Ni 元素对 Sn2.5Ag0.7Cu0.1RE/Cu 无铅微焊点界面 IMC 和力学性能的影响

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摘 要: 以 Sn2.5Ag0.7Cu0.1RE 无铅钎料为研究对象,借助扫描电镜和 X 衍射等检测方法研究了 Ni 元素对 Sn2.5Ag0.7Cu0.1RE/Cu 无铅微焊点界面 IMC 和力学性能的影响. 结果表明,添加适量 Ni 元素能显著细化 Sn2.5Ag0.7Cu0.1RE 钎料合金初生 β-Sn 相和共晶组织,抑制焊点界面区 $(Cu,Ni)_6Sn_5$ 金属间化合物的生长和表面粗糙度的增加,提高无铅焊点抗剪强度. 当 Ni 元素添加量为 0.1% 时,钎料合金组织细小均匀,共晶组织所占比例较多; 焊点界面 IMC 薄而平整, $(Cu,Ni)_6Sn_5$ 颗粒尺寸小,对应焊点抗剪强度最高为 45.6 MPa,较未添加 Ni 元素焊点提高 15.2%.

关键词: Sn2.5Ag0.7Cu0.1RExNi 无铅钎料; 焊点; 金属间化合物; 力学性能
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0 序 言

随着电子器件向超高密度、微型化发展,开发出可以替代 SnPb 钎料具有环境友好、高强韧性的无铅钎料是微电子连接材料研究的热点之一[1]. SnAgCu 系无铅钎料以其优良的综合性能成为 SnPb 钎料最有潜力的替代品之一[1,2]. 随着研究深入,采用微合金化的方法,降低 SnAgCu 系无铅钎料中 Ag 元素含量以降低钎料制造成本已成为发展趋势[3],尤其是国内独具特色的 SnAgCuRE 系无铅钎料具有更广阔的应用前景[3,4].

无铅焊点界面处形成的金属间化合物(IMC)作为连接的基础,其几何形态尺寸与微连接焊点可靠性密切相关. 粗大的界面 IMC 会导致其内部裂纹的萌生和扩展从而降低焊点的可靠性[5]. 避免微连接焊点界面生成粗大、过厚的 IMC 已成为人们关注的问题. 研究表明,微量 Ni 元素不仅能提高无铅钎料合金的润湿性和力学性能,而且能较大幅度的改善微连接焊点的蠕变性能等[6],为通过微合金化提高无铅钎料合金的强韧性,以解决该类焊点的脆弱性问题提供了有效途径. 但关于 Ni 元素对此类焊点界面 IMC 和力学性能的研究却鲜见文献报道[6,7]. 因此文中研究了添加 Ni 元素对 Sn2.5Ag0.7Cu0.1RE/Cu 微连接焊点界面 IMC 和力学性能的影响,以期为开发微电子行业需求的高强韧高可靠性无铅钎料提供借鉴.

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1 试验方法

钎料合金熔炼是采用 99.9% 以上纯度的 Sn，Ag，Cu，Ni 元素及含 Ce 和 La 元素的混合稀土(RE),在真空度为 5×10^{-3} Pa 的非自耗电炉 ZHW-600A 中先制备 RE 元素与 Cu 元素中间合金,再制备 Sn2.5Ag0.7Cu 0.1RExNi 钎料合金. Ni 元素添加量分别为 0, 0.05%, 0.1%, 0.3%, 0.5%.

钎焊试验采用如图 1 所示搭接试样,钎料合金轧制成 4 mm×15 mm×0.1 mm 片状,采用 22% $ZnCl_2$ + 2% NH_4Cl 钎剂进行炉中钎焊,钎焊温度为 270 ℃,钎焊时间为 240 s. 室温抗剪强度测试使用

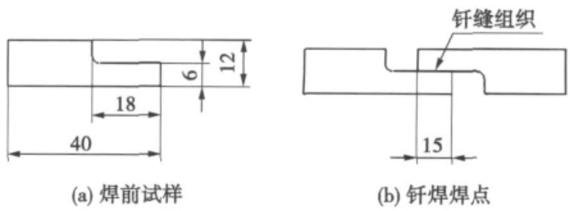


图 1 钎焊焊点试样(mm)
Fig. 1 Test specimen of solder joint

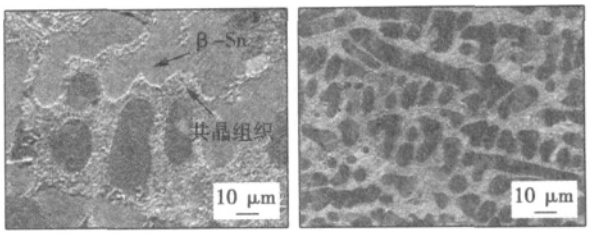
AG-I250KN 万能试验机，拉伸速率为 1 mm/min，试验结果取 3 次测量的平均值.

