Ni-Cr-Co-W-Mo-Ta-B 合金钎料的特性

李　文[1,2]，　金　涛[2]
(1. 沈阳理工大学 材料科学与工程学院，沈阳　110159;
2. 中国科学院 金属研究所，沈阳　110016)

摘　要：采用超声气体雾化法制备了Ni-Cr-Co-W-Mo-Ta-B合金粉. 利用SEM研究了合金粉的微观形貌和化学成分分布；利用DSC分析了合金粉的熔化特性；采用热轧工艺制备Ni-Cr-Co-W-Mo-Ta-B合金柔性布作为中间层合金. 测定了TLP连接镍基高温合金后试样在室温下的断裂强度和1 010 ℃/248 MPa下的持久寿命. 结果表明，Ni-Cr-Co-W-Mo-Ta-B合金粉呈规则的球形，化学成分均匀，其完全熔化温度为1 127 ℃；TLP连接镍基高温合金后在室温下的断裂强度和1 010 ℃/248 MPa下的持久寿命与母材相当.

关键词：Ni-Cr-Co-W-Mo-Ta-B合金粉；镍基高温合金；TLP连接；力学性能
中图分类号：TG406　　文献标识码：A　　文章编号：0253-360X(2012)12-0106-03

李　文

0　序　　言

铸造镍基高温合金为了满足优异的综合性能，加入了多种合金元素，特别是加入了Al，Ti元素，导致合金熔焊时的焊接性较差，限制了熔焊技术的应用[1]. 高温钎焊或瞬态液相连接(transient liquid phase bonding，简称TLP连接)，是有效连接镍基高温合金的连接技术[2-7]，并且中间层合金钎料的选择及其特性至关重要. 目前用于连接镍基高温合金的中间层合金主要有两种类型：一是使用主组元和母材基本相近的共晶类合金或相对简单的三元或四元合金，如Ni-B，Ni-Si，Ni-Cr-B，Ni-Cr-P，Ni-Cr-Si-B等，这些中间层合金能广泛地用于多种材料的连接. 二是以镍基高温合金成分作为基本成分，使中间层合金成分合理地接近所连接的基体金属的成分，并加入适量的降熔点元素，如硼、硅等，以便获得合适的熔化温度. 尽管镍基高温合金最重要的强化机理之一是形成γ′[Ni_3(Al，Ti)]沉淀强化相，但设计中间层合金时通常需要去掉基体合金中的Al，Ti元素，以避免在接头中形成有害的第二相，接头区中的Al，Ti元素可通过连接过程中从母材向接头区的扩散而得到补偿.

文中采用超声气体雾化方法制备了一种用于TLP连接镍基高温合金的Ni-Cr-Co-W-Mo-Ta-B中间层合金，利用扫描电镜(SEM)和热分析方法(DSC)研究了中间层合金的特性，并测定了TLP连接接头的拉伸和持久性能.

1　试验方法

试验所用镍基高温合金具有γ+γ′两相组织，是γ′沉淀强化合金. 用纯度大于99%(质量分数)的镍、铬、钴、钨、钼、钽以及镍硼合金配制Ni-Cr-Co-W-Mo-Ta-B合金，其成分(质量分数，%)为Cr6.5，Co5.5，W5.5，Mo2.0，Ta3.0，B4.0，其余为Ni. 将配制好的合金在真空感应炉中熔炼，并将液态合金浇铸成合金锭作为母合金. 利用超声气体雾化法制备出Ni-Cr-Co-W-Mo-Ta-B合金粉，利用SEM对合金粉的微观组织和成分分布进行分析，利用DSC测定合金粉的固液相线温度. 向合金粉中添加少量的粘结剂，采用热轧工艺制备出具有良好柔韧性又有一定强度的Ni-Cr-Co-W-Mo-Ta-B合金柔性布.

用线切割将镍基高温合金试棒加工成直径为13 mm，长33 mm的待连接试样，待连接试样的连接面用800号砂纸机械磨光，在连接前用丙酮超声清洗，然后将两个待连接试样之间置入Ni-Cr-Co-W-Mo-Ta-B中间层合金柔性布，组成连接试样，连接试样在$1\times10^{-3}\sim5\times10^{-3}$ Pa的真空条件下加热至1 220 ℃，保温16 h，然后在真空样品室中随炉冷却. 对连接后的试样参照基材的热处理工艺进行固溶和时效处理，并分别测试和比较了TLP连接试样和镍基合金基材在室温下的断裂强度和1 010 ℃/248 MPa下的持久寿命.

