

直接扩散连接制备多芯 Bi 系超导带材超导接头

郭 伟, 邹贵生, 吴爱萍, 任家烈*

(清华大学 教育部先进成形制造重点实验室, 北京 100084)

摘 要: 采用扩散连接方法对 61 芯 Bi 系高温超导带材(BSCCO)进行连接, 研究了连接温度、保温时间、连接压力对接头超导电性的影响规律, 并对超导接头的组织进行了微观分析. 结果表明, 连接温度对接头的超导性能影响较大, 保温时间和连接压力在一定的范围内, 对接头的超导性能影响不大; 当连接温度为 820 °C, 保温时间 120 min, 连接压力 3 MPa 时, 接头获得最佳的超导电性能, 接头的超导性能达到了原始母材的 65.9%. 微观分析表明, 接头界面区域组织致密, 主要由 Bi-2223 相和少量的 Bi-2212 相构成.

关键词: 铋系高温超导带材; 扩散连接; 超导电性; 微观组织

中图分类号: TG453.9 **文献标识码:** A **文章编号:** 0253-360X(2009)02-0125-04



郭 伟

0 序 言

随着资源的日益紧张和能源价格的高涨, 节能降耗成为国民经济可持续发展的必然发展要求, 超导特别是高温超导技术有望成为解决能源危机的重要措施之一. 由于高温超导材料具有特殊性能, 将在重大科学工程、医疗、交通(磁悬浮列车)、军事、航空航天等领域得到广泛的应用. 因此, 近些年有关高温超导材料的制备和应用的研究已成为超导科学技术领域的热点. Bi 系多芯高温超导带材是目前最为成熟的超导材料, 也是最有应用前途的超导材料之一. 然而, 在制备长距离(≥ 1 km)多芯 Bi 系超导带材方面, 由于带材本身的特性, 却遇到了许多困难, 同时在制备超导电机绕组、超导线圈等超导器件过程中常常会遇到超导带材的连接问题. 目前, Bi 系高温超导带材的连接问题已经成为制约其进一步产业化的关键技术之一.

高温超导材料本身是一种银包陶瓷氧化物的多层多介质的复杂结构, 超导带材特殊的应用决定连接接头不仅要满足一定的力学性能, 更重要的是接头要具有超导性能. 人们在尝试了熔化焊^[1]、微波连接^[2]、软钎焊^[3]等方法后, 认为传统的连接方法很容易改变高温超导带材特殊的织构组织或使得超导

材料高温分解或者在接头处引入非超导相, 使接头失去超导性能. 近几年, 国外许多国家的学者基于超导带材的制备原理, 采用先高温冷压后高温热处理的方法对超导带材的连接进行了广泛的研究^[4-10]. 然而这种方法的后续热处理时间很长(50 到几百小时), 大大延长了生产的周期, 并且不利于现场施工, 且在大气中长时间的热处理也会对高温超导带材的超导性能带来不利的影响. 近年来, 作者采用直接扩散连接的方法对 61 芯 BSCCO ($(\text{Bi Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ 和少量 $(\text{Bi Pb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$) 带材的连接问题进行了研究, 在提高接头超导性能的前提下, 大大缩短了接头制备的周期.

在扩散连接过程中, 连接温度、保温时间、连接压力是影响超导带材扩散连接接头性能的主要影响因素. 因此, 研究各个工艺参数对接头超导电性的影响, 对制定多芯带材超导连接工艺和研究其接头连接机理有着重要的作用.

1 试验方法

试验所用的材料是北京英纳超导技术有限责任公司提供的 61 芯 Bi 系高温超导带材, 其横截面的宽度和厚度分别为 4.3 mm 和 0.22 mm, 临界电流 I_c 约为 90 A (在 77K 温度和自场条件下), 其微观形貌如图 1 所示.