将钎焊好的试样沿纵向剖开，打磨抛光后经 4% HNO_3 + 1% HCl 酒精溶液侵蚀，采用 JSM-5610LV 扫描电镜观察焊点界面 IMC 形貌；利用 AutoCAD 软件测量界面 IMC 面积以求得 IMC 厚度，测量结果取五个随机区域的平均值；使用 D8 ADVANCE 型 X 衍射仪对钎料及焊点进行物相分析；将焊点放入 13% 的 HNO_3 酒精溶液中，经超声波清洗，钎料基体被腐蚀掉，而界面 IMC 得以保留，观察界面 IMC 俯视形貌；基于定量金相学原理[8] 测量界面 IMC 颗粒平均截线长（L）以定量表征界面（Cu，Ni）$_6$$Sn_5$ 颗粒大小.

2 试样结果与分析

2.1 钎料合金显微组织

图2 为 Sn2.5Ag0.7Cu0.1RExNi 钎料合金的显微组织. 可以看出钎料合金是由初生相 β-Sn 和共晶组织组成. 对钎料合金进行 X 衍射分析表明，内部存在 Cu_6Sn_5 和 Ag_3Sn 相，结合 Sn-Ag-Cu 三元相图，共晶组织包括颗粒状的 β-Sn+Cu_6Sn_5 和针状的 β-Sn+Ag_3Sn，以及 β-Sn+Cu_6Sn_5+Ag_3Sn 三元共晶组织. 钎料合金添加 Ni 元素后，经能谱分析 Cu_6Sn_5 相内部存在一定量 Ni 元素，共晶组织中可能生成了以 Cu_6Sn_5 为基(Cu，Ni)$_6$$Sn_5$ 相. 这是由于 Ni 元素和 Cu 元素具有相同的晶体结构，钎料熔炼过程中 Ni 原子置换出 Cu_6Sn_5 中部分 Cu 原子形成了(Cu，Ni)$_6$$Sn_5$ 相[9]. 对比图 2a 和图 2b，添加适量 Ni 元素后初生 β-Sn 相和共晶组织均有明显的细化；当 Ni 元素添加量为 0.1% 时，钎料合金组织细小均匀，且共晶组织所占比例较多，这可能是由于在钎料合金凝固过程中，Ni 元素为先析出的富锡相提供了更多的形核质点，有利于改善钎料合金力学性能.



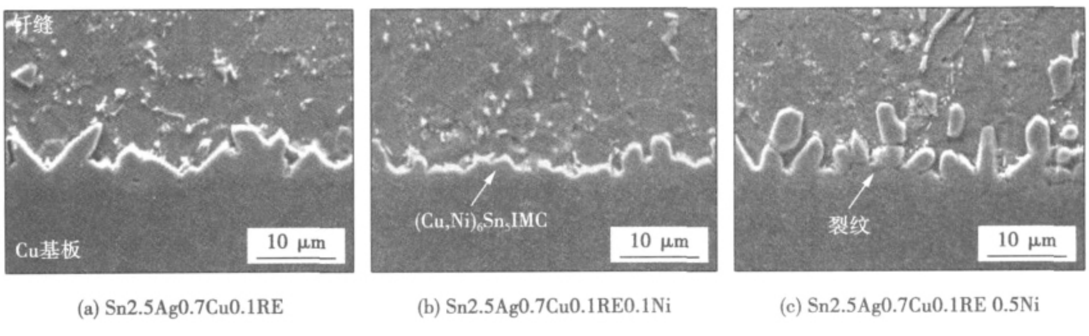
(a) Sn2.5Ag0.7Cu0.1RE (b) Sn2.5Ag0.7Cu0.1RE0.1Ni

