

钛基钎料真空钎焊立方氮化硼的分析

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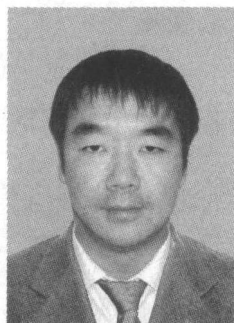
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摘 要: 采用 Ti-Zr-Ni-Cu 钎料在优化钎焊温度和时间下对 CBN 磨粒进行了真空钎焊试验, 实现了 CBN 与钢基体的高强度连接. 采用 SEM 对 CBN 表面化合物三维形貌进行了观察分析, 采用 EDS 分析了 CBN 表面化合物及钎料与钢基体界面成分变化, 采用 XRD 对焊后的 CBN 磨粒及其表面的化合物进行了物相分析, 最后对 CBN 试样进行了断口分析. 结果表明, CBN 表面生成了 Ti 元素的针状、块状化合物 TiB_2 和 TiN 磨粒与钎料间界面形成化学冶金结合, 这正是 CBN 与 Ti-Zr-Ni-Cu 有良好润湿性和高强度连接的主要原因. 断口形貌的分析表明, CBN 与 Ti-Zr-Ni-Cu 钎料间的断口发生在 CBN 磨粒内部, 说明 CBN 磨粒与 Ti-Zr-Ni-Cu 合金钎料的结合强度大于 CBN 磨粒本身的强度.

关键词: 真空钎焊; 钛基钎料; 立方氮化硼

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0 序 言

立方氮化硼 (CBN) 具有高的硬度和良好的化学稳定性, 它不与铁族金属及其合金发生亲和作用. 而随着工业技术的发展, 硬韧类难加工材料如钛合金、高温合金以及金属间化合物等的应用越来越广泛, 目前这些材料的磨削加工多采用电镀和烧结的 CBN 超硬磨料砂轮. 但传统的电镀或烧结 CBN 砂轮中 CBN 磨粒仅仅是通过结合层金属的机械包埋镶嵌作用与工具基体相互连接, 结合力较低, 使得重负荷工作环境下由于磨粒极易从结合层脱落导致砂轮过早失效. 目前, 国内外正在通过钎焊技术开发新一代超硬材料磨料砂轮, 期望通过钎料与磨粒及基体在高温下的化学冶金反应使三者之间形成牢固的化学冶金结合以满足磨削加工要求^[1,2]. 目前关于 CBN 的钎焊问题, 国内外有许多学者进行了相关的研究.

Chattopadhyay^[1]、肖冰等人^[2]采用银基含 Ti 元素钎料对 CBN 进行了真空钎焊, 发现了 Ti 元素在 CBN 表面有 Ti 元素富集, 确定了界面处部分新生化合物的种类.

南京航空航天大学的丁文锋等人^[3]采用 Ag

Cu-Ti 钎料进行了钎焊 CBN 试验, 发现了 CBN 与钎料界面处微观组织的分层结构, 并对形成机理作了细致的分析. 卢广林等人^[4]采用添加不同比例活性 Ti 元素的 Ag-Cu 基钎料对 CBN 进行钎焊, 研究了 CBN 的焊接性. 迄今为止, 尽管该项研究采用含 Ti 元素的银基钎料对 CBN 钎焊已经取得了重要的进展, 并对钎焊界面微结构以及活性元素在磨粒与钎料界面之间的特征进行了详细的报道, 但采用银基钎料成本较高, 而采用钛基钎料进行 CBN 钎焊的研究尚未见报道.

作者采用以活性元素 Ti 元素为基的钎料对 CBN 磨料进行了钎焊试验, 着重分析了两种界面 (CBN 磨粒与钎料之间的界面以及钎料与钢基体之间的界面) 的微结构, 以期对钎焊 CBN 砂轮基础研究做一些有益探索.

1 试验方法

试验采用基体材料为 45 钢, 尺寸为 $\phi 70 \text{ mm} \times 10 \text{ mm}$, 磨料为 YBN-65 型 CBN 粒度直径为 $\phi 150 \sim \phi 180 \mu\text{m}$ 钎料为 Ti-Zr-Ni-Cu 合金粉末, 具体成分为 (质量分数) 37.5% Zr, 15% Cu, 15% Ni, 余量为 Ti 元素. 基体表面钎料用量大约为 100 mg/cm^2 , 采用精度为 0.1 mg 的 Adventure 型分析天平进行称量. 具体工艺过程为: 首先对钢基体、磨粒作表面去油、去