扩散连接试验是在专用超导扩散炉中进行, 连接气氛为大气. 为了获得超导接头, 超导带材表面的

收稿日期: 2008-09-20

基金项目: 国家自然科学基金面上和重点项目(50575114, 50635050); 北京市自然科学基金项目(3052010); 中国博士后科学基金项目(20080430360)

*参加项目研究工作的人员还有王延军

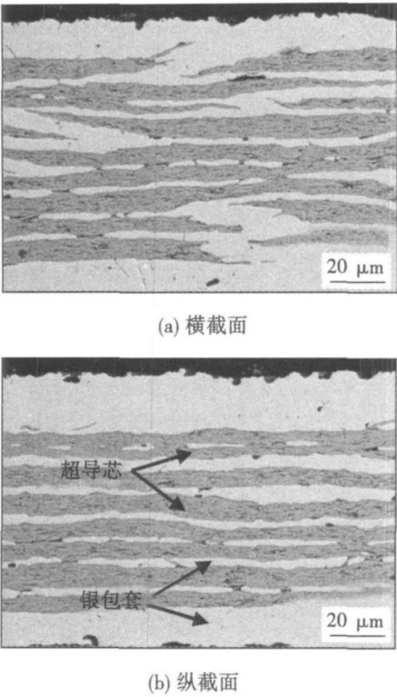


图 1 61 芯 Bi 系超导带材微观形貌

Fig. 1 Microstructures of 61-filament superconducting tape

银包套必须事先采用机械或化学方法去除. 连接试样前期准备工作如下: (1) 首先制作扩散连接窗口, 采用机械和腐蚀相结合的方法去除超导带材搭接部位的 Ag 合金外包套, 获得一定尺寸的窗口如图 2 (上), 腐蚀液为 75% 的氨水和 25% 的双氧水组成的混合溶液; (2) 按试样窗口外形精确装配如图 2 (下); (3) 在一定的工艺条件下, 在专用超导扩散炉中进行扩散连接.

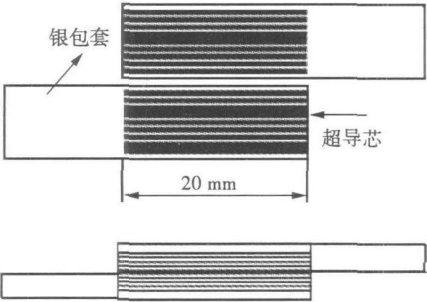


图 2 超导带材接头尺寸及装配

Fig. 2 Dimension of superconducting type joint and its assemble

采用国际上标准的四引线法测试接头的超导临界电流, 来表征接头的超导性能. 试验设备采用清华大学应用超导中心制备的临界电流测试专用设

备, 其中测试电压节点包含整个接头区域. 接头超导电性能测试位置如图 3 所示. 采用 b-e 之间的临界电流 I_c 与原始带材的临界电流值的比值表征接头的超导性能, 称为临界电流比率 CCRo(critical current ratio).

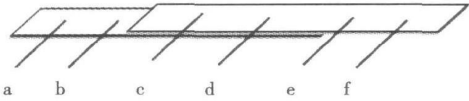


图 3 超导带材扩散连接接头超导电性能测试位置示意图

Fig. 3 Sketch of measure position for superconducting property of joint

2 试验结果与分析讨论

2.1 连接温度的影响

连接温度是影响超导带材扩散连接的最主要的影响因素. 一方面, 对于 Bi 系高温超导带材来说, 其主要成分 Bi-2223 相是一种非稳态组织, 在连接温度区间范围内带材本身就会发生部分分解反应; 另一方面, 温度是影响元素扩散的最主要的因素之一. 扩散接头的超导性能是以上两个方面综合作用的结果, 图 4 为连接温度对接头临界电流的影响.

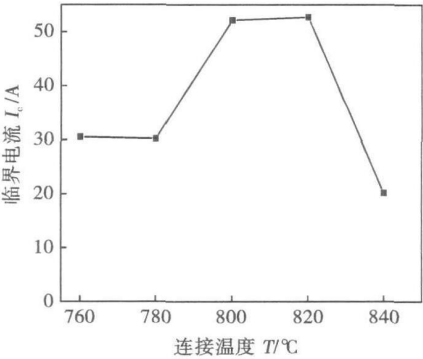


图 4 连接温度对接头超导性能的影响

Fig. 4 Effect of bonding temperature on superconducting property of joints

试验结果表明, 当连接温度较低时 (760 ~ 780 $^\circ\text{C}$), 原子的扩散能量低, 原子的扩散距离短, 接头扩散界面的间隙愈合需要较长的保温时间和较大的连接压力, 而过大的连接压力和保温时间对高温超导带材本身的性能又有不利的影响; 因此, 当连接温度较低时, 接头的临界电流值较低 (30 A). 随着连接温度的提高, 接头的超导性能也相应提高, 当温