图2 不同 Ni 元素添加量下钎料合金组织形貌
Fig. 2 Microstructure of SnAgCuRExNi solder

2.2 焊点界面 IMC

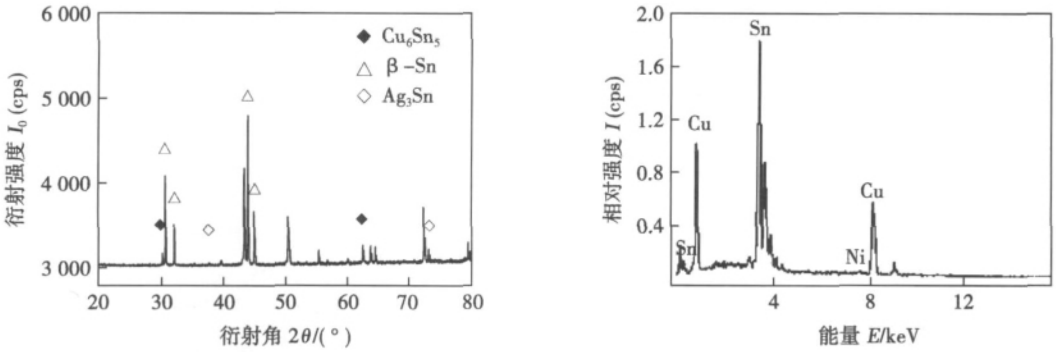
图3 为 Sn2.5Ag0.7Cu0.1RExNi/Cu 焊点界面显微组织. 可以看出，界面生成了一层扇贝状的 IMC，厚度在 3 ~ 4 μm. 由图 4 Sn2.5Ag0.7Cu0.1RExNi/Cu 焊点 X 衍射图谱和能谱分析结果可知，该 IMC 为 Cu_6Sn_5；添加 Ni 元素界面 IMC 则是以 Cu_6Sn_5 为基的(Cu，Ni)$_6$$Sn_5$. 靠近铜基板侧还有可能生成少量 Cu_3Sn，由于其厚度极薄而不易被检测到. 在钎焊过程中，由于液态钎料内 Sn 原子向铜基板侧扩散速率较快，此时会首先形成激活能较低的(Cu，Ni)$_6$$Sn_5$ 相；而随着(Cu，Ni)$_6$$Sn_5$ 厚度的增加，Sn 原子向铜基板侧扩散逐渐受到阻碍，当铜基板侧 Sn 原子供给不足时，非稳态的(Cu，Ni)$_6$$Sn_5$ 将和过量的 Cu 原子反应生成 Cu_3Sn 相. 对比图 3 三种焊点界面 IMC 形貌可以看出，添加 0.1% Ni 元素后，焊点界面(Cu，Ni)$_6$$Sn_5$ 整体厚度较薄且比较平整；添加过量 Ni 元素，则使焊点界面(Cu，Ni)$_6$$Sn_5$ 厚度增加，粗糙度变大；当 Ni 元素添加量为 0.5% 时，界面(Cu，Ni)$_6$$Sn_5$ 粗糙度最大，内部还存在较多裂纹，且部分粗大的(Cu，Ni)$_6$$Sn_5$ 的顶端已经开裂.

图5 为 Ni 元素对 Sn2.5Ag0.7Cu0.1RE/Cu 焊点界面(Cu，Ni)$_6$$Sn_5$ 厚度影响. 随着 Ni 元素添加量的增加，(Cu，Ni)$_6$$Sn_5$ 厚度呈对号形变化趋势. 在 Ni 元素添加量为 0.05% 和 0.1% 时，(Cu，Ni)$_6$$Sn_5$



(a) Sn2.5Ag0.7Cu0.1RE (b) Sn2.5Ag0.7Cu0.1RE0.1Ni (c) Sn2.5Ag0.7Cu0.1RE 0.5Ni

图3 不同 Ni 元素添加量下界面 IMC 形貌
Fig. 3 Microstructure of interfacial IMC at SnAgCuRExNi/Cu solder joints



(a) 未添加Ni元素焊点XRD衍射分析　(b) 0.1%Ni元素焊点能谱分析

图 4　Sn2.5Ag0.7Cu0.1RExNi 焊点界面 IMC XRD 和 EDX 分析

Fig. 4　XRD and EDX results of Sn2.5Ag0.7Cu0.1RExNi joints

厚度最薄；当 Ni 元素添加量为 0.5% 时，(Cu，Ni)$_6$Sn$_5$ 厚度基本和未添加 Ni 元素焊点 Cu_6Sn_5 厚度相同. 这表明添加适量 Ni 元素能抑制界面 IMC 的生长；这可能是由于 Ni 元素在冷却的过程中起到了结晶核心的作用，增加了界面间元素扩散的阻力，阻碍了 IMC 的过快长大.

