不同方向表现出差异。

SYNL的研究团队将最小厚度达4.8纳米、共6 层的层状材料碲化镓置于两层10纳米、左右厚度的 氮化硼之中,达到对碲化镓的封装保护。室温下, 少数层碲化镓的电导率沿着不同方向呈现出近似正 弦振荡的周期性变化,表现出与硒化锡、 磷化锗 相似的随着方向变化的各向异性电阻率,且差别最 大的两个方向上电阻率比值在10以内。

通过施加垂直电场,碲化镓的电导率各向异 性的比值能够从10倍飙升至5000倍,远超目前报道 的具有面内电学各向异性的其他体系。这些现象和 数据表明,电子沿着二维碲化镓不同晶格方向的传 输能力,能够在电场的调控下达到三个数量级的差 别。例如,在没有电场施加的情况下,沿着y"车 道"上的电子通过率为沿着x"车道"上的十倍左 右。但是,一旦施加外电场,且达到一定强度,两 垂直"车道"上"车辆"通过率的差别可以高达 5000倍。也就可以想象成我们的交通状况,施加电 场就相当于在我们的y方向亮起了"绿灯","电 子车辆"顺利大量地通过,而在x方向亮起了"红 灯","电子车辆"听话地几乎不通过,x、y"车 道"上的"电子车流"形成鲜明的差别。也就是 说,外电场起到了二维电子"交通管制"的作用。

基于这些发现,SYNL的研究团队进一步构建 了全范德华组装的各向异性二维碲化镓浮栅存储器 件,并演示了该器件中优异的存储器性能:通过一 次门电压擦写,在该浮栅操控的原型存储器件中可 同时实现x和y方向(两者方向垂直)两组信息存 储。

众所周知,受晶格对称性的影响,晶体材料中 热导率、电导率、介电常数、拉曼张量等基本物理 量常常呈现出内禀的各向异性。例如,石墨中ab面 内的电导率比面外(c方向)高三个量级,这种面内外 的强各向异性在三维块体范德华材料中比较常见。 近年来,随着二维材料研究的发展,各种面内的各 向异性新现象不断涌现。其中,晶格对称性较低的 二维范德华材料(例如SnSe、GeP等)的拉曼各向异 性、电导率面内各向异性等现象受到越来越多的关 注和深入的研究,基于此的原型器件也亟待设计和 开发。然而,目前报道的二维极限下导电各向异性 值(比如,面内某方向最大电导率与面内另一方向 最低电导率的比值)均在10以内,数值偏小,不利 于新型器件的开发应用。另一方面,能否通过某些 快速方便的手段(例如门电压)来调控电学的各向 异性,也是一个极具挑战性的问题。

二维极限下碲化镓纳米电子器件展示出了门电 压可调的、面内巨各向异性电阻效应,解决了上述 挑战。为实现新型的逻辑运算及存储单元提供了新 思路,比如方向性多值浮栅存储器等。从科幻角度 来描述的话,就是有那么一种可能,各向异性存储 器中一次性写入的数据可以沿一个方向读取是一本 小说,沿另一个方向读取则是一部电影。

3.12.1.2 基于头发上的AZO/ZnO/PVK/ PEDOT:PSS异质结柔性光电子器件

柔性光电子技术是一种将电子器件和电路制 作在柔性塑料或薄金属基板上,从而使光电子器件 具有一定的可弯曲性和部分延展性的新兴光电子技 术,其在信息、能源、医疗、国防等领域具有广泛 的应用前景。目前,柔性光电子器件的制备普遍都 是通过在柔性基底直接生长光敏感材料或者是将已 经制备好的光电材料转移至柔性基底来实现的。然 而,这些用于商业应用的柔性基底要么不可生物降 解要么制备过程复杂并且昂贵,导致其在制备或者 处理过程中对环境造成污染。因此,寻找合适的基 底对于制备价格低廉和环境友好的光电子器件至关 重要。而且,作为紫外光敏感材料,ZnO由于丰富 的表面态和氧气的吸附/解吸附过程导致了其光响 应度低和响应长等问题。

针对这一系列问题,我们首次利用人类头发作 为柔性基底,采用低温合成方法在人类头发上构建 了AZO/ZnO/PVK/PEDOT:PSS异质结构。基于该结 构的光电探测器显示出非常优异的紫外光电响应性 能、机械柔韧性和长期稳定性,其光响应时间仅为 110 ms,光响应度可高达81.6 mA/W。通过将7个光 电探测器作为7像素点所形成的柔性紫外图像传感 器在紫外光照下可以准确的显示出0-9的阿拉伯数 字。同时,通过对两个光电探测器在电路中的不同 集成方式也可实现AND、OR和NAND门的逻辑功 能。并且,在不同弯曲条件下器件的性能仍然保持 不变,证明了其在高性能柔性光电子器件方面的潜



图1 少数层GaTe各向异性浮栅存储器件的操控演示:通过一次门电压擦写,实现了x和y方向(两者垂直)两组信息存储。



图2 集成在人类头发上的AZO/ZnO/PVK/PEDOT:PSS柔性紫外光电探测器及其在柔性光控逻辑电路和紫外图像传感器中的应用。

在应用价值。该项工作为使用人类头发作为柔性基 底并获得高性能柔性光电子器件提供了一个新的设 计思路和可行性工艺。

3.12.1.3 纳米碳催化反应机理和结构功能关系研 究

纳米碳材料在气相、液相和电催化领域的应 用是国际化学、能源和材料领域的热点研究方向之 一。我们近年来持续围绕纳米碳催化开展工作,并 从初期的新型碳基材料制备开发逐渐升级到对碳催 化反应本质过程以及碳材料催化反应结构-功能关 系规律的系统研究工作。利用自主设计的催化活性 中心化学定量、模型催化剂、原位光谱和控制表面 反应等实验方法先后实现了碳催化烷烃脱氢反应活 性中心定性与定量、催化反应动力学模型建立、催 化剂本征催化活性测试和比较,解决了碳催化反应 机理研究的一系列难点问题。

本年度,我们在上述研究成果的基础上又进



图3 氮掺杂和未掺杂碳纳米管催化剂在乙苯氧化脱氢反应中 本征催化活性的比较。

一步、首次利用以反应机理为基础的微观反应动力 学方法成功揭示杂原子修饰的纳米碳材料在烷烃氧 化脱氢反应中的构效关系规律。相关研究结果表 明:杂原子并不总是对提升纳米碳催化烷烃脱氢的 反应活性起到促进作用,适当的反应条件选择是展 示掺杂纳米碳材料高催化活性的关键。更加重要的 是反应动力学和催化剂结构分析结果表明氮杂原子 对催化烷烃脱氢反应的促进作用主要是基于其向纳 米碳材料的电子转移、提升碳材料的亲核性、亦即 提高纳米碳断裂烷烃分子中C-H键的反应活性(Appl Catal B-Environ. 258 (2019) 117982)。这部分研究工 作首次在原子和分子层次上揭示了杂原子对纳米碳 材料催化反应活性的影响规律及其背后的物理化学 本质,为建立系统的碳催化理论体系、指导高效碳 基催化材料设计制备及推动其工业应用打下了坚实 的基础。

3.12.1.4 3D打印制备微流体三维太赫兹波光子晶 体器件

太赫兹波是指频率在0.1 THz到10 THz范围的 电磁波,介于微波与红外之间。太赫兹波由于自身 的特点,如THz脉宽在皮秒级可方便的进行时间分 辨的研究、能量低不易破坏被检测物质、非极性物 质吸收小可探测材料内部信息等等,在通信、雷 达、电子对抗、电磁武器、天文学、医学成像、无 损检测、安全检查等领域具有广阔的应用前景。 三维太赫兹波光子晶体是一种重要的太赫兹元器 件。3D打印是制备三维太赫兹波光子晶体的重要 技术,然而金属三维太赫兹波光子晶体仍然难以制



图4 微流体三维太赫兹波光子晶体器件3D打印与不同介质 太赫兹响应示意图。

备。现有器件一旦制备成型,其太赫兹响应特性一 般难以实时调整。生物、化学样品中水分对于太赫 兹波的严重吸收也制约着太赫兹波对于此类样品的 无损探测。

在近期工作中,我们应用玻璃胶浆料,通过 3D打印技术制备出微流体三维太赫兹波光子晶体 器件,成功解决了这些问题。通过在器件内部构造 三维微流体通道,注入液态金属就可以制备出金属 三维太赫兹波光子晶体,大大简化了制备工艺,降 低了成本。这些微流体三维太赫兹波光子晶体器件 的太赫兹响应特性可以通过原位注入不同介质进行 实时调控,无需改变器件形状或施加外场,非常适 宜器件的集成与应用。微流体通道降低了生物、化 学样品中的水分对太赫兹波的吸收,从而在微流体 三维太赫兹波光子晶体器件中成功实现对水中细 胞、盐类、纳米材料等的无损探测。因此,这些微 流体三维太赫兹波光子晶体器件具有广阔的应用前 景。相关研究结果发表在ACS Appl. Mater. Inter. 11 (2019) 41611。

3.12.1.5 脱合金腐蚀制备多孔材料强度与弹性模 量之间的统一关联

脱合金腐蚀是近年来发展起来的制备多孔材料,特别是纳米多孔金属的重要手段。由于尺寸效应,脱合金腐蚀制备的纳米多孔金属具有高强度和高比强度;该材料也是研究纳米晶体力学行为的理想模型材料。但由于纳米多孔金属中普遍存在大量悬空孔棱,其力学性能无法用经典Gibson-Ashby模型定量描述。这成为实现其理论强度,以及建立宏观-微观力学性能关联的巨大障碍。虽已提出了多个修正模型,但由于尺寸效应的干扰而难以实验验证。

本工作通过熔体腐蚀制备结构尺寸较为粗大 且一致的多孔Fe-Cr,并研究其强度和弹性模量与 相对密度之间的关系。在此情况下,尺寸效应干扰



图5 金属熔体脱合金腐蚀制备的多孔Fe_{0.80}Cr_{0.20}及其力学性能。(a)多孔Fe_{0.80}Cr_{0.20}的扫描电镜照片,相对密度: 0.30;(b)多孔Fe_{0.80}Cr_{0.20}的强度与相对密度的关系;(c)多孔Fe_{0.80}Cr_{0.20}的杨氏模量与相对密度的关系;(d)多孔Fe_{0.80}Cr_{0.20}强度和杨氏模量之间的关系;(b-d)中实线是基于不同模型中的指数关系拟合的结果。

可忽略不计。研究发现虽然多孔Fe-Cr的强度和弹 性模量与相对密度之间的关系都偏离Gibson-Ashby 模型的预测,但强度和弹性模量之间仍然符合 Gibson-Ashby模型所预测的指数为3/4的统一关系。 这一重要实验结果进一步支持了我们前期提出的基 于表观相对密度的修正模型。这一强度与弹性模量 之间的统一关系也成为判断文献中关于G-A修正模 型正确与否的重要判断依据。本工作进一步完善了 对脱合金腐蚀制备多孔与纳米多孔金属材料力学行 为的认识,对于制备高强度高塑性纳米多孔材料以 及对金属微观变形行为的研究具有推动作用。该工 作发表于Acta Mater. 186 (2020) 105。

3.12.1.6 大直径耐蚀合金管材热挤压技术

无缝管材作为管道材料广泛应用于化工、发 电(含核电)、海洋工程等领域,其中直径超过 0.5米的主管道用大直径管材尚未国产化,目前全 部需要进口。制备的难点主要是,该类材料热挤压 温度高、区间窄(不足200℃),变形抗力大,挤 压大直径管除需要大吨位挤压设备外,对模具、润 滑、温度控制等有极高要求。面向化工领域对该类 管材的需求,我们联合辽阳石化机械设计制造有限 公司、青海康泰锻铸有限公司,开展了大直径厚 壁8825合金(Incoloy825)管材热挤压技术研究工 作,目前已取得阶段性成果。

在精确控温方面,我们指导参研单位通过优化 转运过程压缩了转运时间;课题组开发的润滑膜拼 接覆盖技术达到较好保温效果。自主开发的多层复 合润滑材料,将石墨润滑、玻璃润滑有机结合,达



图6大直径高镍耐蚀合金管。

到了优良的保温、润滑效果,挤压表面质量良好。 经初步试验,首次在国内成功挤压出直径1.2m、壁 厚45mm、长度超过10m的大直径化工主管道管材 样品。

大直径耐蚀合金管材热挤压技术的突破,将有 力促进我国实现该类管材的国产化,为保证相关化 工、发电、海工装备的自主可控做出贡献。



3.12 Joint Research Division

DIVISION HEAD: LU Ke

RESEARCH GROUP LEADERS: (8)

JIN Haijun (Nanoporous Metals) JIANG Xin (Thin Film Materilas and Interfaces) QI Wei (Catalysis and Energy Materials) Li Qi (Functional Materials for Environmental Applications and Sustaniability) TAI Kaiping (Thermoelectric Materials and Devices) HAN Zheng (Quantum Materials and Quantum Devices) SU Guoyue (Metal Profiles and Reliability) SHANG Jianku (Water Purification Materials)

3.12.1 Summary of Scientific Activities

The Joint Research Division integrates groups from different disciplines to conduct cutting-edge research in materials science. It provides a platform that encourages innovation, facilitates interdisciplinary research collaborations, and promotes interaction between basic science and application-orientated research. The mission is to build a team of excellent scientists, provide supports for research into emerging new materials and challenging applications, strengthen both basic research and technological innovations, make major breakthroughs and even lead the research in key areas of materials science internationally.