收稿日期：2011-10-08

2　试验结果与讨论

Ni-Cr-Co-W-Mo-Ta-B 是一种用于 TLP 连接镍基高温合金的中间层合金. 它以被连接的镍基高温合金的成分作为基本成分,将其中的铝、钛排除在外,再加入少量的降熔点元素硼,以满足对中间层合金熔化温度的要求. 采用超声气体雾化法制备得到的 Ni-Cr-Co-W-Mo-Ta-B 中间层合金粉,其颗粒为比较规则的球形,如图 1 所示.

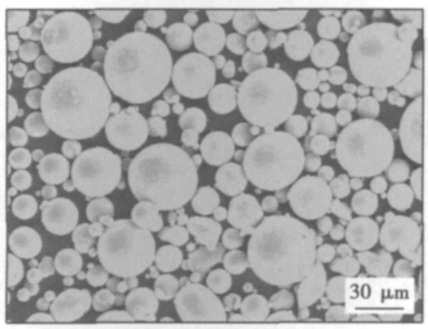

图 1　Ni-Cr-Co-W-Mo-Ta-B 粉的 SEM 形貌
Fig. 1　SEM morphology of Ni-Cr-Co-W-Mo-Ta-B

图 2 是 Ni-Cr-Co-W-Mo-Ta-B 颗粒的元素分布

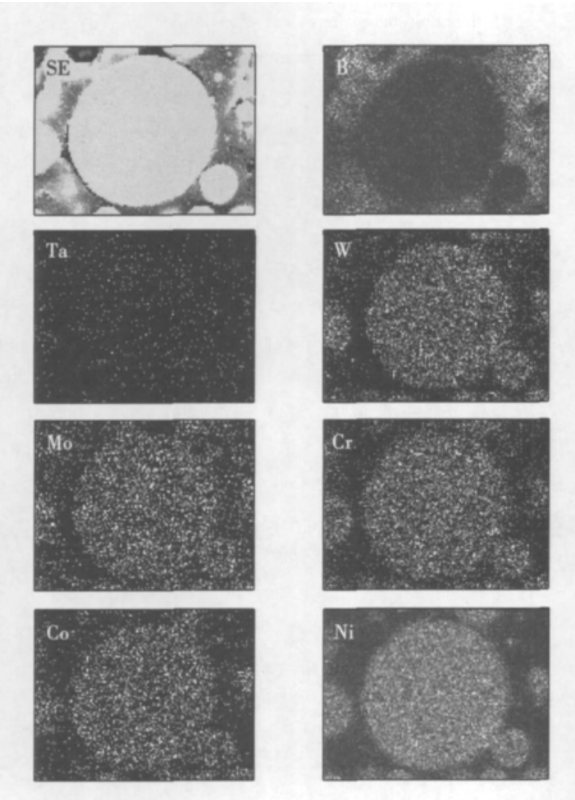

图 2　Ni-Cr-Co-W-Mo-Ta-B 颗粒 SEM 元素分布
Fig. 2　Element distribution maps for Ni-Cr-Co-W-Mo-Ta-B particle by SEM

SEM 面扫描分析,可见各元素的分布是均匀的. 超声气体雾化法是借助于快速凝固技术,使熔化后的合金液流经雾化喷嘴时,在高压气体撞击下破碎成很小的金属液滴,增大了熔体的散热面积,使熔体在极短的时间内快速凝固,因此这种在急冷条件下形成的合金可以看作是被冻结了的金属熔体,保持着液态时良好的化学成分均匀性,而具有稳定和均匀的成分是作为中间层合金的基本要求.

图 3 为 Ni-Cr-Co-W-Mo-Ta-B 合金粉的 DSC 分析曲线. 可见随着温度的升高,样品在 1 056 ℃开始熔化,在 1 127 ℃完全熔化,在此期间是一个吸热峰,因此 Ni-Cr-Co-W-Mo-Ta-B 合金粉的固、液相线温度分别为 1 056 ℃和 1 127 ℃,中间层合金的熔化温度直接关系到连接时所选择的工艺参数,连接温度一般至少应高于完全熔化温度 30 ~ 60 ℃[8],实际设计的 TLP 连接温度为 1 220 ℃.