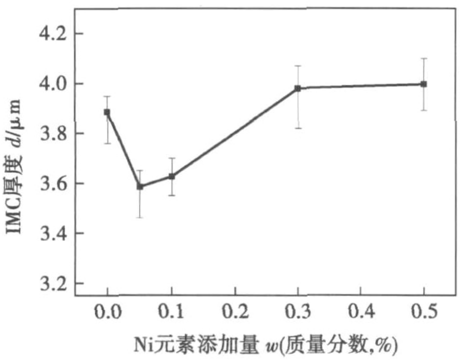


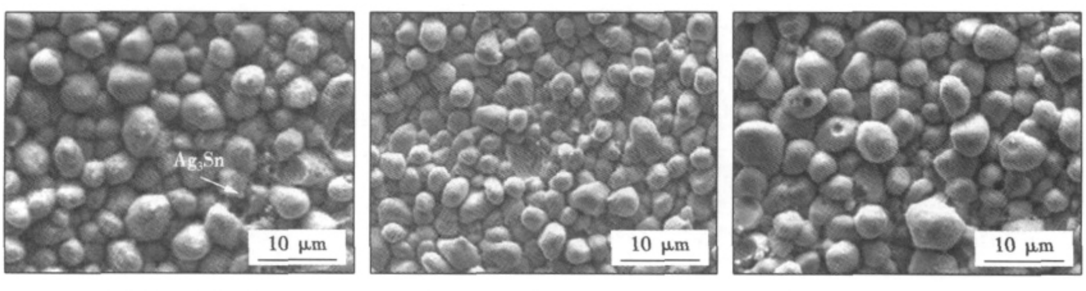
图 5　不同 Ni 元素添加量下(Cu，Ni)$_6$Sn$_5$ IMC 厚度

Fig. 5　Relationship between (Cu，Ni)$_6$Sn$_5$ thickness and Ni content

图 6 为不同 Ni 元素添加量下界面(Cu，Ni)$_6$Sn$_5$ 俯视形貌. 可以看出，其俯视形貌呈鹅卵石状，颗粒平均直径在 2 ~ 4μm；这种向钎料内部长大的鹅卵石状颗粒尺寸越大，越容易在应力作用下萌生裂纹，从而降低焊点力学性能. 在(Cu，Ni)$_6$Sn$_5$ 表面还分布着一些颗粒状的物质，能谱分析表明，该颗粒为 Ag_3Sn，其形成可能是由于界面处大量 Sn 原子参与反应生成(Cu，Ni)$_6$Sn$_5$，使得其与液态钎料界面处富含 Ag 原子，这些 Ag 原子在钎料凝固过程中就会和 Sn 元素结合成 Ag_3Sn 相，这些细小弥散分布的 Ag_3Sn 颗粒往往对焊点的力学性能是有益的. 基于定量学原理测得 Ni 元素添加量为 0，0.1% 和 0.5% 时(Cu，Ni)$_6$Sn$_5$ 颗粒平均截线长(定量表征粒子大小)分别为 2.98 μm，2.50 μm，3.16 μm；添加 0.1% Ni 元素焊点界面(Cu，Ni)$_6$Sn$_5$ 颗粒平均截线长最小，即添加适量 Ni 元素能抑制界面(Cu，Ni)$_6$Sn$_5$ 颗粒的生长；添加过量 Ni 元素，这种抑制效果会逐渐减弱；当 Ni 元素添加量为 0.5% 时，对界面(Cu，Ni)$_6$Sn$_5$ 颗粒的生长已经起不到抑制作用.