The major achievements of this year include:

(1) We developed a thermoelectric (TE) material comprising of highly ordered Bi_2Te_3 nanocrystals anchored on a single-walled carbon nanotube (SWCNT) network, which shows high thermoelectric performance and exceptionally high flexibility.

(2) We devised a full-2D GaTe floating-gate-memory (FGM), which enables a prototype device of directional floating gate memory, showing great potential for future nanotechnology such as novel directional sensor/memories and etc.

(3) We fabricated a high-performance, flexible UV-image sensor and flexible photon-triggered logic gates, by integrating organic/inorganic hybrid heterostructures on human hair.

(4) We revealed for the first time the structure-function relation regularity and physical-chemical nature of the promotion effect of heteroatoms to nanocarbon catalysts, which is important to the design and potential practical applications of nanocarbon catalysts with high efficiency.

(5) We reported the direct writing of metal 3D terahertz photonic crystals (TPCs) for Terahertz technology applications.

(6) A universal scaling relationship between the strength and Young's modulus was observed in dealloyed porous $Fe_{0.80}Cr_{0.20}$, which proves that the G-A scaling equations are valid for dealloyed materials as long as the "apparent relative density" is properly considered, as we proposed earlier.

(7) By the control of temperature of the billet, the lubrication of extrusion, we extrude a large-diameter Incoloy825 pipe with 1.2 meters in diameter successfully, which have important applications in the areas such as chemical industry, power generation and oceanographic engineering industry.

3.12.1.1 Gate-Tunable Giant Anisotropic Resistance in 2D GaTe

Researchers from SYNL found that electrons in twodimensional world may flow in an anisotropic manner, leading to conductivity difference along different crystallographic directions. Furthermore, this manner is gate tunable. i.e., a vertical electrical field can change the directional difference of resistance/resistivity in 2D.

We encapsulated 4.8 nm few-layered GaTe (~ 6 layers) in between two h-BN flakes with thickness at the order of 10 nm. With the h-BN protection, few-layered GaTe can retain its pristine physical properties, and the resistance

exhibits ellipsoidal dependence with respect to different directions. This behavior is similar to those reported in SnSe, GeP.

Surprisingly, when subjected to a perpendicular electrical field, the ratio between maximum and minimum resistance along different directions in 2D GaTe can be gate-tuned from less than 10 to up to 5000, far above in-plane anisotropic resistance found in any other 2D systems. The above experimental observation resembles the scenario that when the electrons move in the 2D crystal, a vertical electrical field can act as traffic control: electron 'traffics' in x direction are allowed/stopped with/ without vertical electrical fields, giving rise to maximum



Fig. 1: Directional functioning in 2D-GaTe FGT. One gate programming can store two data sets at different output levels.

three orders of magnitudes in the total traffic along y and x directions.

Based on this, the team from SYNL further devised a full-2D GaTe floating-gate-memory (FGM) using the vdW vertical assembly technique. It turned out that in this novel type of 2D-FGM shows excellent memory properties, with on/off ratios retained larger than 10⁷ and retention time above 10⁵ s. Among all the 2D FGM devices reported, the 2D GaTe FGMs have so far the best memory performances. Moreover, it is found that when testing the 2D GaTe FGM devices along x and y directions, the memory performance are also larger different from each other, originated from the giant anisotropic resistance in the few-layered GaTe channel. In other words, there is possibility that in future disks made by GaTe FGMs, one can read the data out of a same disk but totally different information, by simply swapping the reading directions.

GaTe in the 2D limit shows gate-tunable giant anisotropic resistance, which enables a prototype device of directional floating gate memory, showing great potential for future nanotechnology such as novel directional sensor/ memories and etc.

3.12.1.2 ZO/ZnO/PVK/PEDOT:PSS Flexible Optoelectronic Devices Integrated on Human Hairs

As an emerging photoelectric technology, flexible optoelectronics with excellent flexibility and ductility are fabricated on flexible plastics or thin metal substrates and show extensive applications in information, energy, medical treatment and national defense, etc. Generally, flexible devices were fabricated through the direct growth or transfer of nanomaterials on flexible substrates. Therefore, substrate selectivity is a crucial concern in the design and development of flexible optoelectronic devices. Unfortunately, most of the flexible substrates used for commercial applications are either non-biodegradable or expensive. As a result, developing suitable substrates for the preparation of flexible devices is vital for cost-effective and environmentally friendly applications. Additionally, ZnO nanostructures, as one of the excellent photoelectronic components, can be grown on arbitrary substrates through the seed layer deposition and low temperature growth process but the long photoresponse time (from seconds to hours) arising from O₂ adsorption/desorption at crystal



Fig. 2: Flexible AZO/ZnO/PVK/PEDOT:PSS UV photodetector integrated on human hair and its application in flexible photon-triggered logic functions and UV-image sensors.

SYNL

surface and rich surface states greatly limits its practical applications in flexible electronics. To overcome these problems, we created Al-doped ZnO (AZO) / ZnO nanorods (NRs) / poly (9-vinylcarbazole) (PVK) / poly (3,4-ethylen-edioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) organic / inorganic hybrid heterostructures on human hair using low-temperature deposition methods. A high-performance ultraviolet (UV) photodetector based on the hair-based heterostructure shows a fast response speed (110 ms), high photoresponsivity (81.6 mA W⁻¹), specific UV-detection wavelength, and excellent flexibility and stability over extended periods. A high-performance, flexible UV-image sensor was prepared using 7 hairbased heterostructures as 7 image pixels to identify target Arabic numerals from 0 to 9. Flexible photon-triggered logic gates, including AND, OR and NAND gates, were also created through rationally combining the hair-based heterostructures in circuits. Moreover, the performance of the devices remains unchanged under different bending conditions, proving their outstanding stability and superior flexibility. The results obtained in this work demonstrate the possibility of using the human hair as fibre-shaped flexible substrate and the potential of using hair-based heterostructures as building blocks to create various functional optoelectronic devices.

3.12.1.3 Reaction Mechanism and Structure-Function Relations for Nanocarbon Catalysts

Nanocarbon materials exhibit intriguing catalytic

activity in gas phase, liquid phase, electrochemistry and other energy related reaction systems, which became a hot topic in the field of chemistry, energy and material science. We have focused on the research field of carbon catalysis, since 2008, and we have updated our research emphasis from nanocarbon material synthesis at initial stage to the studies on the nature of nanocarbon catalysis and the basic theory of carbon catalyst structure-function relations. We have successfully solved or revealed a series of fundamental frontier scientific questions or challenges, including identification and quantification of active sites, kinetic reaction models, intrinsic catalytic activity measurements and comparisons etc., in the research topic of reaction mechanism of nanocarboncatalysis using our own developed unique experimental strategies, such as active site titration, model polymer catalysts, in situ spectroscopy and control surface reactions etc.



Fig. 3: Comparisons of the intrinsic catalytic activity of nitrogen doped- and undoped- carbon nanotube catalysts in ethylbenzene oxidative dehydrogenation reactions.

This year, we made further progress in this direction based on the previous findings. We have revealed for the first time the structure-function relations for hetero-atom doped nanocarbon catalytic materials via classical kinetic strategies. The corresponding results have shown that heteroatoms, such as nitrogen atoms, do not always bring positive effect to the catalytic reactivity of nanocarbon materials in alkane ODH reactions, and the rational choice of the reaction conditions is the key to show the unique and advanced catalytic activity of heteroatom doped nanocarbon materials. More importantly, the detailed reaction kinetic analysis and structural characterization results have shown that the promotion effect of nitrogen atoms mainly comes from the electron transfer from pyridinic nitrogen to carbon matrix, which could effectively enhance the nucleophilicity and thus improve the catalytic activity of nanocarbon catalysts for C-H bond activation (Appl. Catal. B-Environ. 258 (2019) 117982). The present research revealed for the first time the structure-function relation regularity and physical-chemical nature of the promotion effect of heteroatoms to nanocarbon catalysts, and this basic structure-function relation is considered as the foundation for the establishment of the theoretical systems for nanocarbon catalysis and the important guidance for the rational design and potential practical applications of nanocarbon catalysts with high efficiency.

3.12.1.4 Direct Writing of Microfluidic Threedimensional Photonic Crystal Structures for Terahertz Technology Applications

Terahertz technology is one of the most frontier technologies which has received much attention due to its wide range applications from the unique properties of terahertz irradiation. Locating between infrared and microwave in the electromagnetic spectrum, the terahertz radiation possesses specific properties like wide bandwidth, transparency in most dielectrics, spectroscopic fingerprinting, low photon energy and non-ionization. Thus, it has great potential for many technical applications, including wireless communication, security, medical and biological applications, food and agriculture technology, astronomy, analytical science, and environmental monitoring. As an important type of terahertz devices, terahertz photonic crystals (TPCs) are artificial materials with periodic structures which could shape the flow of tetrahertz irradiations effectively. Among them, threedimensional photonic crystals (3D-TPCs) could find more technical applications because they could possess bandgaps for all directions due to their periodic variations in all three orthogonal directions. Although 3D printing technique had been demonstrated as a powerful approach to create 3D-TPCs with various material systems of ceramics, composites, and polymers, it is still a challenge to produce metallic 3D-TPCs. Furthermore, most 3D-TPCs had fixed terahertz responses because their materials and structures were fixed after they were created, while the capability of changing terahertz response is highly desirable for 3D-TPCs to possess specific functionalities.

On the other hand, terahertz technology is promising as a key technique for biological and chemical detections due to its nondestructive and non-ionization nature. However, its practical applications are still limited because water in these samples could severely attenuate terahertz irradiations by absorption. One proposed solution was to decrease the distance that terahertz irradiation goes through liquid samples to reduce its absorption by water, so microfluidicassisted terahertz technology could be a promising approach. Although one-dimensional and two-dimensional photonic crystals and waveguides had been created to solve this problem, their linear and planar geometries could not accurately mimic the three dimensional nature of most biological systems. Furthermore, it was difficult



Fig. 4: The schematic illustration of the direct-writing of microfluidic three-dimensional photonic crystal structures via a layer-by-layer building process and their different terahertz properties by in situ changing the injected fluidic media in real time without structure change.

to couple THz irradiation into their fiber or waveguide and their fabrication processes were generally expensive.

In this work, microfluidic 3D-TPCSs were assembled with a glass cement ink by the direct writing technology. Microstructured channels with a reverse woodpile structure were embedded inside these microfluidic 3D-TPCSs, which allowed the injection of various fluidic media into them for different terahertz technique applications. By the creation of microfluidic 3D-TPCSs, metal 3D-TPCs could be easily obtained through the injection of a liquid alloy of EGaIn into these microfluidic 3D-TPCSs. By in situ changing the injected fluidic media of different dielectric properties, these microfluidic 3D-TPCSs could demonstrate different terahertz properties in real time without structure changes, which could be beneficial for their integration into various terahertz devices for a wide range of applications. Due to their microstructured channels, the absorption of terahertz irradiation by water could be largely reduced in them, which endowed them the capability to be used as real time, nondestructive biological and chemical detectors. Thus, novel functionalities could be introduced into these microfluidic 3D-TPCS-based THz devices, and they have a great potential for various technical applications.

3.12.1.5 A Universal Scaling Relationship Between the Strength and Young's Modulus of Dealloyed Porous Materials

The mechanical properties of dealloyed nanoporous metals typically deviates from Gibson-Ashby (G-A) scaling laws. The fact that ligament strength is strongly affected by size has become an obstacle to understanding the relationship between structural topology and mechanical response of dealloyed nanoporous metals, and the failure of G-A scaling laws in dealloyed nanoporous materials.

In this study, we studied the mechanical properties of porous $Fe_{0.80}Cr_{0.20}$ prepared by liquid metal dealloying. The ligament diameters of these samples are stabilized at approximately 4 micron, so that the ligament strength is constant in all samples. The variation of strength (or flow stress) and Young's modulus with relative density, on a log-log scale, is nonlinear. Both properties decrease more steeply with decreasing relative density at lower relative density. These results are similar to the observations in nanoporous gold prepared by (electro) chemical dealloying but deviate from G-A scaling laws. However, the strength of the porous $Fe_{0.80}Cr_{0.20}$ plotted against the Young's modulus on a log-log scale exhibits a linear relation in the full range, with a slope of approximately 3/4 that matches



Fig. 5: Structure and Mechanical properties of porous $Fe_{0.80}Cr_{0.20}$ prepared by liquid metal dealloying. (a) A scanning electron micrograph of porous $Fe_{0.80}Cr_{0.20}$ with relative density of 0.30; (b) Variation of the strength with relative density in a log-log plot; (c) Variation of the Young's modulus with relative density; (d) Variation of the strength with Young's modulus; The solid lines in parts (b-d) are linear fits of the data from the different power relations in theoretical models.



perfectly with the standard G-A prediction. This confirms the significant role played by "dangling ligaments" in the deformation of dealloyed porous materials: Coarseninginduced pinch-off of some ligaments is responsible for the anomalously low strength and stiffness of dealloyed porous materials; the load-bearing network remains selfsimilar, and its mechanical response follows the standard G-A scaling laws, despite the fact that the porous material itself may not do so. Our study confirms that, for dealloyed porous materials, the G-A scaling relations are valid if the apparent relative density or, alternatively, genusdensity-related pre-factors are introduced. The universal scaling relationship reported in this study may also act as a criterion for assessing the validity of any model or modified scaling equations that are proposed to quantify the mechanical properties of dealloyed materials, and other porous materials including the ones developed by 3D printing.