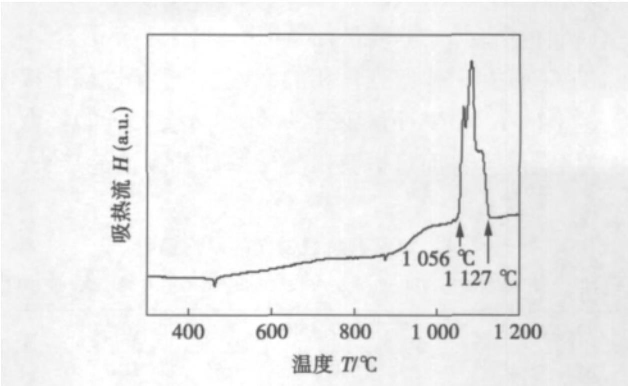

图 3　Ni-Cr-Co-W-Mo-Ta-B 合金粉的 DSC 曲线
Fig. 3　DSC curve of Ni-Cr-Co-W-Mo-Ta-B powder

图 4 为 Ni-Cr-Co-W-Mo-Ta-B 中间层合金柔性布. 金属粉末柔性布是将特殊性能固体颗粒材料与粘接剂混合,经滚压轧制制成. 超声气体雾化后得到的 Ni-Cr-Co-W-Mo-Ta-B 金属粉末呈球形,具有不同的粒度,将金属粉末分级,并选取颗粒直径小于 45 μm 的合金粉末作为试验样品,选用的粘接剂不仅有连接颗粒的功能,而且在随后的连接加热过程

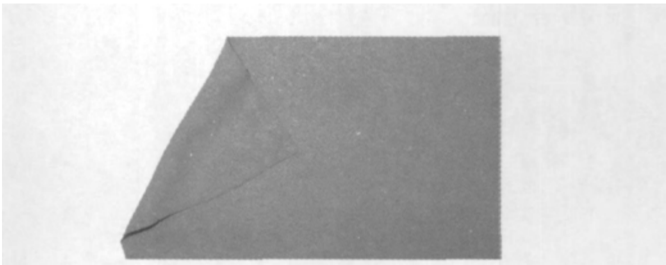

图 4　Ni-Cr-Co-W-Mo-Ta-B 合金柔性布
Fig. 4　Ni-Cr-Co-W-Mo-Ta-B flexible insert alloy

中全部挥发，对连接过程无不良影响．采用热轧工艺，将加入粘接剂的合金粉末制备成具有良好柔韧性又有一定强度的柔性布，使分散的金属粉末变成一个整体，可以方便地制成多种形状，并能与多种表面相贴合，便于装配．

利用 Ni-Cr-Co-W-Mo-Ta-B 合金柔性布作为中间层合金，在 1 220 ℃，16 h 条件下对镍基高温合金进行 TLP 连接后，参照基材的热处理工艺进行固熔和时效处理，分别测定了 TLP 连接试棒和母材在室温下的断裂强度和 1 010 ℃/248 MPa 下的持久寿命，其结果如表 1 和表 2 所示．可见 TLP 接头在室温下的断裂强度和 1 010 ℃/248 MPa 下的持久寿命与母材相当．一方面利用快速凝固技术制得的 Ni-Cr-Co-W-Mo-Ta-B 合金粉化学成分均匀，同时降熔点元素硼的原子半径很小，扩散速度快，大大减少了接头出现脆性相的可能性；另一方面镍基高温合金中最重要的强化机理之一是形成 γ′沉淀强化相，虽然研制的 Ni-Cr-Co-W-Mo-Ta-B 中间层合金不含 Al 和 Ti 等形成 γ′弥散强化相的元素，但连接过程中接头区上的 Al 和 Ti 元素依靠从母材向接头区的扩散而得到补偿，进而可以获得类似基体的高性能接头．

表 1 室温下断裂强度的平均值

Table 1 Average value of tensile tests at room temperature

试样	断裂强度 σ_b/MPa	断裂位置
TLP 连接	1 046	基材
基体金属	1 020	—

表 2 1 010 ℃/248 MPa 下的持久性能

Table 2 Stress rupture properties at 1 010 ℃/248 MPa

试样	持久寿命 t/h	断裂位置
TLP 连接	45.93	接头
基体金属	45.28	—

3 结 论

（1）利用超声气体雾化法制备 Ni-Cr-Co-W-Mo-Ta-B 合金粉，合金颗粒呈规则的球形，化学成分均匀，合金的完全熔化温度为 1 127 ℃.