2.3　焊点力学性能

图 7 为 Ni 元素对微连接焊点抗剪强度的影响. 可以看出，随着 Ni 元素添加量的增加焊点抗剪强度



(a) Sn2.5Ag0.7Cu0.1RE　(b) Sn2.5Ag0.7Cu0.1RE0.1Ni　(c) Sn2.5Ag0.7Cu0.1RE 0.5Ni

图 6　不同 Ni 元素添加量下焊点界面(Cu，Ni)$_6$Sn$_5$ 俯视形貌

Fig. 6　Top-view morphology of (Cu，Ni)$_6$Sn$_5$ at SnAgCuRExNi/Cu solder joints

逐渐增加. 当 Ni 元素添加量为 0.1% 时,焊点抗剪强度达到最大值为 45.6 MPa,较未添加 Ni 元素焊点抗剪强度提高 15.2%; 随 Ni 元素添加量的继续增加,焊点抗剪强度则呈下降趋势,当 Ni 元素含量为 0.3% 时,焊点抗剪强度已基本与未添加 Ni 元素焊点相同. 钎焊过程中粗大、过厚的焊点界面 IMC 脆硬相在应力作用下往往容易萌生裂纹及裂纹扩展,降低焊点力学性能[10]. Ni 元素添加量为 0.1% 时,焊点界面区 IMC 厚度较薄且平整,$(Cu,Ni)_6Sn_5$ 颗粒尺寸小,内部基本见不到裂纹,对应焊点抗剪强度最高; 当 Ni 元素添加量为 0.5% 时,由图 6c 可知,在焊点界面 IMC 较厚且内部已经存在较多数量的裂纹,部分 $(Cu,Ni)_6Sn_5$ 颗粒已经完全脱落,这有可能是焊点强度降低的原因.

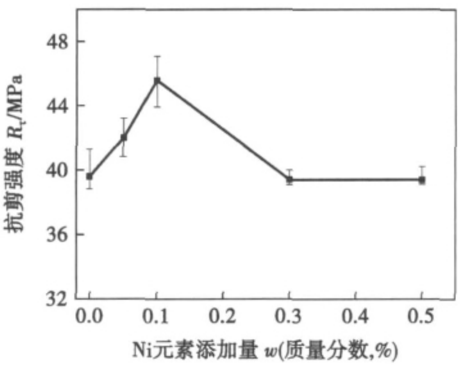


图 7 Ni 元素添加量对焊点抗剪强度影响

Fig. 7 Effect of Ni on shear strength of solder joints

3 结 论

(1) 添加适量 Ni 元素能细化 Sn2.5Ag0.7Cu0.1RE 钎料合金初生 β-Sn 相和共晶组织. 当 Ni 元素添加量为 0.1% 时,钎料合金组织细小均匀,且共晶组织所占比例多.

(2) Sn2.5Ag0.7Cu0.1RE/Cu 焊点界面生成一层扇贝状的 $(Cu,Ni)_6Sn_5$,俯视形貌呈尺度不均匀的鹅卵石状. 适量 Ni 元素能抑制焊点界面区 $(Cu,Ni)_6Sn_5$ 的生长,降低界面 IMC 表面粗糙度,提高焊点抗剪强度. 当 Ni 元素添加量为 0.1% 时,界面 IMC 薄而平整,$(Cu,Ni)_6Sn_5$ 颗粒尺寸小,对应抗剪强度最高为 45.6 MPa,较未添加 Ni 元素焊点抗剪强度提高 15.2%.

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Abstract: A new modified technology is put forward in which weld shaping with trailing impact rolling is used (WSTIR). The integrated device of WSTIR has also been designed. Tensile test and fatigue test has been carried out respectively for under-matched equal load-carrying capacity joints after modifying. Tensile test results show that tensile fracture occurs in the base metal near the weld toe and tensile strength reaches the tensile strength of base metal for equal load-carrying capacity joints after WSTIR. Fatigue test results show that the fatigue life of equal load-carrying capacity joints after WSTIR is significantly greater than the original welded joints. The weld toe arc transition can reduce stress concentration, thereby improve fatigue carrying capacity of WSTIR joints. The results of tensile and fatigue test show that the modified flat-reinforcement joints have the same load carrying capcity with base metal. This shaping method with WSTIR will greatly promote the practical application in engineering for the undermatching equal load-carrying capacity joints.