3.12.1.6 Hot Extrusion Technology for Large Diameter Corrosion-resistant Alloy Tubes

Corrosion resistant alloy seamless pipes are widely used as pipeline in chemical industry, power generation (including nuclear power) industry, oceanographic engineering industry and other fields. Among which, the Main Line used pipes, whose diameter is greater than 0.5 meters, have not been produced localized. They still need import at present. The difficulties in manufacturing of those large pipes mainly include high hot extrusion temperature, narrow temperature range (less than $200\Box$), great deformation resistance, high requirements for mold, lubrication, temperature control, etc. In order to meet the demand of chemical industry for the pipe, the research group, in cooperation with Liaoyang Petrochemical Machinery Designing Manufacturing co.,LTD., and Qinghai Kang-Tai Forging & Casting co.,LTD., carry out this large diameter No8825 alloy (Incoloy825) pipe hot



Fig. 6: Photograph of a large diameter corrosion-resistant alloy tube.

extrusion research project.

By optimizing the process, the transfer time of the hot billet is shortened and temperature drop is significantly reduced. By taking the lubrication film splicing and covering technology developed by the research group, the hot billet is better insulated. By using a kind of innovative multi-layer composite lubrication, excellent thermal insulation and lubrication effect is achieved. After preliminary test, a large-diameter nickel-iron-chromium alloy No8825 main pipe sample is extruded successfully, whose dimension is: 1.2m in diameter, 45mm in wall thickness and 10m in length.

The breakthrough of hot extrusion technology for large diameter corrosion-resistant alloy pipes will strongly promote the localization of such pipes, and contribute to the independent control of related chemical, power generation and oceanographic equipment.



3.13 量子材料联合研究分部

研究分部主任: 贾金锋

研究组负责人(1人)

贾金锋 (量子材料)



3.13.1 研究工作简述

量子材料联合研究分部将对超导材料、关联材料、拓扑材料、低维材料等前沿量子材料体系涉及到 的一系列的基础科学问题进行系统深入地研究,研制新型量子材料原型器件。重点发展新型量子材料的 合成制备、纳米结构可控加工、基本物性研究、异质结构的构筑、以及异质结构中新现象探索。同时开 发新型实验技术与设备,在更低温度、更小空间尺度、更短时间尺度上研究低维材料中电子的基本物理 规律。重点关注量子材料在信息光电子器件、超导器件、显示器件、化学催化、电池、载药等领域的应 用。

2019年度,本研究部年度工作综述如下:

利用分子束外延生长技术在国际上首次成功制备出高质量大范围原子级平整的拓扑绝缘体/超导体异 质结。为构造人工拓扑超导体,和在磁通涡旋中探测Majorana零能模提供了很好的平台。随后通过一系 列实验工作证明在拓扑绝缘体/超导异质结磁通涡旋中存在Majorana零能模。这些工作获2016年教育部自 然科学一等奖以及2019年国家自然科学二等奖。

制备出原子级平整的拓扑晶体绝缘体/超导体异质结。发现超导近邻效应比目前已知的绝大多数异 质结体系的超导近邻效应都要强,而且在该异质结体系中观测到拓扑超导电性存在的有力证据。拓扑晶 体绝缘体/超导体异质结具有拓扑超导电性和很强的超导近邻效应,为下一步在该体系中探测Majorana零 能模,以及研发拓扑超导器件打下了基础。系统地测量了双原子层FeSe薄膜在其表面吸附不同量的钾原 子时的超导能隙和抗磁响应,从抗磁的角度首次证实了该体系的超导特性,同时还发现该超导体系的临 界温度与测量得到的超流密度呈线性关系,这表明FeSe薄膜的临界温度的高低是由相刚度而非配对势决 定,即呈现出很强的非传统超导特征,对进一步深入理解FeSe衍生的超导体的高温超导特性提供了非常 重要的信息。

2019年从上海交通大学申请200万元配套资金用于该部量子材料微纳加工平台设施的建设,完善量子 材料加工测试平台在拓扑量子材料和原型器件方面研究的能力,提升拓扑量子计算、二维晶体器件以及 超导材料等方面的器件自主研发能力。

2019年度,在国际学术刊物发表论文55篇。

3.13.1.1 拓扑晶体绝缘体拓扑超导电性的探测

理论计算表明超导的拓扑晶体绝缘体是一种新 型的拓扑超导体。虽然人们已经在拓扑晶体绝缘体 中诱导出超导电性,但是实验测得的超导能隙特征 和普通超导体的能隙特征类似,这使得超导的拓扑 晶体绝缘体是否具有拓扑超导电性存在争议。

研究团队在拓扑晶体绝缘体Sn_{1-x}Pb_xTe与超导体Pb形成的异质结中发现了超导拓扑晶体绝缘体存在拓扑超导电性的证据。利用分子束外延生长技术,制备出原子级平整的拓扑晶体绝缘体Sn₁₋xPb_xTe与超导体Pb形成的异质结(图1(a))。由于超导针尖具有更高的能量分辨率,通过对比在Sn₁₋xPb_xTe和Pb岛上测得的超导能隙,发现Sn_{1-x}Pb_xTe的超导能隙具有"peak-dip-hump"特征(图1(b),(c))。 这与理论计算的超导拓扑绝缘体和拓扑晶体绝缘体 在具有拓扑超导电性时的超导能隙特征一致。 $Sn_{1.x}Pb_x$ Te的超导能隙的衰减长度在4.2K大于200 nm(图1(d))。另外准粒子干涉技术进一步证明在Sn1-xPbxTe的超导能隙里有无能隙的表面态存在(图1(e),(f))。

该工作在拓扑晶体绝缘体中首次观测到peakdip-hump型超导能隙特征以及超导能隙内存在四重 对称性干涉图,为超导拓扑晶体绝缘体存在拓扑超 导电性提供了有力的证据,也为研究其它拓扑材 料的拓扑超导电性提供了一种有效的表征方法。 另外拓扑晶体绝缘体Sn_{1-x}Pb_xTe与超导体Pb形成的 异质结在4.2K下具有很强的超导近邻效应,为今后 研制大尺寸拓扑超导器件以及探测拓扑晶体绝缘 体Majorana零能模提供了新的平台。该成果发表在 Adv. Mater. 31 (2019) 1905582。



图1 Sn_{1-x}Pb_xTe-Pb异质节。(a)原子级平整的Sn_{1-x}Pb_xTe-Pb异质节STM图(150x150nm²)。(b)Pb岛和(c) Sn_{1-x}Pb_xTe 岛上用超导针 尖测的超导gap的dI/dV谱;(d) Sn_{1-x}Pb_xTe超导能隙随距离的变化;(e)和(f)分别为倒空间和实空间中在Sn_{1-x}Pb_xTe超导gap内零 能处测的准粒子干涉图。

3.13.1.2 FeSe薄膜原位抗磁测量

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近期国内外有多个课题组发现,在FeSe薄膜表面,吸附上适量的K原子,可以改变FeSe薄膜的超导能隙的大小。这是因为K原子的电负性非常小, 很容易转移一部分电子给FeSe薄膜(图2(a)),因此,控制K原子的吸附量,即是控制了FeSe薄膜所能获取的电子数量,从而有望达到对FeSe超导特性的调控。不过,仅仅是确定了能隙大小的改变对于超导的研究是不够的。对一个材料具有超导特性的判断依据是要测量到它的零电阻和迈斯纳效应(完 全抗磁性)。然而,对于表面吸附了K原子的FeSe 薄膜而言,这种物性测量是很困难的。其原因在于 K原子具有非常强的化学活性,使得该薄膜样品无 法脱离超高真空环境,也就无法接受传统实验技术 手段的物性测量。

研究团队将普通的STM的核心部件进行改造, 使其具有普通STM的一切基本功能之外,还能对样 品进行双线圈交流互感的原位测量。实验中,对同 一块高质量的双层FeSe薄膜样品表面进行了不同覆 盖度K原子的吸附(图2(b)),并对每个K覆盖度下 的FeSe薄膜采集了多种实验数据,从而得到了一系



图2 双原子层FeSe掺K原位抗磁测量。(a)原理图;(b)样品STM图;(c)Tc随K覆盖度的变化;(d)超导能隙与Tc的比值随着K 覆盖度的变化;(e)Tc与超流密度的变化关系。

列实验结果:1,超导转变温度Tc随着K原子覆盖 量的增加呈现先升后降的Dome型变化(图2(c)), 这虽然与众多非常规超导材料很相似,但却是在 FeSe衍生超导材料当中首次观察到如此完整而连 续的相变行为;2,超导能隙与超导转变温度的比 值随着K覆盖度的增加并不是一个恒定的值(图 2(d)),这意味着超导配对势无法决定超导转变温度的高低;3,超导转变温度与超流密度呈现线性的变化关系(图2(e)),这意味着相刚度是决定转变温度高低的主要因素。这一系列实验测量有助于进一步理解和调控铁基超导电性。该成果发表在*Phy. Rev. Lett.* 123 (2019) 257001。



3.13 Quantum Materials Joint Division

DIVISION HEAD: JIA Jinfeng

RESEARCH GROUP LEADER: (1)

JIA Jinfeng (Quantum Materials)



3.13.1 Summary of Scientific Activities

Research at the Quantum Materials Joint Division focuses on the novel quantum materials such as superconducting materials, correlation materials, topological materials, low-dimensional materials. The research area includes the synthesis and characterization of nanostructured quantum materials and their heterostructures, the development of new technologies and instruments to probe the novel physics at lower temperature, smaller spatial scale, shorter time scale. The ultimate goal is to understand the basic mechanisms of the quantum materials, and to seek the protentional applications in superconducting device, optoelectronic device, chemical catalysis and so on.

The major achievements of 2019 include:

(1) Obtain the second prize of National Natural Science Award in 2019 based on a series of works on the realization of Majorana zero modes in Bi₂Te₃-type topological insulator-superconductor heterostructures.

(2) Atomically flat topological crystalline insulator-superconductor heterostructures $Pb_{1-x}Sn_xTe-Pb$ are successfully fabricated by molecular beam epitaxy. The superconducting proximity effect in the heterostructures is unexpectedly strong even at 4.2 K. Evidences to support the topological superconductivity in the heterostructures are observed.

(3) A multifunctional STM is developed which enables in situ four-point-probe electrical measurement and two-coil mutual inductance measurement. The diamagnetic response of K-adsorbed multilayer FeSe films are in situ detected in ultrahigh vacuum.

3.13.1.1 Superconductivity of Topological Surface States and Strong Proximity Effect in Pb_{1-x}Sn_xTe-Pb Heterostructures

A topological superconductor (TSC) is characterized by having a pairing gap in the bulk and gapless Andreev bound states at its boundary, which is topologically distinct from a conventional superconductor (SC). TSCs contain Majorana zero modes (MZMs) which obey non-Abelian statistics, thus exhibiting great potential applications in fault-tolerant topological quantum computing. After the realization of topological insulators (TIs), the search for TSCs in real materials has already been a very hot topic in condensed matter physics. Natural TSCs are rarely found, but topological superconductivity can be induced in TIs through chemical doping and superconducting proximity effect. Topological crystalline insulators (TCIs) are topologically nontrivial states of matter that the gapless surface states are protected by crystalline symmetry instead of time-reversal symmetry. The first class of TCIs has been recently predicted and verified in the SnTe-type IV-VI semiconductors with a rock-salt crystal structure. Superconducting TCIs are expected to form a new type of TSCs that multiple MZMs bound to a single vortex may be supported under the protection of lattice symmetries. The bulk superconductivity of TCIs has been induced

through chemical doping and proximity effect. However, STM experiments still display the conventional full gaps in the superconducting TCI, so the existence of topological superconductivity in TCIs remains controversial. In this work, we fabricated atomically flat lateral and vertical Pb_{1,x}Sn_xTe-Pb heterostructures by molecular beam epitaxy (MBE). The superconductivity of the Pb_{1-x}Sn_xTe-Pb heterostructures can be directly investigated by in situ low temperature STM/STS. The superconducting proximity effect in the heterostructures is unexpectedly strong even at 4.2 K. The features of the tunneling spectra taken on superconducting Pb_{1-x}Sn_xTe show a peak-dip-hump character rather than the peak-shoulder character seen in conventional SCs such as Pb, which is in agreement with the existence of topological odd-parity pairing. Quasiparticle interference (QPI) patterns taken at the zero energy in the superconducting gap of Pb_{1-x}Sn_xTe show a fourfold symmetry, indicating the presence of gapless ingap states. The superconducting TCI is predicted to be a new class of TSC supporting MZMs protected by lattice symmetries. Our results suggest that the Pb₁ Sn_yTe-Pb heterostructures have great potential application in topological superconducting devices to detect and manipulate MZMs in the future. The relevant work was published in Adv. Mater. 31 (2019) 1905582.