（2）采用 Ni-Cr-Co-W-Mo-Ta-B 合金粉作为中间层合金进行 TLP 连接后，在室温下的断裂强度和在 1 010 ℃/248 MPa 下的持久寿命与母材相当．

参考文献：

[1] 庄鸿寿．高温钎焊［M］．北京：国防工业出版社，1989.

[2] Nishimoto K, Saida K, Kim D, *et al*. Bonding phenomena and joint properties of transient liquid phase bonding of Ni-base single crystal superalloys［J］. Welding in the World, 1998, 41(2): 121－131.

[3] 李 文，金 涛，胡壮麒．镍基单晶高温合金瞬态液相连接接头的微观结构和结晶学取向［J］．金属学报，2008，44(12)：1474－1478.
Li Wen, Jin Tao, Hu Zhuangqi. Microstructure characteristics and crystallographic orientation of transient liquid phase joint of Ni-based single crystal lsuperalloy［J］. Acta Metallugica Sinica, 2008, 44(12): 1474－1478.

[4] 李 文，金 涛，孙晓峰，等．急冷 Ni-Cr-B 合金钎料的制备及其可焊性［J］．焊接学报，2002，23(6)：82－84.
Li Wen, Jin Tao, Sun Xiaofeng, *et al*. Preparation of rapidly quenched Ni-Cr-B alloy ribbon and its weldability［J］. Transactions of the China Welding Institution, 2002, 23(6): 82－84.

[5] 曲文卿，王奇娟，张彦华．铝基复合材料与铝合金的 TLP 扩散连接［J］．焊接学报，2002，23(6)：67－70.
Qu Wenqing, Wang Qijuan, Zhang Yanhua. TLP diffusion bonding of aluminum base composite and aluminum alloy［J］. Transactions of the China Welding Institution, 2002, 23(6): 67－70.

[6] Liu Jide, Jin Tao, Zhao Nairen, *et al*. Temperature dependence of deformation mechanism in bonding zone of TLP joint of nickel base single crystal superalloy［J］. Science and Technology of Welding and Joining, 2007, 12: 381－384.

[7] 张贵峰，张建勋，王士元，等．瞬态液相扩散焊与钎焊主要特点之异同［J］．焊接学报，2002，23(6)：92－96.
Zhang Guifeng, Zhang Jianxun, Wang Shiyan, *et al*. Similarities and differences in main characteristics between transient liquid phase bonding and brazing process［J］. Transactions of the China Welding Institution, 2002, 23(6): 92－96.

[8] 邹 僖．钎焊［M］．北京：机械工业出版社，1995.

作者简介：李 文，女，1964 年出生，博士，教授．主要研究镍基高温合金的连接．发表论文 20 余篇．Email：wenli@imr.ac.cn

Abstract: Based on the section analysis of three-dimensional model of friction stir welding, the evolution of the joint section of the welding process was established. The forming process of friction stir welding was divided into extrusion stage, migration stage, backfilling stage and shoulder effect stage. The first three stages which were affected by stir pin were analyzed. The analysis of the material migration processes of the first three stages pointed out that the original surface and the residual oxides were migrated to the retreat side in the extrusion stage, the onion ring structure was formed, the oxides were fragmentated and dispersed in the migration stage and the onion ring structure was fully formed in the backfilling stage. The studies showed that if the above three stages could not effectively complete the forming processes, the superposition effect of a variety of defects forming mechanisms would lead to the formation of the final defects. The results show that the four stages of the forming process established by using the section analysis can be used to explain the forming mechanisms of FSW joints and the causes of the "S line" and other defects.

Key words: friction stir welding; section analysis; joint forming; defect

Effects of welding heat source parameters on residual stress and distortion in thin plate joint WANG Nengqing, TONG Yangang, DENG Dean (College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China). pp 97 – 100

Abstract: The thermo-elastic-plastic finite element method (FEM) has been widely used to predict temperature field, residual stress distribution and deformation. However, how to choose the parameters of moving heat source model for given welding conditions heavily depends on a analyst's experience. It is necessary to clarify the influence of heat source parameters on residual stress and deformation. Therefore, an attempt was made to examine the influence of heat source parameters on residual stress and deformation in a thin plate joint using thermo-elastic-plastic FEM with Goldak heat source model in the current work. The simulation results show that the heat source parameters have no significant effect on residual stress, but have effect on welding deformation to some extent.