污处理,接着将 Ti-Zr-Ni-Cu钎料置于钢基体表面,并在钎料上分布 CBN磨粒,钎焊接头如图 1所示,然后在 VOQ2—80型真空炉中加热至合适的钎焊温度保温 5 min,最后随炉冷却至 200 ℃取出。

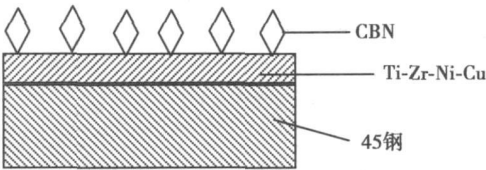


图 1 Ti-Zr-Ni-Cu钎焊 CBN接头示意图
Fig 1 Schematic diagram of joint framework

钎焊温度的选择根据实际生产过程和钎料熔化温度的范围来确定。钎焊温度 T 分别为 930 950 970 990 ℃。

由于钎料对 CBN相对于钢基体的润湿性较差,因此文中重点考虑了 CBN与钎料的界面。在钎焊过程中 CBN与钎料中 T 元素发生润湿反应,在表面生成了新的化合物,文中首先采用硝酸对焊后的 CBN进行深腐蚀,而 TN TB_3 TB 等是耐腐蚀的,因此 CBN及表面的化合物与基体可以脱离。

对 CBN表面化合物的三维形貌和成分采用日本电子公司 (JEOL) JSM—6300型扫描电镜 (SEM) 及美国 KEVEX公司 X射线能谱仪 (EDS) 进行分析,使用 X射线衍射仪 (日本理学公司的 D max) 进行相分析。

2 试验结果与分析

2.1 界面微观组织分析

CBN以 $B-N$ 原子沿四面体杂化轨道形成的共价键结合,很难被一般液态金属所润湿,一般焊接材料很难实现 CBN与金属基体的连接。通过钛基钎料中活性的 T 原子,其对 $B-N$ 原子有较强的化学亲和力,使钎料与 CBN之间发生化学反应,实现 CBN与金属基体的连接。

试验发现,活性的 T 元素极易被氧化,钎焊加热和保温阶段真空度需保证高于 10^{-3} Pa,当低于此真空度时很难实现 CBN与基体的连接。Ti-Zr-Ni-Cu钎焊 CBN试验中,各个钎焊温度的焊接效果见表 1。从表 1中可以看出,钎焊温度存在一个合适的范围,钎焊温度在 950 ~ 970 ℃时,试样表面成形美观,钎料与 CBN的结合强度较高,温度过高或过低对 CBN的焊接性都不利。

真空钎焊 CBN磨粒的整体形貌如图 2所示,可

表 1 钎焊温度对焊接性的影响			
Table 1 Effect of brazing temperature on weldability			
钎焊温度 $T/^\circ\text{C}$	润湿性	成形	结合强度
930	差	差	低
950	好	好	高
970	好	一般	一般
990	好	差	低

以看出 Ti-Zr-Ni-Cu钎料对 CBN磨粒表现出很好的浸润性,CBN磨粒与钎料的加热过程中发生了润湿反应,钎料沿 CBN磨粒侧面达到了一定的高度,并将 CBN磨粒包裹起来。

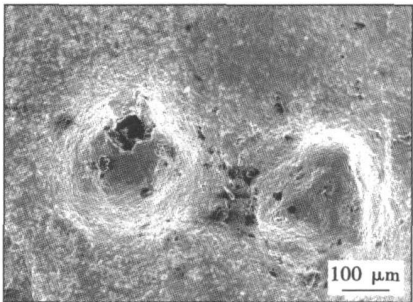


图 2 Ti-Zr-Ni-Cu钎焊 CBN形貌 (SEM)
Fig 2 Morphologies of brazed CBN

为深入分析钛基钎料中 T 元素与 $B-N$ 元素的相互作用,对焊后的 CBN试样进行深腐蚀,图 3为深腐蚀后 CBN表面的三维化合物形貌,从图 3中的 A、B处可以明显看到许多块状、棒状和细针状的化合物从 CBN表面生长出来。其能谱见图 4可以看出明显是由 $B-N-T$ 元素组成,各种元素的成分 (原子分数,%) $B18.5$ $N23.6$ $Ti57.9$,由此可以判断其为 $B-N-T$ 生成的化合物。