Fig. 1: $Sn_{1-x}Pb_xTe-Pb$ heterostructure. (a) STM topography of an atomically flat lateral $Pb_{1-x}Sn_xTe-Pb$ heterostructure; (b-c) dI/dV spectra taken on (b) Pb and (c) $Sn_{1-x}Pb_xTe$ using superconducting tips; (d) Spatial evolution of the superconducting gap as a function of the distance to the Pb island edge; (e) QPI pattern and (f) dI/dV map inside the superconducting gap of $Pb_{1-x}Sn_xTe$.

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3.13.1.2 Diamagnetic Response of Potassium-Adsorbed Multilayer FeSe Film

Carrier doping is an effective approach to the realization of high-temperature superconductivity in cuprates and iron pnictides, resulting in a dome-shaped relation between critical temperature (T_c) and doped carrier density. Similarly, in the case of a single unit-cell (1UC) layer of FeSe film grown on a SrTiO₃(001) substrate (STO), electron transfer from the STO substrate to the FeSe layer is believed to play an essential role in the emergence of a large superconducting energy gap (ranging from 10 to 22 meV) and a high Tc value (ranging from 20 to 109 K in different studies). For a multilayer FeSe film on STO, in contrast, no superconducting like energy gap could be observed, indicating that the electron doping is very limited to the first FeSe layer in close proximity to the STO substrate. Alternatively, researchers found another strategy to enhance superconductivity in multilayer or bulk FeSe by depositing alkali-metal (K or Na) atoms on the surface. Such a top-down electron doping at appropriate K coverage (K) results in a superconducting like energy gap closing at a temperature as high as ~48 K. However, the superconductivity in the K-adsorbed FeSe multilayers has not been verified yet via measurements of zero resistance or the Meissner effect, which requires in situ experimental techniques to overcome the problem from

vulnerability of K adatoms to air. In contrast, the nature of the superconductivity in K/FeSe films has not been well studied yet. Moreover, a dome-shaped relation between the energy gap and doping level has been discovered in K/FeSe films, while only discrete T_c values were found in FeSe thin flakes by continuously tuning carrier concentration with a solid ionic gating technique. It is therefore very natural to raise questions whether a continuous dome-shaped phase diagram exists or not in a FeSe-derived superconductor.

Based on a commercial STM with a four-electrode piezo scanner tube, we developed a multifunctional STM that enables in situ four-point-probe electrical and two-coil mutual measurement inductance measurement in additional to general STM/S. We succeed in observing diamagnetic response of K/FeSe multilayers at various K_c, and thus reveal a continuous dome-shaped (T_c, K_c) phase diagram and experimental evidence for the macroscopic superconductivity in a K/FeSe film. Besides T_c, the information about the superconducting energy gap (ΔE), penetration depth (λ) and superfluid density (ps) is also collected at various K's, from which spatial inhomogeneity of ΔE , quadratic low temperature variation of λ and an approximate linear relation between T_c and ρ s are revealed. These discoveries may be helpful for further understanding of superconductivity in FeSe-derived superconductors. The relevant work was published in Phy. Rev. Lett. 123 (2019) 257001.



Fig. 2: K-adsorbed Multilayer FeSe Film. (a) Schematic diagram; (b) STM image; (c) Evolution of Tc as a function of coverage of K (K_c); (d) Ratio of superconducting gap and T_c vs K_c; (e) Approximate linear relationship between T_c and superfluid density.



3.14 东北大学联合研究分部

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3.14.1 研究工作简述

东北大学联合研究分部主要围绕材料腐蚀与防护的核心科学与技术问题,针对远洋、深海、深地、 极地、微生物、高温等环境特征,开展的腐蚀试验设备研制、材料腐蚀机理等方面的研究工作,并在耐 蚀-功能性材料、新型防护涂层、腐蚀监检测等防腐蚀技术的原理与设计、制备新技术、性能提升及工程 应用探索等方面取得突破。主要研究领域包括:轻金属表面处理、油气工业腐蚀与防护、海洋环境腐蚀 与防护、微生物腐蚀、高温腐蚀与防护等。

2019年度,本研究部取得的重要进展有:

(1)针对中国石油天然气资源开发过程中特有的深地腐蚀问题,建立了系列性的"Fe-Cr-Cl-CO₂-H₂O"五元高温高压E-pH图。在E-pH图的基础上,建立了"压力-温度-流体-应力"四自由度的腐蚀寿命预测模型。从热力学和动力学角度,实现对苛刻油气环境下材料腐蚀的预测。系统回答了"材料在苛刻油气环境下会不会腐蚀?多久会发生腐蚀?",这两个长期困扰我国西部油气资源开发过程中的腐蚀问题。

(2)突破性研制新型Co(OH)₂修饰TiO₂纳米管—Al-Zn-In-Mg-Ti复合光阳极材料,对Q235碳钢提供了双 重电化学阴极保护。在浸泡后期,Al牺牲阳极保护效率降低的情况下,TiO₂纳米管层起到较好的光电化 学补充保护作用,显著地延长了牺牲阳极材料的使用寿命,为海洋金属腐蚀防护方法设计与研制提供了 新思想。

(3)发现植物源的儿茶精水合物(Catechin hydrate)可以作为既能杀菌又能抑制微生物腐蚀的多效绿色环 保型杀菌剂和缓蚀剂。其不仅可以有效抑制细菌的生物被膜的形成基因使其具有出色的抗菌性能,还具 备优良的缓蚀性能和生物安全性,实现了"绿色杀菌、一剂多效",为开发绿色环保无污染型杀菌剂和 防治微生物腐蚀提供了新途径。

(4)发明了一种含氟化物 (CaF₂) 搪瓷涂层。搪瓷[SiO₄]网络结构具有较高的热稳定性,并且搪瓷中 CaF₂与熔融铝液反应后,在搪瓷/熔融铝液界面形成气相氟化铝,降低铝液在搪瓷表面的润湿性,进而提 高搪瓷涂层的抗铝液腐蚀性能。该研究为在熔融铝液环境下服役的各种金属结构件材料提供了一种新的 高温防护涂层方案。

2019年度,在国际学术刊物发表论文55篇。

3.14.1.1 油气环境下金属材料的E-pH图及腐蚀预测

我国西部石油天然气资源的开发,面临着世界 范围内都极为罕见的高温、高压、高盐分、高浓度 H₂S/CO₂气体、应力与流体协同作用的苛刻油气环 境的挑战。这是中国特有的腐蚀环境,国外没有相 关研究报道。由于无法预测油管的腐蚀寿命,给设 计、管理和决策带来了巨大的困难,材料腐蚀问题 极其严重,经济损失以数十亿计。相图是预测合金 显微组织和力学性能最重要的工具,是金属材料研 究中最基础的内容之一。E-pH图是金属腐蚀的电纶 学相图,对于腐蚀研究的重要性不言而喻。建立研 刻油气环境下的E-pH图,必须考虑高温、高压、腐 蚀气体以及CI、CO₃²离子等多因素耦合的影响, 其复杂程度远超出常规E-pH图所考虑的范围。在国 际上,苛刻油气环境下材料的E-pH图一直处于空白 状态,对于材料发生腐蚀的可能性都无法判断。

为此,通过校正高温高压条件下的热力学参 数(焓、熵、自由能、热容、离子活度),综合 考虑合金各组元与H2O、Cl⁻、CO3²⁻的共同作用, 建立了系列性的"Fe-Cr-Cl-CO₂-H₂O"五元E-pH 图。在E-pH图的基础上,将原本相互分散、割裂的 Sridhar模型、开路电位模型、点缺陷模型、 "花边 -内切"成长模型、Gutman模型有机地整合起来, 建立了"压力-温度-流体-应力"四自由度的腐蚀寿 命预测模型。从热力学和动力学角度,实现对苛 刻油气环境下材料腐蚀的预测。这些工作系统回 答了"材料在苛刻油气环境下会不会腐蚀?多久 会发生腐蚀?",这两个长期困扰我国西部油气 资源开发过程中的腐蚀问题。目前已被中石化西 北局用于指导顺北超深油井的选材,相关工作发表 在Electrochim. Acta 293 (2019) 116和J. Electrochem. Soc. 166 (2019) C539 上。



图1 根据热力学相图(a)和点蚀寿命模型(b),可以定量回答"材料在苛刻油气环境下会不会腐蚀?多久会发生腐蚀?"的问题。

3.14.1.2 新型Co(OH)₂修饰TiO₂纳米管--Al-Zn-In-Mg-Ti复合光阳极材料设计及研制

海洋环境下牺牲阳极保护是最常用防护手段之一。但传统Al-Zn-In-Mg-Ti牺牲阳极在海洋环境下 消耗快、易海生物附着,性能及寿命都有待大幅度 提高。光催化牺牲阳极本身不消耗,不易海生物吸 附,在海洋环境下非常具有优势。但因其自身很难 实现高的防护性能,并且夜间失效,一直不能有效 应用。

本工作由刘莉教授与刘岗研究员合作研究, 首次创新性地设计并研制了将传统Al-Zn-In-Mg-Ti 牺牲阳极材料与Co(OH)₂修饰TiO₂纳米管光催化材 料相结合的新型复合光阳极材料。基于形貌、成 分、电化学保护性能的长期变化等测试结果,提 出了复合光阳极通过TiO₂纳米管层和牺牲阳极基 体层共同提供电子的方式,并实现了对Q235碳钢 提供了双重电化学阴极保护。在浸泡后期,复合 光阳极中的牺牲阳极基体层保护效率降低的情况 下,TiO₂纳米管层起到了较好的光电化学补充保 护作用,可实现牺牲阳极材料的寿命延长。该工 作得到国际同行高度肯定,以及审稿人评价; "A new Al photoanode coating based on titanium, cobalt and sacrificial materials was proposed and designed to provide new ideas for cathodic protection in the marine environment. The topic is interesting and deserves attention." 为海洋环境中金属的腐蚀防护方法设 计与研制以及光催化材料应用提供了新的设计思 想。该工作发表于J. Electrochem. Soc. 166 (2019) H3215。

3.14.1.3 绿色环保多功能微生物腐蚀抑制剂

海洋用钢铁材料的最主要破坏形式就是腐蚀, 其中因海洋微生物引起的腐蚀约占海洋材料腐蚀的 70-80%,引起的损失高达上千亿美元。海洋环境 中,材料表面形成的生物被膜是导致微生物腐蚀的 主要原因之一。生物膜下材料的物理化学环境发生 改变,如溶解氧、离子浓度、pH值等,同时伴随 着微生物对电化学反应的催化过程,最终导致材料 的严重腐蚀。防止微生物腐蚀的关键就是如何有效 去除生物膜,目前最常用有效的方法就是使用杀菌



图2 新型光催化复合牺牲阳极材料形貌、性能及原理示意图。

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图3 植物源的儿茶精水合物(Catechin hydrate)可以作为绿色环保无污染型杀菌型。不仅具有优良的抗菌的性能,抗生物被膜性能,还具备优良的缓蚀性能,实现了"一剂多效"。

剂,但绿色环保的杀菌剂种类非常有限。杀菌剂的 大量使用不仅大幅度提升了微生物的耐药性,并且 对环境保护及生物健康造成极大的损害。寻找既能 杀菌又能抑制微生物腐蚀和腐蚀的多效绿色环保杀 菌剂是目前面临的世界难题。

我们发现植物源的儿茶精水合物(Catechin hydrate),可以作为绿色环保无污染型杀菌型。其 不仅具有优良的抗菌的性能,抗生物被膜性能,还 具备优良的缓蚀性能,实现了"一剂多效"。儿茶 素在500pm高浓度时对细胞依然没有明显毒性,说 明了其优良的生物安全性。我们发现儿茶素可以抑 制细菌的生物被膜的形成基因,从而抑制细菌生物 被膜的形成。通过量子化学计算也验证了儿茶素 具备优良的缓蚀性能和在金属材料表面成膜的能 力。相关工作分别发表在Corro. Sci. 157 (2019) 98 和Bioelectrochemistry 128 (2019) 193上。

3.14.1.4 耐熔融铝液腐蚀搪瓷涂层

热浸镀广泛应用于建筑、家电、车船等行业, 在国民经济中占有很大比重。2017年,我国仅热浸 镀锌钢板产能即达9300万吨。当前,我国热浸镀金 属的制品率(14%)远低于工业发达国家(58%),最直 接的原因就是锌、铝等液态金属导致的不锈钢设备 腐蚀。国内对液态金属腐蚀机理以及腐蚀与摩擦磨 损的协同作用研究尚处于起步阶段,腐蚀设备的维 修周期仅有14天。热浸镀设备的液态金属腐蚀问题 已受到了包括首钢、唐钢、鞍钢等众多大型钢铁企 业的密切关注。

