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Wetting behavior and interfacial interactions of molten Cu50Ti alloy with hexagonal BN and TiB_2 ceramics

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ABSTRACT

Wetting behavior of molten Cu50Ti alloy on hexagonal BN (*h*-BN) and TiB_2 ceramics has been studied under vacuum using a modified sessile drop method. Final contact angles of 8° and 3° are obtained at 1000 °C on *h*-BN and TiB_2, respectively. Interaction occurs at the interface between the molten alloy and BN, leading to the formation of a reaction layer containing TiB and Ti nitrides. Interfacial interaction of Cu50Ti with TiB_2 results in the formation of densely packed TiB layer about 60–100 μm thick and the detachment of TiB_2 grains. Spreading wetting of liquid Cu50Ti on *h*-BN is mainly controlled by the reactions between Ti and BN at the triple line. For Cu50Ti/TiB_2 system, spreading is mainly limited by the interfacial reaction in the first stage, and is possibly influenced by both the diffusion of boron atoms and viscous friction of the liquid in the second stage. Finally, brazing of graphite to CuCrZr alloy has been realized using Cu50TiH_2 with ceramic additives (including BN and TiB_2) as composite fillers. The joints exhibit favorable interfacial bonding between the filler layer and the substrates. The ceramic reinforcements in the filler layer could contribute to the improvement of the shear strength.

1. Introduction

Brazing technology, as one of the most effective joining techniques, has been widely used for the fabrication of ceramic/metal joints. For example, carbon/metal (including graphite/Cu and carbon-carbon composite/Cu-clad Mo) joints have been prepared by brazing for the industry applications [1–3]. However, one of the major issues for brazing ceramics to metals is the existence of large residual stresses, which are mainly generated by the mismatch of coefficient of thermal expansion (CTE) and elastic modulus between the substrates [4,5]. The residual stresses of joints may lead to cracks in the ceramic and even the failure of joints upon cooling from the processing temperature.

The metal interlayers and composite fillers have been introduced to alleviate the residual stresses of the ceramic/metal joints [6–14]. The composite fillers are generally composed of active metal brazes and ceramic reinforcements. The residual stresses of joints may be relaxed by the introduction of ceramic reinforcements with relatively low CTE. In addition, the ceramic additives in the composite fillers are assumed to be distributed uniformly in the filler layer, which can develop the reinforced structure in the joints. Halbig et al. [11] studied the brazing of SiC using Ag–Cu–Ti braze alloys reinforced with SiC particulates. Based on the theoretical calculations, the CTE of the braze with the incorporation of about 45 vol% SiC could decrease by nearly 45–60%. As reported in Ref. [13], the synthesized TiB whiskers contributed to the strength improvement of Al_2O_3/Ti–6Al–4V joints.

It should be noted that the microstructure and properties of the joints may be influenced by the wettability and interactions between liquid metal brazes and ceramic reinforcements. Thus, it is crucial to study the wetting behavior between the metal brazes and ceramic reinforcements prior to the design and preparation of the composite fillers for joining. The reinforcements used in the composite fillers generally include carbides, nitrides, borides, and so on. Among them, BN and TiB_2 ceramics have been used as reinforcements in Refs. [13,14].

Extensive studies have been performed on the wetting of BN by liquid metals [15–22]. Naidich et al. [15] measured the contact angles in the range of 135–150° at 1000–1500 °C for the metals with a negligible (Ag, Sn, Au) or weak (Ge, Ga, Cu) affinity for both N and B, and contact angles lower than 90 ° for ferrous metals. For Al/BN system, nearly perfect wetting is achieved at 1000 °C and a continuous AlN layer is formed at the interface by the reaction between liquid Al and BN [16]. Nicholas et al. [18] studied the wetting of BN by addition of Ti to Cu and Ag–Cu. Very low contact angles were obtained at both 1150 °C and 950 °C. Furthermore, the

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wetting of BN by liquid alloys including Si, Ni–Mo (0–40 wt%), GaSb, InSb, and Al–Si has been reported in Refs. [19–22].

Investigations on the wetting of TiB_2 by liquid metals, including Cu, Au, Ni, Al, Fe and Ti, have been extensively carried out [23–31]. For Cu/TiB_2 system, both wetting and non-wetting contact angles have been reported by different researchers [23]. The molten Cu and Au show a good wetting on non-stoichiometric TiB_2 substrates ($TiB_{1.9}$ and $TiB_{1.95}$). Some limited boride dissolution and alteration of the substrate composition occur at the TiB_x/Cu and TiB_x/Au interfaces [24–26]. In the case of Ni/TiB_2 system [23], TiB_2 is dissolved into the liquid Ni, resulting in a good wetting in either high vacuum or neutral gas environments. Weirauch Jr et al. [27] investigated the wettability of molten aluminum drops on four different types of TiB_2 substrates. The effect of the substrate microstructure on the wetting kinetics has been discussed. Mutale et al. [28] introduced the spreading wetting of TiB_2 substrates by molten aluminum in the temperature range between 660 °C and 760 °C in different fluxes. Ghetta et al. [29] performed the study on the wetting of sintered TiB_2 by pure iron and iron containing dissolved TiB_2. The wetting deteriorated with the increase of oxygen content in the TiB_2 substrates. Xi et al. [30–31] presented a good wetting of molten Al, Ti and Ti–Al alloys on TiB_2. The formation of TiB occurs at the interfaces of Ti/TiB_2 and $Ti_{74.3}Al_{25.7}$/TiB_2.

In this study, the wetting behavior and interfacial interactions of Cu50Ti alloy with *h*-BN and TiB_2 ceramics have been investigated. Such a study can provide a reference for joining graphite to Cu alloys with the composite fillers composed of Cu50Ti metal braze and ceramic reinforcements (including BN and TiB_2).