Key words: heat source; welding residual stress; welding deformation; numerical simulation

Effects of laser shock wave on salt spray corrosion of X70 pipeline steel welded lines WU Yongzhong, KONG Dejun, LONG Dan, FU Guizhong (College of Mechanical Engineering, Changzhou University, Changzhou 213016, China). pp 101 – 105

Abstract: The surface of X70 pipeline steel welded line was treated by laser shock wave, and the corrosion performances before and after laser shock processing were analyzed by salt spray corrosion test in artificial atmosphere. The surface morphologies, chemical elements and phase constituent were observed with SEM (scanning electron microscope), EDS (energy dispersive spectrometer) and XRD (X-ray diffraction), respectively, and the effects of laser shock processing on the corrosion mechanism were discussed. The results show that tensile residual stress exists in the surface of X70 pipeline steel welded lines in primitive state, which improves stress corrosion crack with the interaction of corrosive medium Cl^-. Spelling corrosion occurs with the interaction of boundary corrosion. The grain refinements are produced in the welded lines by laser shock processing, and the strengthened layer is formed on the surface, which improves corrosion resistance of the welded lines.

Key words: laser shock processing; X70 pipeline steel; welded line; salt spray corrosion

Characteristics of Ni-Cr-Co-W-Mo-Ta-B brazing filler

LI Wen[1,2], JIN Tao[2] (1. College of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110159, China; 2. Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China). pp 106 – 108

Abstract: Ni-Cr-Co-W-Mo-B alloy powder was prepared by gas atomization. The particle morphology and element distribution of the powder were investigated by SEM. The melting characteristics of the Ni-Cr-Co-W-Mo-Ta-B powder were evaluated by DSC. The Ni-Cr-Co-W-Mo-Ta-B flexible insert alloy cloth was obtained through a thermal rolling technology. The bonding strength at room temperature and stress rupture life at 1 010 ℃/248 MPa were measured. The results indicate that Ni-Cr-Co-W-Mo-Ta-B particles existas ball-shape and the element distributions are homogeneous in the particles. The liquidus temperature of the alloy is 1 127 ℃. The tensile strength at room temperature and stress rupture life at 1 010 ℃/248 MPa of the completed joints are almost identical to those of the superalloy substrate when the Ni-base superalloy was bonded by the transient liquid phase (TLP) bonding using Ni-Cr-Co-W-Mo-Ta-B powder as an insert alloy.

Key words: Ni-Cr-Co-W-Mo-Ta-B powder; Ni-base superalloy; TLP bonding; mechanical properties

Study of pulse combustion welding rod for vertical weld

WU Yongsheng, WANG Jianjiang, XIN Wentong, LIU Haodong (The Institute of Advanced Materials, Ordnance Engineering College, Shijiazhuang 050003, China). pp 109 – 112

Abstract: A new type of manual SHS welding rod called the pulse combustion rod is introduced, which is used in the urgent repair of war. Firstly, the problems and insufficiency of the normal manual SHS welding rod (normal combustion rod for short) are analyzed in the vertical weld. The pulse combustion rod is designed with structure and constitution presented. Then vertical weld experiment is carried out, in which low carbon steel is used as the base metal. By analysis with SEM, XRD and EDS, the results show that weld seam is composed of Fe-riched phase and Cu-riched phase, with a few of α-Fe but a little of Fe-Ni, ε-Cu and Cu0.81Ni0.19 contained in Fe-riched phase, and with much ε-Cu but a little of Cu0.81Ni0.19, α-Fe and FeNi contained in Cu-riched phase. Dendritic Fe-riched phase distributes in the solid solution of Cu-riched phase. The weld seam alloy has a good bond with the base metal. The aim of double sides forming is obtained by single side welding. The mechanical properties test of weld joint presents that tensile strength is up to 367MPa and the hardness of weld alloying zone is 143.8 HV.

Key words: pulse combustion welding rod; vertical weld; microstructure and property