作为腐蚀防护用的WC-Co金属陶瓷复合涂层, 则由于孔隙率高、耐磨耐蚀性差,在液态金属腐蚀 以及热浸镀钢带的摩擦磨损协同破坏下,服役寿命 短,表面状态差导致热浸镀产品质量严重下降。搪 瓷就是在金属表面通过特殊工艺涂烧一层或多层不 透明的非金属无机材料,使金属与无机材料在高温 下发生物理化学反应,析出晶体并形成化学键,把 两者牢固结合成一个整体,因而具有抗冲击、耐腐 蚀、光滑美观、绝缘、耐热、耐磨等优点,有望替 代传统WC-Co复合涂层,成为热浸镀设备用新型 的腐蚀防护涂层体系。研究发明了一种含氟化物 (CaF₂) 搪瓷涂层, 搪瓷[SiO₄]网络结构具有较高 的热稳定性,且搪瓷中CaF,经与熔融铝液反应后在 搪瓷/熔融铝液界面形成气相氟化铝,降低铝液在 搪瓷表面的润湿性,进而提高搪瓷涂层的抗铝液腐 蚀性能。该研究为在熔融铝液环境下服役的各种金 属结构件材料提供了一种新的高温防护涂层方案, 相关结果发表在Corros. Sci. 148 (2019) 228。



图4 304不锈钢以及涂覆搪瓷涂层经750℃熔融铝液腐蚀不同时间后截面形貌:(a)304不锈钢腐蚀60分钟,腐蚀层厚度~300 μm;(b)搪瓷涂层腐蚀30小时后表面完好,未形成连续腐蚀层;(c)氟化铝750℃的热力学平衡状态图,存在多种气相氟化 铝。



3.14 Northeastern University Joint Division



DIVISION HEAD: WANG Fuhui

RESEARCH GROUP LEADERS: (4)

ZHANG Tao (Surface Treatment of Light Alloys)LIU Li (Marine Corrosion and Protection)XU Dake (Microbiology Induced Corrosion)Chen Minghui (High Temperature Corrosion and Protection)

3.14.1 Summary of Scientific Activities

The research directions of the Northeastern University Joint Division mainly focus on the core scientific and technological issues of corrosion and protection for the materials. According to the different characteristic corrosion environments such as ocean, deep sea, poles, high temperature and the presence of microorganisms, we conduct researches on the development of corrosion test equipments, material corrosion mechanisms and corresponding protection technologies. We have advanced the design and preparation of corrosion-resistant functional materials, novel protective coatings, and better understanding for the principles of corrosion monitoring, detection, and anti-corrosion technologies for engineering applications. The major research interests of our division include: surface treatment of light alloys, corrosion and protection in oil and gas industry and marine environment, microbiologically influenced corrosion, and high temperature corrosion and protection.

We have published 55 peer-reviewed papers in 2019, and the main progresses are shown as follows:

(1) We successfully establish the quinary Fe–Cr–Cl– CO_2 – H_2O E-pH diagram under extreme environment, on the basis of which, the new four-variance model can predict the lifespan under corrosion by combining all the existing models. This work contributes to answer the key questions to determine the occurrence of corrosion and when it will occur, addressing the knottiest concerns that trouble the oil-drilling enterprises in western China.

(2) We design a novel composite photoanode material, which combines the traditional Al-Zn-In-Mg-Ti sacrificial anode material and $Co(OH)_2$ modified TiO₂ nanotube photocatalyst material for the first time. At the late stage of immersion, when the protection efficiency of the sacrificial anode matrix layer in the composite photoanode is reduced, TiO₂ nanotube layer plays a better complementary role in photoelectrochemical protection, which can prolong the life of the sacrificial anode material.

(3) We discover the catechin hydrate, an effective eco-friendly multifunctional chemical with excellent antibacterial, antibiofilm and anticorrosion activities, possessing strong potential to be applied in the marine, oil and gas industries to solve the global concerns caused by the microbiologically influenced corrosion. Catechin hydrate, originated from the aromatic and medicinal plant, can inhibit the corrosion induced by Pseudomonas aeruginosa with an excellent inhibition efficiency of 99.8%.

(4) We develop a novel enamel coating containing fluoride (CaF_2) . The $[SiO_4]$ network structure of enamel has high thermal stability, and CaF_2 is easy to react with molten aluminum to form gaseous aluminum fluoride at the interface of enamel/molten aluminum, which reduces the wettability of aluminum onto the enamel surface and improves the corrosion resistance of enamel coating. This study provides a new high temperature protective coating for various metallic equipment served in molten aluminum environment.

3.14.1.1 Pourbaix Diagrams and Life Prediction for Stainless Steel in Extremely Aggressive Oil & Gas Environment

The exploitation of oil & natural gas in western China is suffering from the most extreme environment in the world, in which high temperature, high salinity, high concentration H_2S/CO_2 and complicated synergistic effect between stress and flow coexist. This extreme drilling conditions is peculiar to China, which has never been reported and dealt with elsewhere in the world. The difficulty in predicting the lifespan of pipelines brings a series of problems to oil-drilling companies for the design, management and decision-making of their oil extraction behavior. The failure of these pipelines due to corrosion will instantaneously lead to the loss of billions of dollars. Phase diagram is the most fundamental tool in metallurgy and materials science, which helps predict the microstructure and mechanical properties of alloys. The E-pH diagram is the "phase diagram" in electrochemistry, but it thermodynamically predicts the electrochemical reactions, which justifies its usefulness in corrosion





Fig. 1: (a) Pourbaix diagrams of HP-13Cr stainless steel and (b) the prediction for pit depth as a function of well depth after 6 years of service in the extremely aggrassive environment.

science. However, the E-pH diagram under extreme environment has yet to be established, which obstructs corrosion scientists to predict the possibility of pipelines to corrode. The establishment of E-pH diagram under extreme environment is much more complicated than its equivalent under normal conditions, since it needs to consider the synergistic effect of high temperature, high pressure, corrosive gas and corrosive anions (Cl- and CO_{2}^{2}). Our research group strives to establish the quinary Fe-Cr-Cl-CO₂-H₂O E-pH by fully comprehending the synergistic effect of different element, and correcting the thermodynamic parameters (entropy, enthalpy, Gibbs free energy, heat capacity and ionic activities) under extreme environment. On the basis of the E-pH diagram, the new four-variance model predict the lifespan under corrosion by combining the existed models, such as the Sridhar Model, the Open Circuit Model, the Point Defect Model, the Lacy Model and the Gutman Model. The current work contributes to answering the question concerning the possibility of corrosion to occur and how long it takes to occur. These questions are the most difficult ones that trouble the oil-drilling enterprises in western China. The model has also been successfully applied by Northwest Bureau of Sinopec to the select of pipeline. For the detailed version of this work, please refer to the published articles: *Electrochimi. Acta* 293 (2019) 116 and *J. Electrochem. Soc.* 166 (2019) C539.

3.14.1.2 A New Co(OH)₂/TiO₂ Photocatalytic Composite AI-Zn-In-Mg-Ti Sacrificial Anode Material

Sacrificial anode protection is one of the most commonly used protection methods in the marine environment. However, the traditional Al-Zn-In-Mg-Ti sacrificial anode consumes fast and is easy to be attached to marine organisms in the marine environment. Its performance and life span need to be greatly improved. The photocatalysis sacrificial anode itself is not consumed and is not easy to be adsorbed by marine organisms, so it has a great advantage in the marine environment. However, it is difficult to achieve high protection performance and failure at night,



Fig. 2: Schematic diagram of morphology, performance and principle of a new $Co(OH)_2/TiO_2$ photocatalytic composite Al-Zn-In-Mg-Ti sacrificial anode material.

so it has not been effectively applied. In this work, a new composite photoanode material, which combines the traditional Al-Zn-In-Mg-Ti sacrificial anode material and Co(OH), modified TiO, nanotube photocatalyst material was studied for first time. Based on the long-term test results of morphology, composition and electrochemical protection performance, the way of composite photoanode providing electrons through TiO, nanotube layer and sacrificial anode substrate layer is proposed, and the dual electrochemical cathodic protection for Q235 carbon steel is realized. At the later stage of immersion, when the protection efficiency of the sacrificial anode matrix layer in the composite photoanode is reduced, TiO, nanotube layer plays a better complementary role in photoelectrochemical protection, which can prolong the life of the sacrificial anode material. This work has been highly recognized by the international peers and evaluated by the reviewers; "A new Al photoanode coating based on titanium, cobalt and sacrificial materials was proposed and designed to provide new ideas for cathodic protection in the marine environment. The topic is interesting and deserves attention. "Provides a new design idea for the design and development of corrosion protection methods

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of metals in the marine environment and the application of photochemical materials. This work was published in *J. Electrochem. Soc.* 166 (2019) h3215.

3.14.1.3 Catechin Hydrate as a Multifunctional Eco-friendly Biocorrosion Inhibitor

Corrosion still remains a tenacious problem of iron and steel materials in marine environment. Microbiologically influenced corrosion (MIC) accounts for most of the material damages in marine environment, the losses of which amounts up to hundreds of billions dollar losses annually worldwide. The biofilm is responsible for MIC, thus how to mitigate MIC mainly focuses on the treatment of the biofilm. Biocide is the most common and effective method to treat biofilm, while it is not "green", and long term and high dosage treatment escalates the resistance of the biofilm and the pollution to the environment. An eco-friendly MIC inhibitor is desired to solve this global concern. Catechin hydrate (CH), originated from the aromatic and medicinal plant, was evaluated for its antimicrobial, antibiofilm and anticorrosion activities for 304L stainless steel against marine corrosive biofilm by



Fig. 3: Schematic illustration of an eco-friendly multifunctional biocorrosion inhibitor, catechin hydrate, for its antibacterial, antibiofilm, and anticorrosion properties.

means of surface analysis, electrochemical measurements and quantum chemical calculations. Results showed that CH inhibited the biofilm formation and killed mature biofilms. Electrochemical data demonstrated that CH inhibited the corrosion induced by Pseudomonas aeruginosa with an excellent inhibition efficiency of 99.8%. It was also found that CH significantly downregulated the expressions of critical genes for quorum sensing and biofilm formation as revealed by qPCR data. The scanning electron microscopy and transmission electron microscopy images showed that the antibacterial mechanism of CH was by damaging the cell membranes and thus leading to the leakage of the cell constituents. This study demonstrated that CH is an effective eco-friendly multifunctional chemical with excellent antibacterial, antibiofilm and anticorrosion activities, possessing strong potential to be applied in marine, oil and gas industries.

3.14.1.4 Enamel Coating Resistant to Molten Aluminum Corrosion

Hot dip galvanizing is widely used in construction, household electrical appliances, vehicle and ship industries, and occupies a large proportion in the national economy. In 2017, China's capacity of hot-dip galvanized steel plate reached 93 million tons. At present, the rate of hot-dip products in China (14%) is far lower than that in developed countries (58%), the most direct reason of which is the corrosion of stainless steel equipment caused by liquid metals such as zinc and aluminum. In China, the research on corrosion or tribocorrosion in liquid metals is still in its infancy, and the maintenance period is only 14 days. Accordingly, corrosion of liquid metal in hot dip galvanizing equipment aroused close attention from many large iron and steel enterprises, including Shougang, Tanggang and Angang . The WC-Co composite coating for corrosion protection, due to its high porosity, poor wear resistance and corrosion resistance, has a short service life and poor surface state, which leads to a serious decline in the quality of hot-dip products under condition and tribocorrosion in the liquid metals.

Enamel is to burn one or more layers of non-metallic inorganic materials on the metal surface by a special process, so that the metal and inorganic materials will have physical and chemical reactions at high temperature, form chemical bonds, and firmly combine the two into a whole, so it has the advantages of impact resistance, corrosion resistance, smooth and beautiful appearance, insulation, heat resistance, wear resistance, etc., and is expected to replace the traditional WC-Co composite coating to be used on hot dipping equipment. A kind of enamel coating containing fluoride (CaF₂) was developed. The [SiO₄] network structure of enamel has high thermal stability, and CaF, is easy to react with molten aluminum to form gaseous aluminum fluoride at the interface of enamel/molten aluminum, which reduces the wettability of aluminum onto the enamel surface and improves the corrosion resistance of enamel coating. This study provides a new high temperature protective coating for various metallic equipment served in molten aluminum environment, and the relevant results are published in Corros. Sci. 148 (2019) 228.



Fig. 4: Cross-sectional morphologies of 304 stainless steel with or without enamel coating after corrosion in molten aluminum at 750°C for different times: (a) the 304 stainless steel, 60 min corrosion, forming a \sim 300 µm thick corrosion layer; (b) the enamel coating, 30 h corrosion, stable and without corrosion; (c) thermodynamic equilibrium diagram of volatile aluminum fluorides at 750°C.