2. Materials and methods

2.1. Wetting of Cu50Ti alloy on h-BN and TiB_2

Hexagonal BN (*h*-BN) ceramics (Φ 20 mm × 5 mm) with a purity over 99 wt%, and TiB_2 ceramics (20 mm × 20 mm × 3 mm) with 4–5 wt% sintering aid containing Ni, were used as the wetting substrates. Both the *h*-BN and TiB_2 ceramics were supplied from Key Laboratory of Automobile Materials, Jilin University, China. The surfaces of the substrates were mechanically ground and subsequently polished using diamond suspensions.

The Cu50Ti alloy with 50 wt% Ti was prepared from high-purity Cu (99.999 wt%) and Ti (99.995 wt%) plates by arc-melting in a purified Ti-gettered argon atmosphere. The molten alloy was turned in a water-cooled copper crucible and remelted for four times by electromagnetism stirring to ensure a good homogeneity. Then, the alloy was cut into small cubic pieces weighing about 150 mg. The ceramic substrates and the Cu50Ti alloy pieces were ultrasonically cleaned in ethanol prior to wetting tests.

The dispensed drop method is unsuitable in our study because of a severe reaction of the Ti-containing melts with the drop dispenser made of alumina. Accordingly, a modified sessile drop method described elsewhere [32] was adopted. The solid bulk alloy, rather than the liquid alloy droplet, was dropped on the substrate surface from the alumina tube. Fig. 1 gives the schematic of the modified sessile drop method. The distance between the end of the tube and the substrate surface was about 6 mm. The ceramic substrate was placed in the vacuum chamber and kept to a horizontal position, while the Cu50Ti alloy specimen was stored in a stainless-steel tube outside the chamber. The chamber was evacuated to a vacuum about 2×10^{-4} Pa at room temperature, and then heated to the testing temperature of 1000 °C at a rate of 20 °C/min. Then, the solid Cu50Ti alloy was delivered to the surface of the ceramic through an open alumina tube which was connected with the stainless-steel tube. Indeed, the alloy was not melted when it contacted the substrate surface. The melting and

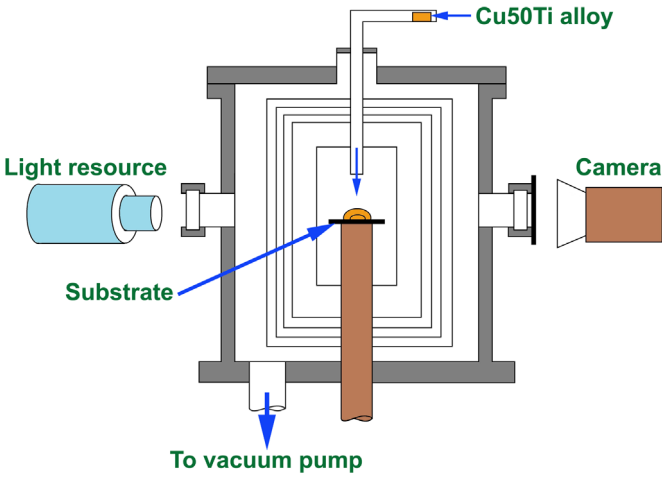

Fig. 1. Schematic of the modified sessile drop method.

spreading processes of the Cu50Ti alloy on the ceramic were monitored by a high-speed CMOS camera (frame rate of 120 fps and resolution of 640 × 480 pixels). The time-dependent variation in contact angle during isothermal wetting at 1000 °C was tracked. Both the contact angle (the error of 0.5°) and drop diameter were measured from the droplet images by using an axisymmetric-drop-shape analysis (ADSA) program.

2.2. Joining of graphite/CuCrZr using composite fillers

The commercial graphite (10 mm × 10 mm × 10 mm) with a density of 1.9 g/cm^3 and purity of 99.99% was purchased from Changsha Aobo Carbon Co., Ltd., China. The commercial CuCrZr alloy (10 mm × 10 mm × 10 mm) with a nominal composition of Cu- (0.4–1) Cr- (0.03–0.15) Zr (in wt%) and a density of 8.9 g/cm^3 was supported from Shenzhen Heshuo Metal Products Co., Ltd, China. Both the graphite and CuCrZr alloy were used as joining substrates. The substrates were polished with 1.0 μm diamond paste and then ultrasonically cleaned in alcohol prior to brazing experiments.

The composite filler was composed of Cu powders, TiH_2 powders (replacement of Ti powders, to avoid the oxidation during the mechanical milling) and ceramic additives. The detailed description of Cu powders and TiH_2 powders could be found in Ref. [33]. BN powders with the size of about 1 μm and purity of 99.0%, and TiB_2 powders with the size of about 3–5 μm and purity of 99.5%, were supported from Qinhuangdao Eno High-Tech Material Development Co., Ltd, China. The powders of Cu, TiH_2 and ceramic additives were mixed together by mechanical milling to obtain Cu50TiH_2+BN (or Cu50TiH_2+TiB_2) composite filler. The weight ratio of Cu and TiH_2 powders was kept at 1:1, and the content of ceramic additives was 2 wt% in the composite filler.

Considering that the melting temperature of the powder filler could be lower than that of bulk alloy, the joining temperature was set at 950 °C (with the holding time of 10 min). The detailed joining procedure and the shear strength measurement of joints were described in Ref. [33].

2.3. Microstructure characterization

The wetting specimens for cross-section view were prepared in an epoxy mount and then polished. The microstructure of the cross-section was characterized by a scanning electron microscope (SEM, Quanta200, Holland) equipped with an energy dispersive X-ray spectrometer (EDS, SDD Inca X-Max50, Holland). The phase identification of interfacial area was determined by an X-ray