度达到 800 ℃时, 接头的临界电流值达到 50 A 左右, 当温度为 820 ℃时, 接头的临界电流值达到最大值(52.73 A), CCRo 达到 65.9%。继续提高连接温度, 当温度达到 840 ℃时, 接头的临界电流迅速下降到 20 A 左右, 这是因为在 840 ℃高温下, 带材中超导相发生部分分解反应生成非超导相的结果^[1]。

2.2 保温时间的影响

原子的扩散需要一定的时间, 因此扩散连接过程需要一定的保温时间, 而过长的连接时间将浪费大量能源, 并加剧带材的分解。图 5 为保温时间对接头临界电流的影响。结果表明, 当保温时间达到40 min时, 带材即能实现连接。随着保温时间的延长, 接头的临界电流变化不大。在连接温度为820 ℃, 连接压力为 3 MPa, 保温时间为120 min时, 接头的临界电流达到最大值52.73 A。随后, 进一步延长保温时间, 接头的临界电流值基本不变。总之, 在一定的范围内, 保温时间对接头临界电流的影响不大。

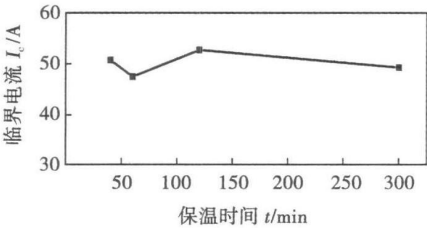


图 5 保温时间对接头超导性能的影响
Fig. 5 Effect of holding time on superconducting property of joints

2.3 连接压力的影响

图 6 为不同连接压力下接头的临界电流值。结果表明, 当连接压力较小时(1 MPa), 接头即能获得

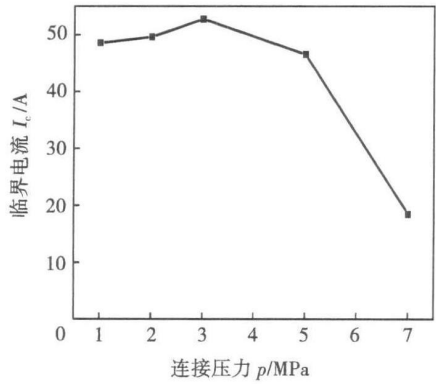


图 6 连接压力对接头超导性能的影响
Fig. 6 Effect of bonding pressure on superconducting property of joints

较高的临界电流(48 A), 随着连接压力的增大, 接头的临界电流缓慢增大, 当连接压力达到 3 MPa 时, 接头具有最好的超导性能(52.73 A)。进一步增加连接压力, 接头的临界电流值逐渐减小, 当连接压力为 7 MPa 时, 接头的临界电流值下降到只有 20 A 左右。这是因为过大的连接压力容易在高温超导带材内部产生较多的微裂纹等缺陷, 使得接头的超导性能大大降低。