3.15 技术支撑部



技术部主任(副):张 磊

技术组负责人(5人)

- 吴 波 (透射技术组)
 谭 军 (扫描技术组)
 王绍钢 (射线技术组)
 姚 戈 (性能技术组)
- 张 磊 (制样技术组)

2019年是技术支撑部开启新征程的一年,在平 台建设规划,管理运行,理化分析能力拓展以及与 大科学装置联合,新分析测试中心基础设施布局等 多方面均取得了新的进展。

3.15.1 建设平台

分析测试平台的建设规划重点是面向材料高端 微分析技术能力的提升。继续强化原子级分辨谱学 分析技术,纳米尺度晶体及缺陷表征,拓展微纳加 工的广度和深度;进一步加强性能测试装备研制等 技术方向的青年高级技术人才的引进和培养;同时 联合大科学装置,来满足高端应用需求的射线技术 提升,并促进技能人才的成长。

在先期分析测试中心仪器装备规划与布局的 同时,分期分批采购设备。2019年度投入超过3500 万元购置包括球差和高分辨透射电镜,X射线微聚 焦荧光谱仪用于微结构与成分分析;添置了热机械 性能、微动疲劳等材料服役性能试验机;以及热分 析、激光热导仪和液相色质联用谱仪等理化测试分 析关键设备。完善改进自主研制的高温洛氏硬度仪 测试装备拟通过标准组织认证;开始逐步推进与上 海光源实验平台的共建联合,依托线站技术能力, 发展与SYNL研究目标相适应的相关配套装备和技 术方法,扩展研究工具与手段,形成具有特色的新 技术能力。

完善了分析测试技术平台管理规范,制定了适应技术支撑部共享平台建设发展的管理条例,改革 了分析测试技术队伍的绩效评估办法。技术支撑人 员以服务为中心,与SYNL的研究任务紧密联系, 创新发展技术装备及方法,立足岗位为创建国际一 流共享材料分析测试平台而努力。

3.15.2 共享运行

所有分析测试设备已全部纳入网上共享管理 系统,实现设备预约、机时记录的一致性。管理数 据的统计与分析更加准确便捷。为适应新的管理规 范,开发了内部经费使用申请与审批微信小程序; 结合技术岗位提出的要求,对共享管理系统进行了 更新升级。

技术支撑部2019年提供研究与服务机时达15 万小时,年培训学生与科研人员1432人次,用于样 品制备的关键设备:透射电镜、扫描电镜、X射线 衍射仪和性能测试的大型设备的运行时间达到10万



图1 技术支撑部微信小程序用于经费申请与设备预约的入 口界面。

小时,电镜类设备年度平均机时达2559小时,为标准负荷1800小时的142%,保持了高负荷运行状态。部分电镜用于科研的机时超过4500小时,接近饱和。设备运行效率保持在高水平,设备机时资源真正实现共享管理。在服务于SYNL科研工作的同时,为航天、交通、大学、研究机构以及地方高科技企业等外部用户提供了及时准确的分析测试与咨询服务。

3.15.3 技术发展

飞行时间二次离子质谱的浓度检出限可达ppm 级,具有全周期表元素、同位素以及分子簇的分析 鉴别能力。除在分析H、Li、Be、B等轻质元素显 示出优势外,近几年二次离子质谱技术在SYNL的 应用随多领域研究工作的开展呈现出新的能力。即 使钢中稀土的含量仅在100 ppm以下,利用氧化态 稀土与稀土二次离子的比值能够区分稀土在钢中以 氧化物还是固溶的形式存在;利用二次离子质谱的 逐层剥离的纵向深度分析技术结合三维分析技术, 可以清晰的分辨出金属与陶瓷异质界面微量的元素 扩散;近来在二维材料的工艺研究中,二次离子质 谱的组分面分布表征和深度分析能力也发挥着不可 替代的作用。与研究工作密切配合的二次离子质谱 分析技术在解决科研工作关键问题的同时,也在持 续努力进步,展示出良好的发展前景。



图2飞行时间二次离子质谱三维数据生成与处理流程示意图。





3.15 Technical Support Division

DEPUTY DIVISION HEAD: ZHANG Lei

TECHNICAL GROUP LEADERS: (5)

WU Bo (TEM Group) TAN Jun (SEM Group) WANG Shaogang (X-ray group) YAO Ge (Property Group) ZHANG Lei (Sample Group) 2019 is a new year for the technical support division (TSD) of the SYNL for plan and reform. New progress has been made in platform construction planning, management and operation, physical and chemical analysis capacity expansion, infrastructure layout of the new analysis and test center, etc.

3.15.1 Constructing Platform

The construction plan of the analysis and testing platform focuses on the improvement of the capability of high-end microanalysis technology of materials. It is required to continue in strengthening the atomic resolution spectroscopy analysis technology, nanoscale crystal and defect characterization, expanding machining capability in micro and nano scale. It also needs to introduce and cultivate young talents to become skillful technical staff. At the same time, we also cooperate with large scientific facilities like synchrotron radiation to meet the needs of high-end applications of X-ray technology.

In 2019, more than 35 million yuan has been invested to purchase equipment, including spherical aberration and high-resolution transmission electron microscopy, X-ray micro focus fluorescence spectrometer for microstructure and component analysis; testing machines for thermomechanical properties, fretting fatigue tester for material service performance evaluation; as well as physical and chemical analysis equipment such as thermal analysis, laser thermal conductivity measurement and liquid chromatography-mass spectrometry. The self-developed high-temperature Rockwell hardness tester was carried on experiment for more and more sample and kept on improvement to pass the certification of the standards organization. We start to build a joint experimental platform with Shanghai Synchrotron Radiation Facility. With the cooperation of various beamlines, relevant supporting equipment and technical methods are expected to be developed for the research objectives of the SYNL.

We have improved the management by formulating the regulations to adapt the TSD development for public technical service. Reformed personal evaluation prompts the technical staff to have more independent innovations in equipment and methods relied on close cooperation with the researchers of the SYNL. Our effort is to create a world-class analysis and testing platform for material research.

3.15.2 Shared Operation

All the equipment has been incorporated into the online sharing management system to achieve the consistency of equipment booking and machine time record. The statistics and analysis of management data are more accurate and convenient. We developed a Wechat small program for the application and approval of the TSD expenses. The software of the management system was updated according to additional requirements of the service process.

In 2019, the TSD provided about 150 thousands hours of machine time for research and service, and trained 1432 students or SYNL employee. The annual average machine time of the electron microscopes reached 2559 hours, which was 142% of the standard load of 1800 hours. Some of the electron microscopes were used for more than 4500 hours, close to saturation of working days. The utilization efficiency of equipment usage is kept at a high level. While serving the scientific research work of SYNL, we also provided timely and accurate analysis, testing and consulting services for external users such as aerospace, transportation, universities, research institutions and local high-tech enterprises.

3.15.3 Developing Technique

The detection limit of time-of-flight secondary ion mass spectrometry (TOF-SIMS) is ppm. The ability covers all elements in periodic table, isotopes and molecular clusters. In recent years, the application of TOF-SIMS in SYNL has shown new capabilities with the extension of research work in many fields. Even if the content of rare earth in steel is less than 100 ppm, the secondary ions ratio of the oxidized species to the non-oxidized species of rare earth can be used to distinguish whether rare earth exists in the form of oxide or solid solution in steel. Threedimensional analysis technology of TOF-SIMS can clearly distinguish the trace element diffusion at a metal/ceramics heterogeneous interface. TOF-SIMS also finds increasing applications for 2D material research.



Fig. 1: 2D crystal characterized by microanalysis techniques, optical microscope, atomic force microscope, selected area electron diffraction and HR-TEM.
4 年度大事记 EVENTS OF THE YEAR



4.1 2019年3月28日,首届建设运行管理委员会、学术委员会第一次会议在北京召开。

4.2 2019年4月26日,成立沈阳材料科学国家研究中心党总支。

4.3 2019年5月6日,材料设计与计算研究部成立。

4.4 2019年6月25日,轻金属材料研究部成立。

4.5 2019年12月31日,李依依院士荣获2019年度辽宁省科学技术最高奖;"金属材料的搅拌摩擦焊接与加工基础研究"获辽宁省自然科学一等奖。

5 附表 APPENDIX

5.1 科研及管理人员 STAFF

5.1.1 中心主任(1人)	5.1.1 DIRECTOR OF SYNL (1)
卢 柯	LU Ke
5.1.2 中心副主任(2人)	5.1.2 DEPUTY DIRECTORS OF SYNL (2)
张劲松* 李秀艳*	ZHANG Jinsong* LI Xiuyan*
(*兼PI)	(*Concurrent Post as PI)
5.1.3 研究部主任(13人)	5.1.3 RESEARCH DIVISION HEADS (13)
陈成黄贾李李卢吕马王王张张**********************************	CHEN Xingqiu [*] CHENG Huiming HUANG Xiaoxu [*] JIA Jinfeng [*] LI Dianzhong [*] LI Yi [*] LU Ke LU Jian [*] MA Xiuliang [*] WANG Fuhui WANG Jingyang [*] ZHANG Jinsong [*] ZHANG Zhidong
(*兼PI)	(*Concurrent Post as PI)
5.1.4 研究组负责人(60人)	5.1.4 PRINCIPAL INVESTIGATORS (60)
陈春林 陈 军 军 王 御 韩 王 明 府 加 黄 時 御	CHEN Chunlin CHEN Minghui CHEN Xian CHEN Xingqiu DU Kui FU Paixian HAN Zheng HU Weijin HUANG Mingxin HUANG Xiaoxu
寅 භ 旭 贾 金 锋 美 辛	HUANG Xiaoxu JIA Jinfeng IIANG Xin
女 「	179

矫义来	JIAO Yilai
金海军	JIN Haijun
李 昺	LI Bing
李殿中	LI Dianzhong
李 峰	LIFeng
李美栓	LI Meishuan
李 琦	
了 · · · · · · · · · · · · · · · · · · ·	LI Viuvan
本 杂	LIVi
丁 权	LIIIChang
刘勾	LIU Chain Tsuan
刘饰川	
刘利	
刘庆	LIU Qing
刘伟	LIU Wei
卢磊	LU Lei
陆善平	LU Shanping
吕 坚	LU Jian
马秀良	MA Xiuliang
马宗义	MA Zongyi
齐伟	QI Wei
任文才	REN Wencai
尚建库	SHANG Jianku
SROLOVITZ David Joseph	SROLOVITZ David Joseph
苏国跃	SU Guoyue
孙东明	SUN Dongming
邰凯平	TAI Kaiping
陶乃镕	TAO Nairong
王建强	WANG Jianqiang
王京阳	WANG Jingyang
王恭丰	WANG Jingfeng
工版 王 拉	WANG Pei
王幻青	WANG Shaoqing
工化内工的程	WANG Xiaohui
工化化	WANG Zhenhua
工场十	WANG Zhenbo
工 快波 公上 可	XU Dake
体入了	YANG Yongjin
初水过	YANG Zhenming
初祝明	ZHANG Bo
状 波 ル ー エ	ZHANG Guangning
张厂半	ZHANG Haifeng
张海峰	ZHANG lie
张洁	ZHANG Jingong
张劲松	
张军旗	
张涛	
朱银莲	ZHU Yinlian

SYNL

5.1.5 技术支撑部负责人(5人)

张 磊* (副主任) 谭 军 王绍钢 吴 波 姚 戈

(*兼组负责人)

5.1.6 科技管理办公室(5人)

时元宝(主任) 陈红梅 聂英石 邢传宇 月 伟

5.1.7 办公室(6人)

刘树伟(主任) 高 李 冬 歳 青 乐 乐

5.1.5 TECHNICAL SUPPORT LEADERS (5)

ZHANG Lei^{*} (Deputy Head) TAN Jun WANG Shaogang WU Bo YAO Ge

(*Concurrent Post as Support Group Leader)

5.1.6 TECHNOLOGY ADMINISTRATION OFFICE (5)

SHI Yuanbao (Head) CHEN Hongmei NIE Yingshi XING Chuanyu YAN Wei

5.1.7 SYNL OFFICE (6)

LIU Shuwei (Head) GAO Feng LI Dongxu LIU Wei LYU Qing YANG Le

5.2 荣获奖励情况

AWARDS AND HONORS

5.2.1 在职人员

卢 柯 Acta Materialia金质奖章(国际材料科学与工程领 域的终身成就奖)

李依依 辽宁省科学技术最高奖

马秀良 亚太材料科学院院士

王京阳 美国陶瓷学会会士

马宗义、肖伯律、倪丁瑞、薛鹏、王东 辽宁省自然科学一等奖

陈先华、王敬丰、彭建、王勇、潘复生 教育部自然科学二等奖

贾金锋、钱冬、刘灿华、高春雷、管丹丹 教育部自然科学二等奖

新千千 电子显微学会议优秀报告奖

李 昺
 日本中子学会青年研究奖
 2019年中国十大新锐科技人物

李 波 国家超级计算广州中心2019 "天河之星"优秀应 用奖

刘 莉 中国腐蚀与防护学会四十年贡献奖"优秀学会工作 者"

刘 洋 中国科学院包头稀土研发中心首届"包头稀土杯" 科技创新邀请赛三等奖

卢 柯 中国科学院优秀研究生导师奖

卢 磊 中国科学院优秀研究生导师奖

陆善平 中信微合金化技术中心中信铌钢科技发展三等奖

5.2.1 BY FACULTY AND STAFF

LU Ke Acta Materialia Gold Medal

LI Yiyi Highest Science and Technology Award of Liaoning Province

MA Xiuliang Academician of Asia Pacific Academy of Materials

WANG Jingyang Fellow of the American Ceramic Society

MA Zhongyi, XIAO Bolv, NI Dingrui, XUE Peng, WANG Dong First Prize of Natural Science Award, Liaoning Province

CHEN Xianhua, WANG Jingfeng, PENG Jian, WANG Yong, PAN fusheng Second Prize of Nature Science Award by Minister of Education, China

JIA Jinfeng, QIAN Dong, LIU Canhua, GAO Chunlei, Guan Dandan Second Prize of Nature Science Award by Minister of Education, China 钱余海
中国腐蚀与防护学会四十年贡献奖—优秀会员
孙鲁超
第九届国际稀土开发与应用研讨会暨2019中国稀土
学会学术年会优秀口头报告
郤凯平
中国科学院"优秀导师奖"
中国科学与技术大学"优秀导师奖"
唐云龙
中国硅酸盐学会微纳技术分会卓越青年讲席