Key words: undermatching welded joints; weld shaping with trailing impact rolling; tensile property; fatigue property

Effect of Ni on interfacial IMC and mechanical properties of Sn2.5Ag0.7Cu0.1RE/Cu solder joints LI Chenyang[1], ZHANG Keke[1], WANG Yaoli[1], ZHAO Kai[1], DU Yile[2] (1. Material Science & Engineering College, Henan University of Science & Technology, Luoyang 471003, China; 2. Luo Yang Ruichang Petro-Chemical Equipment Co., Ltd, Luoyang 471003, China). pp 39-42

Abstract: The effects of Ni on the microstructure and mechanical properties of Sn2.5Ag0.7Cu0.1RE solder and solder joints were studied by using the scanning electronic microscope and X-ray diffraction. The results show that adding proper amount of Ni in Sn2.5Ag0.7Cu0.1RE solder alloys can refine the initial β-Sn phase and eutectic structure, suppress the growth of the $(Cu,Ni)_6Sn_5$ intermetallic compound (IMC) at the interface of solder joints, and reduce the roughness of interfacial IMC, improve the shear strength of the SnAgCuRE/Cu solder joints. The solder alloy structure was fine and homogenous, eutectic structure proportion was large, interfacial IMC was thin and flat and the grain size of (Cu,Ni)6Sn5 was small. The shear strength got the maximum value (45.6 MPa) when the Ni content was 0.1 wt%, which was 15.2% higher than the solder joints without Ni.

Key words: Sn2.5Ag0.7Cu0.1RExNi solder alloys, solder joints; intermetallic compound (IMC); mechanical properties

Microstructure and abrasion resistance of high-chromium open arc hardfacing alloys GONG Jianxun, XIAO Yifeng (School of Mechanical Engineering, Xiangtan University, Xiangtan 411105, China). pp 43-46, 50

Abstract: Wear-resisting alloys containing Cr 21% ~ 23%, C 3.5% ~ 4.2%, Si 1.4% ~ 1.6%, B 0% ~ 1.8% (mass fraction) were deposited by metal powdered-type flux-cored wire self-shielded open arc welding. The effects of B4C content in flux-cored wire on the microstructure and abrasion resistance as well as the solidifying characteristics of weld puddles and the effects of Si, B on the deoxidization of weld beads were studied by the methods of optical microscopy (OM), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). It shows that Si_5C_3 can act as a good homogeneous nucleate core of primary M_7C_3 grain. With the addition of B_4C particles, the volume fraction and the size of primary M_7C_3 grains increase remarkably and their morphology changes from dispersion to aggregation. In addition, the results of wet sand rubber wear tests and the analysis of worn morphology indicate that abrasion resistance depends on the size and the morphology of primary M_7C_3 grains and micro-spalling is the dominating wear mechanism.

Key words: open arc; high chromium; hardfacing; abrasion resistance; microstructure

Interfacial structure and strength of Si_3N_4 ceramics joint brazed with amorphous filler metal and Cu layer ZOU Jiasheng, ZENG Peng, XU Xiangping (Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, China). pp 47-50

Abstract: Si_3N_4 ceramics was brazed with TiZrCuB amorphous filler metal and Cu interlayer, the effect of brazing metal composition and thickness of copper foil on interfacial structure and bonding strength were studied in this paper. The result shows that the joint strength is up to 241 MPa when the brazing temperature is 1 323 K, holding time is 30min, the thickness of Cu interlayer is 70 m and the exerted pressure is 0.027 MPa. the reaction layer is TiN, the interface microstructure is compounds of Si_3N_4/TiN/Ti-Si + Ti-Zr + Cu-Zr + α-Cu; changing the thickness of interlayer can adjust the thickness and composition of the reaction layer; As the thickness of Cu interlayer increases, Ti-Si compound layer has gradually separated from the TiN layer, and it is pushed to the weld center and refined to a granula shape.

Key words: amorphous brazing filler metals; Cu interlayer; Si_3N_4 ceramics; interfacial structure; bonding strength

Diffusion bonding joint of TiAl-based alloy and Ni-based alloy by using composite interlayer LI Haixin, LIN Tiesong, HE Peng, FENG Jicai, WANG Xianjun (State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China). pp 51-54

Abstract: Diffusion bonding of TiAl-based alloy to Ni-based alloy by using Ti/Nb and Ti/Nb/Ni composite interlayer was carried out. The interfacial microstructure and fracture morphology were investigated by scanning electron microscopy and electron probe X-ray microanalysis. The bonding strength of the joints was evaluated through shear test. The results showed that when the interlayer was Ti/Nb, the optimum bonding time was t = 30 min, the maximum shear strength was R_τ = 273.8 MPa, and the fracture occured at the GH99/Nb interface; when the interlayer was Ti/Nb/Ni, the optimum bonding time was t = 60 min, the maximum shear strength was R_τ = 314.4 MPa, the frac-