2.4 接头微观组织

典型的高温超导带材扩散连接接头微观组织, 如图 7 所示。

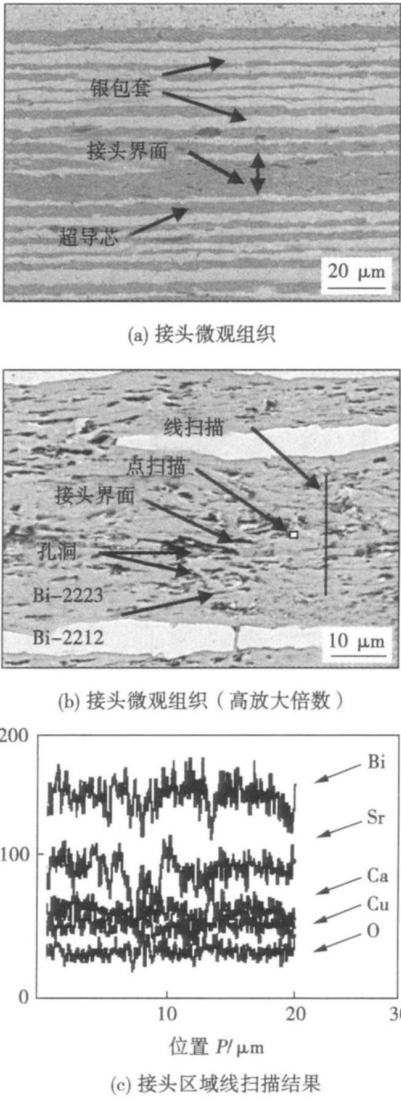


图 7 接头微观组织及能谱分析
Fig. 7 Microstructure and EDS analysis of joint

微观组织显示上下两个超导带材的超导芯已经连接成一体, 形成一个更加宽的超导芯且接头的组织较致密。为了进一步研究接头的结合情况, 对接头界

面的点进行了能谱分析. 结果表明, 接头界面处主要有 Bi, Pb, Sr, Ca, Cu, O 六种元素构成, 其原子数分数(%)为 Bi 8.82-Pb 1.31-Sr 9.38-Ca 9.29-Cu 14.13-O 57.06. 其(Bi, Pb) : Sr : Ca : Cu 比例接近于 2 : 2 : 2 : 3. 结合接头区域的组织形貌, 认为接头界面组织主要由 Bi-2223 相和少量的 Bi-2212 相构成. 点能谱结果与原始母材的超导芯的成分基本相同, 说明带材经过扩散连接的热力作用, 并没有发生明显的相变, 这也是带材接头具有超导性能所必需的基本条件之一. 图 7c 为接头区域的线扫描结果, 表明接头区域主要由 Bi, Sr, Ca, Cu, O 五种元素构成, 且在跨过接头界面的区域内, 分布基本均匀, 说明在界面处形成了连续的成分过渡, 这也反映了接头界面结合良好.

由于接头界面本身不是一个平面, 且主要有脆硬的氧化物陶瓷材料构成, 故增加了界面成形的难度, 且容易造成焊接缺陷, 从而影响接头的超导性能, 使得接头的超导性能离散性较大.

3 结 论

(1) 扩散连接能够实现 Bi 系高温超导带材的连接, 且接头具有超导电性.

(2) 连接温度对扩散接头的超导电性有着显著的影响. 接头超导性能与温度成正态分布, 且温度介于 $800 \sim 820\text{ }^{\circ}\text{C}$ 时, 接头获得最好的超导性能. 在一定的范围内, 保温时间和连接压力对接头的超导性能影响不大. 当连接温度为 $820\text{ }^{\circ}\text{C}$, 保温时间为 120 min, 连接压力为 3 MPa 时, 接头获得最佳的超导电性能, 接头临界电流比率达到 65.9%.

(3) 微观分析表明接头组织结合致密, 接头界面主要由 Bi-2223 相和少量的 Bi-2212 相构成.

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作者简介: 郭 伟, 男, 1976 年出生, 博士. 主要从事新材料的连接研究工作. 发表论文 10 余篇.

Email: gwei@tsinghua.edu.cn

Ltd, Beijing 100176, China). p111—116

Abstract: A powder interlayer with a content 88.5% of superconducting phase 2223 was obtained by combining pressing technology and high temperature sintering from the precursor powders used for fabricating BSCCO tapes. The pressing technology is beneficial to increasing the formation and content of 2223 phase from the precursor powders. A good superconducting bonding quality was achieved using this powder interlayer. The average critical current ratio (CCRo) reached up to 49.9% under the conditions of bonding temperature 800 °C for 2 h at 3 MPa. And it is concluded that the higher the content of 2223 phase in the powder interlayer, the higher the CCRo is. The influences of bonding factors on the joints' microstructures are both obvious and complex, and a further research on this is needed.

Key words: Bi-based superconducting tape; superconducting phase; diffusion bonding

Active brazing of SiO₂ glass ceramic to TC4 alloy LIU Duo, ZHANG Lixia, HE Peng, FENG Jicai (1. National Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China; 2. National Key Laboratory of Precision Hot Processing of Metals, Harbin Institute of Technology, Harbin 150001, China). p117—120