中国硅酸盐学会做纳技术分会早越育牛饼, 沈阳市杰出人才 中国电子显微学会优秀青年学者

张 波 中国腐蚀与防护学会杰出青年学术成就奖

张 峰 第十届中日韩三国新材料国际学术研讨会最佳墙报 奖

张 涛 欧洲腐蚀联盟青年科学家奖

SYNL 2019 年度报告 (ANNUAL REPORT)

5.2.2 研究生

方若翩 中国科学院优秀博士学位论文

杨勇强 中国科学院优秀博士学位论文

程 钊 中国科学院院长特别奖 中国科学技术大学优秀博士学位论文

靳 群 中国科学院院长特别奖

周 鑫 中国科学院院长特别奖 中国科学技术大学优秀博士学位论文

康宇阳 中国科学院院长优秀奖

陈文雄 东北大学轧制技术及连轧自动化国家重点实验室优 秀报告二等奖

关 怀 2019中国材料大会优秀墙报奖

李晓齐 第十四届新型炭材料学术研讨会最佳墙报奖

吴 静 第三届亚洲电化学阻抗谱会议"3分钟报告"三等 奖

张建岗 第四届中国国际复合材料科技大会优秀墙报奖

5.2.2 BY STUDENTS

FANG Ruopian CAS Excellent Doctoral Dissertation Award

YANG Yongqiang CAS Excellent Doctoral Dissertation Award

CHENG Zhao Special Prize of the CAS Presidential Scholarship Excellent Doctoral Dissertation Award, University of Science and Technology of China

JIN Qun Special Prize of the CAS Presidential Scholarship

ZHOU Xin

Special Prize of the CAS Presidential Scholarship Excellent Doctoral Dissertation Award, University of Science and Technology of China

KANG Yuyang Excellent Prize of the CAS Presidential Scholarship

5.3 学术组织与期刊任职 SERVICE

5.3.1 国际学术组织任职 **PROFESSIONAL SOCIETIES** 成会明 **CHENG Huiming** 亚洲碳学会联合会委员 Member, Asian Association of Carbon Groups 成会明 **CHENG Huiming** 单壁碳纳米管的形核与生长机理国际研讨会国际学 Member of International Scientific Committee, 术委员会委员 Single-Walled Carbon Nanotubes 成会明 **CHENG Huiming** 碳国际会议国际咨询委员会委员 Member of International Advisory Committee, Conference on Carbon **CHENG Huiming** 成会明 Member of Program Committee, 新型材料的电学性质国际冬季讨论会国际程序委员

成会明 国际电化学能源科学学会理事

会委员

成会明 亚太能量储存与转换学会中国代表

黄晓旭 国际先进材料加工与制造技术大会副主席

李 昺 J-PARC实验室中子科学评审委员会委员

刘庆 澳大利亚国家轻金属研究中心国际技术委员会委员

卢柯 急冷及亚稳材料国际会议国际咨询委员会委员

卢 磊 国际材料强度大会委员会委员

占 磊 纳米材料国际委员会委员

5.3.1 SERVICE TO THE INTERNATIONAL

Workshop on Nucleation and Growth Mechanisms of

International Winterschool on Eelctronic Properties of Novel Materials

CHENG Huiming Council Member, International Academy of Electrochemical Energy Science and Technology

CHENG Huiming Chinese representative, The Asia-Pacific Association of Energy Storage and Conversion

HUANG Xiaoxu Program Chair, THERMEC

LI Bing Expert Panel Member, Proposal Evaluation Committee of J-PARC

LIU Qing Member, International Technology Committee of the National Light Metal Research Center in Australia

LU Ke Member of International Advisory Committee, International Conference on Rapidy Quenched and Metastable Meterials (RQ)

LU Lei Member, International conference on the Strength of Materials

LU Lei Member. International Committee on Nanostructured Materials

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卢 磊 THERMEC国际咨询委员会委员

吕 坚 科大麻省理工学院研究联盟大学顾问委员会委员

吕 坚 戈登研究会议香港咨询委员会委员

王福会 国际腐蚀工程理事会理事

王京阳 世界陶瓷科学院论坛委员会主席

王京阳 欧洲陶瓷学会国际顾问委员会委员

王京阳 美国陶瓷学会董事会董事

王京阳 美国陶瓷学会Geijsbeek PACRIM International Award奖励委员会委员

王京阳 美国陶瓷学会Edward Orton Jr. Memorial Lecture Award奖励委员会委员

王京阳 美国陶瓷学会工程陶瓷部执行委员会委员

张洁 美国陶瓷学会John Jeppson评奖委员会委员

张洁 美国陶瓷学会工程陶瓷部奖励委员会委员 LU Lei Member, International Advisory Committee of THERMEC

LU Jian Member of University Advisory Board, *HKUST MIT Research Alliance Consortium*

LU Jian Member of Gordon Research Committee's Hong Kong Advisory Board, *Gordon Research Conference*

WANG Fuhui Committee Member, International Corosion Enineering Council

WANG Jingyang President of The World Academy of Ceramics Forum Committee, *The World Academy of Ceramics*

WANG Jingyang Member of International Advisory Board, *European Ceramic Society*

WANG Jingyang Member of Board of Directors, *The World Academy of Ceramics*

WANG Jingyang Member of Geijsbeek PACRIM International Award Committee, *The American Ceramic Society*

WANG Jingyang Member of Edward Orton Jr. Memorial Lecture Award Committee, *The American Ceramic Society*

WANG Jinyang Member of Executive Committee of Engineering Ceramics Division, *The American Ceramic Society*

ZHANG Jie Member of John Jeppson Award Sub-Committee, *American Ceramic Society*

ZHANG Jie Member of Engineering Ceramic Division Award Committee, *American Ceramic Society*

5.3.2 国际期刊任职	5.3.2 SERVICE TO THE INTERNATIONAL JOURNALS
曹艳飞 《材料前沿》编委	CAO Yanfei Member of the Editorial Committee, <i>Advances in Materials</i>
陈先华 《金属学报》(英) 编委	CHEN Xianhua Member of the Editorial Committee, <i>Acta Metallurgica Sinica</i>
陈星秋 《自然科学进展:材料》编委	CHEN Xingqiu Member of the Editorial Committee, Progress in Natural Science, Materials International
陈星秋 《科学报告》编委	CHEN Xingqiu Member of the Editorial Committee, Scientific Report
陈星秋 《中国科学:材料》编委	CHEN Xingqiu Member of the Editorial Committee, Science China Materials
陈星秋 《材料科学技术》编委	CHEN Xingqiu Member of the Editorial Committee, Journal of Materials Science & Technology
陈星秋 《金属》编委	CHEN Xingqiu Member of the Editorial Committee, <i>Metals</i>
成会明 《储能材料》主编	CHENG Huiming Editor-in-Chief, Energy Storage Materials
成会明 《纳米》编委	CHENG Huiming Member of the Editorial Committee, <i>Nano</i>
成会明 《炭素通讯》编委	CHENG Huiming Member of the Editorial Committee, <i>Carbon Letters</i>
成会明 《材料科学技术》编委	CHENG Huiming Member of the Editorial Committee, Journal of Materials Science & Technology
成会明 《材料研究快报》编委	CHENG Huiming Member of the Editorial Committee, Materials Research Letters
成会明 《纳米材料与分子纳米技术》编委	CHENG Huiming Member of the Editorial Committee, Journal of Nanomaterials & Molecular Nanotechnology

成会明 《国家科学评论》编委	CHENG Huiming Member of the Editorial Committee, <i>National Science Review</i>
成会明 《中国科学:材料》副主编	CHENG Huiming Associate Editor, Science China Materials
成会明 《今日应用材料》编委	CHENG Huiming Member of the Editorial Committee, <i>Applied Materials Today</i>
成会明 《先进电子材料》编委	CHENG Huiming Member of the Editorial Committee, Advanced Electronic Materials
成会明 《碳》名誉编委	CHENG Huiming Member of the Editorial Committee, <i>Carbon</i>
成会明 《今日材料-物理》顾问委员会委员	CHENG Huiming Member of the Advisory Committee, <i>Materials Today Physics</i>
成会明 《物理杂志-能源》顾问委员会委员	CHENG Huiming Member of the Advisory Committee, Journal of Physics-Energy
韩 拯 《半导体学报》编委	HAN Zheng Member of the Editorial Committee, Journal of Semiconductors
黄明欣 《金属与材料国际》编辑	Huang Mingxin Editor, <i>Metals and Materials International</i>
黄明欣 《材料科学技术》编辑	Huang Mingxin Editor, Journal of Materials Science & Techonolgy
黄明欣 《材料研究快报》编审委员会委员	Huang Mingxin Member of Editorial Review Board, Materials Research Letters
黄明欣 《冶金、材料交易》编委	Huang Mingxin Member of Editorial Board, Metallurgical and Materials Transactions A
黄明欣 《材料科学技术》编委	Huang Mingxin Member of Editorial Board, <i>Materials Science & Technology</i>
黄晓旭 《纳米材料科学》副主编	Huang Xiaoxu Associate Editor, <i>Nano Materials Science</i>

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李 峰 《储能材料》编委	LI Feng Member of the Editorial Board, Energy Storage Materials
李 峰 《能源化学》编委	LI Feng Member of the Editorial Board, Journal of Energy Chemistry
李 峰 《能源物理》编委	LI Feng Member of the Editorial Board, Journal of Physics: Energy
李美栓 《材料科学技术》编委	LI Meishuan Member of the Editorial Board, Journal of Materials Science & Technology
李扬扬 《美国转化研究》编委	LI Yangyang Member of the Editorial Board, American Journal of Translational Research
李扬扬 《美国核医学与分子影像学》副编辑委员会委员	LI Yangyang Associate Editorial Board Member, American Journal of Nuclear Medicine and Molecular Imaging
李扬扬 《材料快报》副编辑委员会委员	LI Yangyang Associate Editorial Board Member, <i>Materials Letters</i>
李 毅 《材料科学技术》编委	LI Yi Member of the Editorial Committee, Journal of Materials Science & Technology
刘 畅 《纳米材料科学》副主编	LIU Chang Associate Editor, Nano Materials Science
刘 畅 《碳》编辑	LIU Chang Editor, <i>Carbon</i>
刘 畅 《中国科学:材料》编委	LIU Chang Member of the Editorial Committee, Science China Materials
刘宝丹 《科学报告》编委	LIU Baodan Member of the Editorial Board, Scientific Reports
刘 岗 《材料科学技术》编委	LIU Gang Member of the Editorial Board, Journal of Materials Science & Technology
刘 岗 《能源物理》编委	LIU Gang Member of the Editorial Board, Journal of Physics: Energy
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刘洪阳 《今日材料可持续性》编委

刘洪阳 《能源化学》编委

刘 庆 《冶金与材料》编委

卢 柯 《科学》评审编辑

卢 柯 《国际材料研究杂志》顾问委员会委员

卢 柯 《材料科学技术》编委

卢 柯 《冶金、微结构与分析》编委

卢 柯 《材料研究技术》顾问编委会委员

卢 磊 《材料学报》编辑

卢 磊 《材料快报》编辑

卢 *磊* 《材料科学与技术》编委

卢 磊 《中国科学:材料》编委

卢 磊 《金属学报》编委

卢小鹏 《表面与涂层技术》编委 LIU Hongyang Member of the Editorial Board, *Materials Today Sustainability*

LIU Hongyang Member of the Editorial Board, *Journal of Energy Chemistry*

LIU Qing Member of the Editorial Board, Metall. & Mater. Trans

LU Ke Reviewing Editor, *Science*

LU Ke Member of the Advisory Board, International Journal of Materials Research

LU Ke Member of Editorial Board, Journal of Materials Science & Technology

LU Ke Member of Editorial Board, *Metallurgy, Microstructure, and Analysis*

LU Ke Member of Advisory Board, Journal of Materials Research& Technology

LU Lei Editor, *Acta Materialia*

LU Lei Editor, *Scripta Materialia*

LU Lei Member of Editorial Board, Journal of Materials Science and Technology

LU Lei Member of Editorial Board, *Science China Materials*

LU Lei Member of Editorial Board, *Acta Metallurgica Sinica*

LU Xiaopeng Member of Editorial Board, *Surface & Coating technology*

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马秀良 MA Xiuliang 《科学报告》编委 Member of Editorial Board, Scientific Reports 马秀良 MA Xiuliang Member of Editorial Board, 《材料通信》编委 Materials Letters MA Xiuliang 马秀良 《APL Materials》编辑咨询委员会委员 Member of Advisory Board, APL Materials MA Xiuliang 马秀良 Member of Editorial Board, 《当前智能材料》编委 Current Smart Materials MA Zongyi 马宗义 Member of Editorial Board, 《材料科学与工程A》编委 Materials Science and Engineering: A MA Zongyi 马宗义 Member of Editorial Board, 《腐蚀与材料科学创新》编委 Innovations in Corrosion and Materials Science MA Zongvi 马宗义 Member of Editorial Board, 《材料:设计与应用》编委 Journal of Materials: Design and Applications MA Zongyi 马宗义 Member of Editorial Board, 《材料科学技术》编委 Journal of Materials Science & Technology MA Zongyi 马宗义 Member of Editorial Board, 《中国科学:材料》编委 Science China Materials MA Zongyi 马宗义 Member of Editorial Board, 《金属学报》(英)编委 Acta Metallurgica Sinica MA Zongyi 马宗义 Member of Editorial Board, 《中国科学:技术科学》编委 Science China Technological Sciences MA Zongyi 马宗义 Member of Editorial Board, 《焊连接科学技术》编委 Science and Technology of Welding and Joining **REN Wencai** 任文才 Member of Editorial Board, 《中国科学:材料》编委 Science China Materials **REN Wencai** 任文才 Member of Editorial Board,