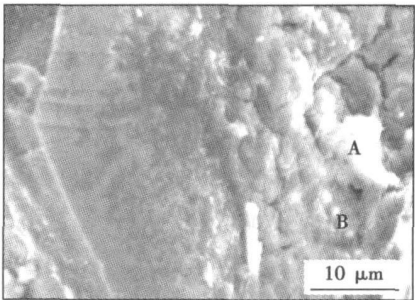


图 3 CBN表面化合物形貌
Fig 3 Morphologies of compound

图 5为 CBN及其表面化合物的 X射线衍射图,从图 5中可见,其主要物相为 CBN, TB_3 TN ,因此

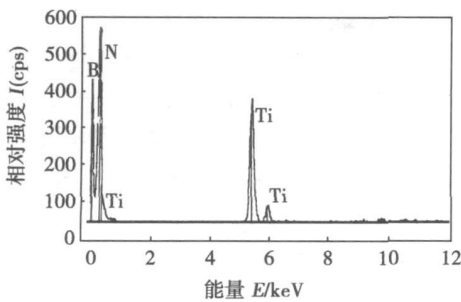


图 4 EDS能谱图
Fig 4 Diagram of EDS

可以确定在 CBN的表面生成了 TiB_2 , TiN 同时由 XRD分析可见, CBN点阵参数未变,说明其生成过程是由直径较小的 B、N原子向钎料扩散,当达到一定浓度时,以外延生长、反应扩散的方式,在 CBN表面形成化合物层。B、N和 Ti的原子半径分别为 0.097、0.067、0.147。需要特别指出的是,尽管表面有一定的化合物生成,但由于化合物相对较少,而 X射线具有较强的穿透能力,因此在对经深腐蚀钎焊试样衍射分析时,相对于表面化合物,内部 CBN磨粒晶体衍射峰更强。

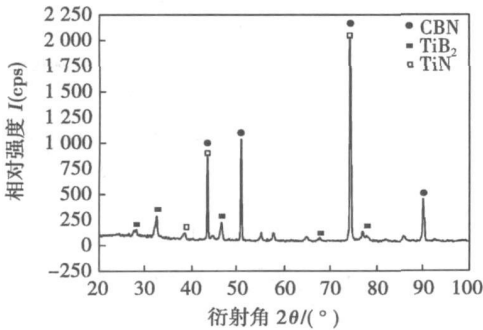


图 5 X射线衍射图谱
Fig 5 X-ray diffraction pattern

2.2 钎料与 CBN界面反应形成机理

选择 $Ti-Zr-Ni-Cu$ 共晶钎料就是因为 Ti、Zr原子与立方氮化硼中的 N、B原子有强的化学亲和性,活性原子 Ti、Zr与共价键结合的 CBN晶体在一定温度能克服激活能而发生界面反应。

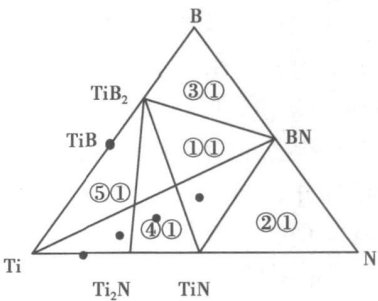
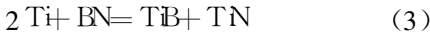
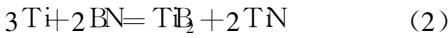
考虑到钎焊过程的环境近似于等压情况,因此利用冶金热力学计算,选用标准 Gibbs自由能作为基本判据,即

$$\Delta G_T^\ominus = \Delta H_T^\ominus - T\Delta S \quad (1)$$

式中: ΔG_T^\ominus 为物质在 T温度时的标准 Gibbs自由能变化值; ΔH_T^\ominus 为物质在 T温度时的相对焓变; ΔS

为物质在 T温度时标准熵变; T为热力学温度。 ΔG_T^\ominus 的值是指示该化学反应能否向指定方向进行的判据。当 $\Delta G_T^\ominus < 0$ 时,反应可以进行; $\Delta G_T^\ominus = 0$ 时,反应处于平衡状态;当 $\Delta G_T^\ominus > 0$ 时,反应则向相反方向进行。王明智等人^[5]采用 DTA测试结果表明,在 473 ~ 1 273 K之间, Ti元素与 CBN有两次反应高峰,分别为 878 K和 1 080 K。在 878 K时有 TiN生成,在 1 080 K时开始出现 TiB_2 、 TiN 。文中的钎焊温度为 950 °C,因此可发生上述两个化学反应。从热力学角度分析 TiN、 TiB_2 、CBN三种物质的生成自由能分别为 -307.6、-288.4、-80.7 kJ/mol,可见 TiB_2 、TiN的生成自由能远低于 CBN,所以试验采用 $Ti-Zr-Ni-Cu$ 钎料钎焊 CBN在热力学上是可行的。