Abstract: SiO₂ glass ceramic was brazed to Ti-6Al-4V (TC4) alloy with commercially available AgCuTi and TiZrNiCu filler foil as braze alloy. SEM and XRD were carried out to study the joint interface and mechanical properties. The experimental result shows that both filler alloy could join SiO₂ glass ceramic to TC4 alloy successfully. The typical interface structure of SiO₂/TiZrNiCu/TC4 joint is SiO₂/Ti₂O+Zr₃Si₂+Ti₅Si₃/(Ti, Zr)+Ti₂O+TiZrNiCu/TiCu/Ti(s, s)/TiZrNiCu+Ti(s, s)+Ti₂(Cu, Ni)/TC4. The typical interface structure of SiO₂/AgCuTi/TC4 joint is SiO₂/TiSi₂+Ti₄O₇/TiCu+Cu₂Ti₄O/Ag(s, s)+Cu(s, s)/TiCu/Ti₂Cu/Ti+Ti₂Cu/Ti-6Al-4V from SiO₂ glass ceramic to Ti-6Al-4V alloy side. The SiO₂/TiZrNiCu/TC4 joints brazed at 880 °C for 5 min has the maximum shear strength 23 MPa, and the SiO₂/AgCuTi/TC4 joint brazed at 900 °C for 5 min obtains the maximum shear strength 27 MPa.

Key words: SiO₂ ceramic; TC4 alloy; brazing; interface microstructure; shear strength

Microstructure and mechanical property of transient liquid phase bonded aluminum silicon alloy joint ZHANG Weihua¹, QIU Xiaoming¹, CHEN Xiaowei¹, ZHAO Xihua¹, SUN Daqian², LI Yongqiang¹ (1. School of Materials Science and Engineering, Jilin University, Changchun 130022, China; 2. Key Laboratory of Automobile Materials, Ministry of Education, Jilin University, Changchun 130022, China). p121—124

Abstract: Microstructure and mechanical property of the transient liquid phase bonded aluminum silicon alloy joints with Cu interlayer were investigated by means of scanning electron microscope, X-ray diffractometry, energy dispersive X-ray spectroscopy and electronic tensile testing machine. The results indicate that Cu interlayer reacts with Al from Al-Si alloy to form eutectic liquid phase, and Si from Al-Si alloy will prevent the reaction to some ex-

tent. The microstructure of the joint consists of α-Al, Si and intermetallic compounds (CuAl₂ and Al₄Cu₉), meanwhile, the amount of the intermetallic compounds decrease with the increasing of bonding time. The fracture occurs at the bonding region/base metal interface during shear strength testing. With the increase of bonding time, the shear strength of the joint increases firstly and then declines while 70.2 MPa can be achieved after bonding at 560 °C for 120 min. In addition, a transition from brittle to hybrid brittle and ductile morphology of the fracture surface was found with the increasing of bonding time.

Key words: aluminum silicon alloy; transient liquid phase bonding; microstructure; mechanical property

Superconducting joint with multifilamentary superconducting BSCCO tapes by diffusion bonding GUO Wei, ZOU Guisheng, WU Aiping, REN Jialie (Key Laboratory for Advanced Manufacturing by Materials Processing Technology, Ministry of Education of P. R. China, Tsinghua University, Beijing 100084, China). p125—128

Abstract: Diffusion bonding of 61-filament high-temperature superconducting tapes has been carried out. The effects of bonding temperature, holding time and bonding pressure on the superconducting properties of the joints were studied. And the microstructures of the joint were examined. The result shows that bonding temperature has a great influence on the superconducting property of the joint, and the effects of holding time and bonding pressure are limited in a certain range. The optimum joints are obtained under the parameters of 820 °C, 120 min and 3 MPa, which reach 65.9% superconducting property of the original superconducting tapes. Microstructures of the joint show that the interface is compact structure and composed of Bi-2223 phase and a small amount of Bi-2212 phase.

Key words: high temperature superconducting BSCCO tape; diffusion bonding; superconducting property; microstructure

Microstructure and mechanical property of ultrasonic soldered joint of AZ31B magnesium alloys GAO Chen, LI Hong, LI Zhuoxin (School of Material Science and Engineering, Beijing University of Technology, Beijing 100124, China). p129—132

Abstract: In order to solve corrosion problem of soldered joint when fluxing agents were used, a technology of ultrasonic soldering was developed. A lap joint of magnesium alloy AZ31B was obtained successfully in air with ultrasonic aided. The microstructure and strength of the joint soldered by this method were studied. The effect of ultrasonic vibration time and width of clearance on shear strength of joint was investigated. The results indicated that ultrasonic vibration can remove the oxide layer on base metal. And the shear strength of joint reaches 80—90 MPa in the appropriate range of vibration time. The shear strength decreases when the width of clearance is too large or too small. The microstructures of joint are mainly α-Mg and Mg-Zn phases and the fracture mode is intergranular fracture.

Key words: ultrasonic soldering; magnesium alloy AZ31B;