《二维材料》编委

2D Materials

SYNL 2019 年度报告 (ANNUAL REPORT)

任文才	REN Wencai
《材料科学技术》编委	Member of Editorial Board,
	Journal of Materials Science & Technology
任文才	REN Wencai
《石墨烯技术》副主编	Associate Editor,
	Graphene Technology
任文才	REN Wencai
《今日材料进展》编委	Member of Editorial Board,
	Materials Today Advances
任文才	REN Wencai
《平面化学》编本	Member of Editorial Board
	FlatChem
	Tuichem
孙左阳	SUN Dongming
11444世北大》后来	Member of Editorial Doord
《忉利竹子仅个》 编安	Journal of Materials Science & Technology
	Journal of Materials Science & Technology
T 15 A	WANC Esta:
土福会	WANG Fuhui
《腐蚀通讯》王编	Editor-in-Chief,
	Corrosion Communications
王福会	WANG Fuhui
《NPJ-材料腐蚀》副主编	Associate Editor,
	NPJ: Materials Degradations
王福会	WANG Fuhui
《材料》编委	Member of Editorial Board,
	Materials
王福会	WANG Fuhui
《防腐方法及材料》编委	Member of Editorial Board,
	Anti-Corrosion methods & Materials
王福会	WANG Fuhui
《国际材料与产品技术》编委	Member of Editorial Board,
	International Journal of Materials and Product
	Technology
	···· 0/
F福全	WANG Fuhui
《中国有色余展学报》(茈)编委	Member of Editorial Board
	Transactions of Nonferrous Metals Society of China
	Transactions of Wongerrous Metais Society of China
于这人	WANG Fuhui
11回4回空谷地》(苏)始禾	Member of Editorial Board
《州仄勿九于报》(天) 编安	Journal of Iron and Steel Research International
	sournal of from and steel Research International
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工砚十	WAINO JIIIgiciig Mambar of Editorial Descrit
《铁和谷金》 编安	iviember of Editorial Board,
	Journal of Magnesium and Alloys
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王京阳 《科学报告》编辑	WANG Jingyang Editor, Scientific Reports
王京阳 《现代陶瓷技术》编委	WANG Jingyang Member of Editorial Board, <i>Ceramics in Modern Technologies</i>
王京阳 《材料工程与性能》编委	WANG Jingyang Member of Editorial Board, Journal of Materials Engineering and Performance
王京阳 《先进陶瓷》编委	WANG Jingyang Member of Editorial Board, Journal of Advanced Ceramics
王胜刚 《腐蚀与材料科学创新》责任编辑(材料科学)	WANG Shenggang Section Editor (Materials Science), Innovations in Corrosion and Materials Science
王晓辉 《先进陶瓷》编委	WANG Xiaohui Member of Editorial Board, Journal of Advanced Ceramics
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徐大可 《Heliyon》 编辑	XU Dake Editor, <i>Heliyon</i>
徐大可 《国际生物腐蚀与降解》编委	XU Dake Member of Editorial Board, International Biodeterioration & Biodegradation
徐大可 《材料科学技术》编委	XU Dake Member of Editorial Board, Journal of Materials Science & Technology
徐大可 《NPJ-材料腐蚀》编委	XU Dake Member of Editorial Board, NPJ: Material Degradation
徐大可 《材料前沿》评审编辑	XU Dake Review Editor, <i>Frontiers in Materials</i>

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徐大可 XU Dake 《生物能源与燃料前沿》评审编辑 Review Editor, Frontiers in Bioenergy and Biofuels 辛仁龙 XIN Renlong 《焊接科学与技术》编委 Member of the Editorial Board, 杨腾 YANG Teng 《科学报告》编委 Member of the Editorial Board, Scientific Reports 曾 尤 ZENG You 《科学报告》编委 Member of the Editorial Board, Scientific Reports (Chemistry) 曾 尤 ZENG You 《材料科学:先进复合材料》编委 Member of the Editorial Board, 张炳森 ZHANG Bingsen 《化学前沿》客座编辑 Guest Editor, Frontiers in Chemistry 张广平 ZHANG Guangping Member of Editorial Board, 《纳米材料科学》编委 Nano Materials Science **ZHANG** Jie 张洁 Member of Editorial Board, 《先进陶瓷》编委 Journal of Advanced Ceramics ZHANG Tao 张涛 Member of Editorial Board, 《金属学报》(英)编委 Acta Metallurgica Sinica **ZHANG** Tao 张涛 Member of Editorial Board, 《NPJ-材料腐蚀》编委 NPJ-Material Degradation **ZHANG Zhidong** 张志东 Editor. 《科学世界》编辑 Scientific World Journal 张志东

《纳米材料》编委

Science and Technology of Welding and Joining

Material Science: Advanced Composite Materials

ZHANG Zhidong Member of Editorial Board, Nanomaterials

5.3.3 国内学术组织任职 SERVICE TO THE DOMESTIC PROFESSIONAL SOCIETIES	刘 畅 中国电工技术学会碳-石墨材料专业委员会副主任 委员
陈星秋 中国材料学会计算材料学分会副秘书长 中国材料学会第七届理事会出版工作委员会委员 成会明 中国电工技术学会碳-石墨材料专业委员会顾问 中国真空学会表面与纳米科学专业委员会委员 中国微米纳米技术学会常务理事	刘 岗 中国材料研究学会青年工作委员会第九届理事会 副主任 中国可再生能源学会光化学专业委员会委员 中国科协先进材料学会联合体第一届青年工作委 员会委员 中国化工学会化工新材料专业委员会专家委员 刘洪阳 中国科学院青年促进会化学材料公会理事
韩 拯 中国材料学会青年理事会理事 胡小强	中国机斗研究学会青年委员会理事会
公司阀门标准技术委员会委员 全国铸造技术标准化技术委员会铸钢分技术委员 会委员 中国机械工程学会铸造公会由法技术委员会委	中国腐蚀与防护学会理争 中国腐蚀与防护学会青年工作委员会副主任委员 中国腐蚀电化学与测试技术专业委员会秘书长
中国机械工程子会按适分会电查技术安贝会安员 黄晓旭 中国科学院学术委员会先进材料领域专门委员会 委员	户 由国材料研究学会疲劳分会理事 中国材料研究学会青年委员会常务理事 国家自然科学基金委员会学科发展战略专家 中国科学技术部"纳米科技"重点专项 指南编制 专家 国家科学技术部"纳米科技" 首体主家如主家
金海军 中国材料学会青年工作委员会理事 中国材料研究学会多孔材料分会委员	采义坤 中国稀土学会稀土在钢中应用专业委员会委员
李昺 中国稀土学会磁制冷材料与技术专业委员会委员 李殿中 中国稀土学会理事 中国机械工程学会铸造分会常务理事 李 峰 中国材料研究学会纤维材料改性与复合技术分会 理事	 吕坚 中国科学院海外评审专家 中国力学学会"中国力学科学技术奖"海外通讯 评审专家 香港工业专业评审局学术顾问委员会成员 香港科技大学霍英东研究所工程材料及可靠性中 心外籍评委 香港研究资助金委员会委员 香港工程师学会(核工程学科建设特别指导委员 人) 本目
中国材料研究学会环境材料分会委员中国颗粒学会理事	会) 妥贝 湘潭大学低维材料及其应用技术教部重点实验室 第三届学术委员会副主任 马嵩
中国腐蚀与防护学会第十届理事会常务理事 中国腐蚀与防护学会第十届高温专业委员会主任 委员 中国硅酸盐学会测试技术分会理事会副理事长 中国空间科学学会第九届空间材料专业委员会委 员	¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬¬
刘宝丹 中国金属学会功能材料分会第五届委员 中国晶体学会稀土晶体专委会 中国颗粒学会超微专委会	辽宁电子显微镜学会常务副理事长 中国科学院东北区域中心电子显微镜学会主席 中国物理学会会员 中国晶体学会理事

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马宗义 中国复合材料学会金属基及陶瓷基专业委员会副主任 粉末冶金产业技术创新战略联盟理事 中国444444444444444444444444444444444444	中国硅酸盐学会特种陶瓷分会理事 中国硅酸盐学会测试分会理事 中国物理学会内耗与力学谱专业委员会副主任
中国钢结构协会粉木冶金分会常分理事中国材料与试验团体标准复合材料领域委员会委员中国有色金属学会金属复合材料专业委员会主任	王绍青 中国计算物理学会第八届理事会理事 中国材料研究学会计算材料学分会第三届委员会
倪丁瑞 中国有色金属学会金属复合材料专业委员会委员	委页 王晓辉 中国硅酸盐学会特种陶瓷分会理事
钱余海 中国腐蚀与防护学会第十届高温专业委员会秘书长	中国青年科技工作者协会理事 王镇波
任文才 中国石墨烯产业技术创新战略联盟标准化委员会主 任	中国有色金属学会理化检验学术委员会委员当的律
全国钢标准化技术委员会碳素材料分技术委员会薄 层石墨材料工作组副组长 中国材料研究学会青年工作委员会第八届理事会理事	辽宁省颗粒学会理事 中国有色金属学会金属复合材料专业委员会副主 任
全国纳米技术标准化技术委员会纳米材料分技术委员会委员	中国复合材料学会金属基复合材料专业委员会委 员 中国有色金属学会青年工作委员会委员
孙东明 辽宁省科学技术协会第九届委员会常务委员 全国纳米技术标准化技术委员会低维纳米结构与 性能工作组委员 中国国际石墨烯资源产业联盟国际标准工作委员 会委员	信运昌 中国材料研究学会青年工作委员会副主任 中国材料研究学会镁合金材料及应用专业委员会 理事 中国机械工程学会材料分会青年工作委员会委员
孙明月 全国塑性工程学会大锻件学术委员会委员 中国材料研究学会青年委员会理事 郃凯平 湖北省发改委功能薄膜材料物理性能检测技术工 程实验宏学术本员	徐大可 中国机械工程学会表面工程分会青年工作委员会 委员 中国腐蚀与防护学会海洋污损防护技术专业委员 会副主任委员
中国材料研究学会热电材料及应用分会委员 谭 军 中国电子显微学会FIB专业技术委员会委员	徐敬军 中国腐蚀与防护学会第十届高温专业委员会委员 中国硅酸盐学会测试技术分会第二届理事会理事
唐云龙 中国电子显微学会物理与材料专业委员会委员	曾 尤 中国复合材料学会理事 中国石墨烯产业联盟标准化委员会委员 中国复合材料学会纳米复合材料分会常务委员
土福会 中国科协先进材料学会联合体首届主席团副主席 中国腐蚀与防护学会理事长 辽宁省化工学会副理事长	张炳森 中国颗粒学会青年理事
王敬丰 十二届中国物理学会内耗与力学谱专委会学术委	张波 腐蚀与防护学会电化学专业委员会委员
员 中国材料研究学会理事 中国材料研究学会镁合金分会副理事长	张广平 中国材料研究学会疲劳分会理事
王京阳 西北工业大学超高温结构复合材料重点实验室学 术委员会委员	张海峰 中国材料研究学会金属间化合物与非晶合金分会 理事 中国兵工学会金属材料专业委员会委员

中国金属学会非晶合金及应用分会委员 辽宁省建设与环境科学发展研究会节能减排与新 能源专业委员会副主任委员 中国材料研究学会空间材料科学技术分会常务理 事

张志东

中国材料研究学会理事 中国物理学会磁学分会委员 中国电子学会应用磁学分会委员 中国稀土学会永磁专业委员会委员 中国稀土学会磁制冷材料与技术专业委员会委员 辽宁省物理学会副理事长

5.3.4 国内期刊任职 SERVICE TO THE DOMESTIC JOURNALS	《复合材料学报)编委 钱余海 《腐蚀科学与防护技术》编委
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丛洪涛 《功能材料》编委	上相云 《中国有色金属学报》 编委 《中国腐蚀与防护学报》编委 《中国表面工程》编委
黄晓旭 《中国科学:技术科学》副主编	王敬丰 《表面技术》编委
李殿中 《材料研究学报》编委 《金属学报》编委	王京阳 《无机材料学报》副主编
李 峰 《新型炭材料》编委 《储能科学与技术》编委	王绍青 《计算物理》编委 肖伯律
李美栓 《金属学报》编委 《中国腐蚀与防护学报》编委	《精密成形工程》编委 辛仁龙 《电子显微学报》编委
刘 畅 《新型炭材料》编委 《功能材料》编委 《科学通报》(中)编委	徐大可 《中国腐蚀与防护学报》编委 曾 尤
刘 岗 《中国化学快报》青年编委 《催化学报》青年编委	《功能材料》编委 张炳森 《中国化学快报》编委
刘莉 《材料保护》编委	张志东 《材料科学与工程学报》编委
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马秀良 《电子显微学报》编委	
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