在钎焊过程中,通过 Ti元素与 CBN的界面反应,降低了 Ti元素的活度,因此 Ti元素继续向 CBN扩散,结合 Ti-B-N三元简化相图^[6-7],如图 6所示,由于 CBN中 B、N两种元素原子分数相同,因此从相图可以初步判断其生成物可能是 TiB_2 和 TiN,即位于相图中的①区。可能发生的化学反应为^[8]



相区① $TiB_2 + TiN + BN$ ② $TiN + BN + N_2$
③ $TiB_2 + B + BN$ ④ $TiN_{1-x} + TiB_2$ ⑤ $Ti + TiB_2$

图 6 Ti-B-N三元相图

Fig 6 Ti-B-N ternary system phase diagram

从相图中可以看出,靠近 CBN的位置即其表面生成 TiB_2 和 TiN是稳定的,这与前面的分析相吻合。

2.3 钎料与钢基体界面的元素扩散与分布

图 7为 $Ti-Zr-Ni-Cu$ 钎料与钢界面微区的 SEM形貌照片及元素线扫描,图中白线为线扫描位置,可以看出界面结合完好,无缺陷。

钎料与钢基体之间存在明显的相互扩散现象,两者形成了冶金结合,并且 Ni、Ti、Zr元素有少量扩散进入钢基体,而 Cu元素几乎没有进入钢基

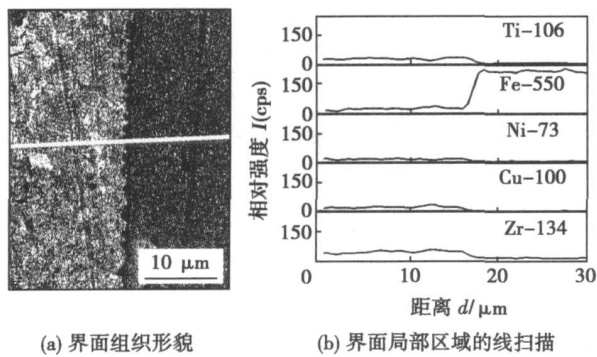


图 7 TiZrNiCu与钢基体的线扫描
Fig. 7 Concentration curves of element in interface between TiZrNiCu filler and steel substrate

体,这可能是因为 Ti Zr原子活性较强,很容易与 Fe元素形成金属间化合物,而 N原子与 Fe原子半径接近,可以形成固溶体。

2.4 钎焊 CBN的断口分析

为确证 TiZrNiCu合金与 CBN界面上的化学冶金结合是否有足够的强度,断口的形貌分析十分有效。对焊后 CBN试样的 30颗磨粒在磨粒顶部施加垂直于磨料的力,使试样分裂成两部分,借助扫描电镜对断口进行形貌观察发现,钎焊的 CBN磨粒大多是 CBN开裂,如图 8所示,充分说明 CBN与钎料之间形成了牢固的化学冶金结合。从图中可以看出,CBN的断口呈脆性断口,明显有解理台阶,而钎料的断口为韧性断口。在图 8中 A B处可以看到,CBN尽管已经开裂,但钎料并没有与 CBN剥离,而仍然牢固地与 CBN连在一起,对 CBN与钎料结合的部位进行能谱测试,可以发现,其主要成分为 Ti B N元素,与前面的分析基本吻合。

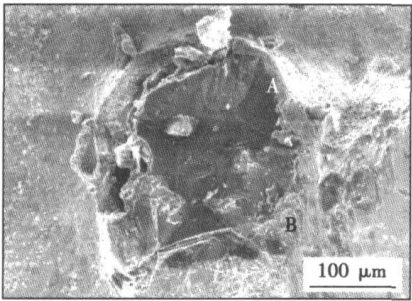


图 8 焊后 CBN断口形貌
Fig. 8 Fracture of surface of brazing CBN

3 结 论

(1)采用 TiZrNiCu钎料钎焊 CBN在 950 ℃

保温 5 min的工艺下,可以实现 CBN的高强度连接,其主要是在 CBN表面有 Ti元素的富集,并在 CBN表面生成 Ti元素的化合物。

(2) TiZrNiCu钎料对 CBN进行钎焊,在 CBN表面可以形成块状、针状的化合物 TiB₃和 TiN

(3)经过钎焊 CBN试样的断口试验,可以发现钎焊 CBN试样的断口发生在 CBN中,充分说明 CBN与钎料之间形成了牢固的化学冶金结合。

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cracks in the whole weld zone were produced. The weld zone was characterized by a large amount of continuously distributed compounds such as TiFe_2 , TiFe and Cr_2Ti . The formation of these kinds of brittle compounds was the main reason of the cracks. The micro-hardness in weld zone was much higher than that in base metal. And TiFe_2 phase was harder than TiFe phase, so the throughout crack was found in the TiFe_2 -rich zone. Direct electron beam welding of these two alloys was hardly completed. Some interlayer alloys have to be used to improve the metallurgical condition and change the kind and distribution of the compounds.

Key words: TA15 titanium alloy; 304 stainless steel; electron beam welding; microstructure; micro-hardness

Analysis on vacuum brazing of CBN grits with Ti-base filler

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Abstract: Ti-Zr-Ni-Cu filler was utilized to braze CBN grits in vacuum furnace at different temperatures and times, and good bonding between CBN and steel substrate was gotten. The microstructure and the element distribution of the bonding interface, as well as the topography and the phase structure of the compounds on the surface of brazed CBN grits were analyzed by SEM, EDS and XRD. The results show that a layer of needle-like, or block-like Ti compounds such as TiB_2 and TiN are formed on the surface of the CBN, thus CBN grits and Ti-Zr-Ni-Cu filler realize chemical metallurgical joining in the interface. And the analysis on fracture appearance shows that the fracture between CBN and Ti-Zr-Ni-Cu filler occurs in CBN, so it can be considered that the joining strength between CBN and Ti-Zr-Ni-Cu filler is higher than that of the CBN.

Key words: vacuum brazing; Ti-base filler; cubic boron nitride

Microstructure of Be/Al/Be joint by welded laser beam

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Abstract: Application of beryllium alloy was joined with laser welding by taking aluminum as transition material. The microstructure and properties of the welded joint were studied by means of scanning electron microscope (SEM), optical microscope (OM), and X ray diffraction apparatus (XRD). The results indicated that the microstructure was composed of quasi-composite compound phase formed by beryllium and aluminum. The shear strength lies between aluminum and beryllium. With percent of beryllium in weld zone being more, the size of beryllium and beryllium particle distribution change, the shear strength of welded joint is higher, the fracture mechanism is transformed from ductile fracture with fractographs of dimples to brittle fracture with quasi-cleavage feature. The intermetallic compound in weld zone is the main cause of fracture for Be/Al/Be laser welded joint.

Key words: beryllium; laser welding; microstructure; shear strength; fracture appearance

Effect of electrode force on welding quality of sheet to tube by single sided spot welding LIANG Caiping, LIU Xiaohang, TIAN Haobin (Mechanics & Electronic Engineering Faculty, Shanghai Second Polytechnic University, Shanghai 201209, China). p 65 – 68

Abstract: Based on the structure characteristics of sheet to tube joined by spot welding, a welding system with servo gun was established. Due to large deformation of the weldments during the sheet to tube welding stage and unreliable ring nugget after welding, a new method was investigated to increase the weld quality based on the electrode force change. The effects of variable electrode force on weld tensile-shear strength and weld deformation were researched. The results show that the weld strength can be increased and weld deformation can be decreased by adjusting the electrode force in welding process. Comparatively, the change of electrode force during holding stage has less influence on weld quality. The studies can contribute to develop welding parameters for sheet to tube joining and to promote the wider application of single sided spot welding in the assembly of auto body.

Key words: single-sided resistance spot welding; servo gun; variable electrode force; welding quality

DSP based digital pulsed CO_2 welding power supply with sloping output characteristics

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Abstract: A digital pulsed CO_2 welding power supply with sloping output characteristics based on digital signal processing controller was developed. It can automatically regulate the slope of external characteristic curves with predominant sloping characteristic algorithm in the welding process, and implement the stability of welding arc in wide field. In this system, the average arc voltage is preset in accordance with the feeding rate of a separate wire feeder, while full-bridge inverted main circuitry can be adopted independently. The digital pulse width modulation signals are generated directly at low hardware expense, and the control strategy is implemented through software. Furthermore, the needed slope rate of output characteristics is calculated with the software, the control signal is created and converted to dual-edge pulse output signal, and the arc voltage is automatically adjusted to maintain a stable arc. The simplified configuration shows high reliability, and the control program can also be updated by means of the upgrade interface for property enhancement. Welding test showed that the pulsed power supply with the sloping output characteristics has high stability and reliability.

Key words: pulsed CO_2 welding; sloping output characteristics; inverted power supply

Effect of flow rate and arc length changes on velocity and temperature field of TIG arc

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Abstract: A steady two-dimensional (2D) axisymmetric