High temperature interaction between molten Ni\textsubscript{50}Al\textsubscript{50} alloy and ZrB\textsubscript{2} ultra-high temperature ceramics

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Abstract: In this work, Ni\textsubscript{50}Al\textsubscript{50} alloy is taken into consideration as potential brazing material for joining ZrB\textsubscript{2} ultra-high temperature ceramic. The results of experimental study on high temperature interfacial phenomena between molten binary Ni\textsubscript{50}Al\textsubscript{50} alloy and polycrystalline ZrB\textsubscript{2}, are shown. A sessile drop method combined with a capillary purification procedure was applied to investigate the wetting behavior of Ni\textsubscript{50}Al\textsubscript{50}/ZrB\textsubscript{2} couple during holding for 400 seconds at temperature of 1688°C (i.e. at $T=1.02T_m$). It was found that the molten Ni\textsubscript{50}Al\textsubscript{50} rapidly wets and spreads over the surface of ZrB\textsubscript{2}, while involved reactive infiltration into the solid substrate allowed reaching a final contact angle of $\sim0^\circ$ in 250 sec. The wetting kinetics was much faster than that reported in the literature for Cu, Ag or Au tested at $T=1.05T_m$. The solidified couple was subjected to SEM/EDS microstructural characterization in order to reveal a course of interfacial phenomena. The results point towards (I) an existence of Ni-enriched Ni-Al/ZrB\textsubscript{2} surface interfacial layer; (II) a formation of infiltration zone assisted by reactively formed Al\textsubscript{2}O\textsubscript{3} due to a reaction with Al-rich melt and (III) a partial transfer of ZrB\textsubscript{2} phase to Ni\textsubscript{50}Al\textsubscript{50} alloy by a dissolution/precipitation mechanism.

Keywords: ultra-high-temperature ceramics; zirconium diboride; composites; joining; wettability; Ni-Al alloys

1. Introduction

Transition metals borides (including TaB, HfB\textsubscript{2} or ZrB\textsubscript{2}) with melting points above 3000°C have been identified as promising candidates for ultra-high applications requesting high thermal fluxes and severe surface stresses (e.g. in sharp leading-edge components) [1]. Among these ultra-high-temperature ceramics (UHTCs), a special attention is given to ZrB\textsubscript{2}, due to its relatively low density as compared to other borides, high strength, hardness, thermal
conductivity and corrosion resistance [2]. A crucial aspect regarding practical implementation of ZrB$_2$ ceramic and composites is their joining to similar (ceramic) or dissimilar (metallic) materials. A proper design and thermal management in ultra-high-temperature devices allow introducing metallic brazing materials to join components made of ZrB$_2$. A successful material candidate should possess a high melting point, excellent oxidation resistance and a good thermophysical/chemical compatibility (reflected e.g. by a good wetting and interfacial bonding) with the UHTC. In this regard, various metallic materials have been examined so far including various (Ag,Cu)-(Ti,Zr,Hf) based alloys [3], boron doped amorphous Ni-base brazes [4] (both having liquidus $T_L$~1050-1150°C) or 60Pd-40Ni and 65Pd-35Co based alloys ($T_m$~1219-1238°C) [5]. In terms of materials having higher melting points, Valenza et al. [6] have performed wettability experiments on ZrB$_2$ ceramics by pure Ni, Ni-17B at.%, and Ni-50B at.% at 1500 and 1200°C by the sessile drop technique. Nevertheless, melting temperatures of either pure nickel ($T_m$=1455°C) or Ni-B alloys ($T_m$=1035-1093°C) do not allow reaching operational temperatures above 1500°C. Furthermore, these materials show a rather poor high temperature oxidation resistance. In order to overcome these limitations, we propose to evaluate a binary nickel-aluminum alloy (Ni$_{50}$Al$_{50}$, at%). This so called β-NiAl nickel aluminide exists as the secondary ordered solid solution over the composition range of ~45–60 at% Ni. For strictly stoichiometric composition (50/50) it melts at $T_m$=1638°C [7]. Due to a high thermal stability of a single phase, excellent oxidation resistance, high hardness and elastic modulus, low density (5.9 gcm$^{-3}$) and low price of raw materials, the NiAl nickel aluminides are being considered as candidates for many high temperature applications beyond nickel superalloys abilities [8] and few successful implementations of NiAl intermetallics have been already reached in coatings technologies [9].

In the present work, the Ni$_{50}$Al$_{50}$ alloy is taken into consideration as a potential brazing material for joining the ZrB$_2$ ultra-high temperature ceramic. Therefore, a specific goal of our research is to evaluate a course of high temperature interfacial phenomena (wettability, reactivity and infiltration) between molten Ni$_{50}$Al$_{50}$ alloy and polycrystalline zirconium diboride.
2. Materials and methods

The binary Ni$_{50}$Al$_{50}$ alloy was fabricated by the electric arc melting technique (Buehler Arc Melter MAM-1) by using properly weight mixtures of pure elements. We used the same hot pressed zirconium diboride that in our previous work [10].

The interfacial phenomena between molten Ni$_{50}$Al$_{50}$ alloy and ZrB$_2$ substrate were examined in a sessile drop experiment by using a capillary purification (CP) procedure (Fig. 1). In the CP procedure, the Ni$_{50}$Al$_{50}$ alloy was initially placed in alumina capillary located above the ZrB$_2$ substrate. After that, the experimental chamber was pumped until a vacuum of 10$^{-6}$ mbar was achieved, and then a heating/cooling procedure was initiated. We used a constant heating rate of 15°Cmin$^{-1}$ to reach temperature of 1688°C ($T=1.02T_m$). At $T=500°C$ flowing argon was introduced in order to suppress the evaporation issues. After reaching the final temperature, a drop of molten alloy was squeezed through the capillary, deposited on the ZrB$_2$ substrate, held for 400 seconds and then cooled down to room temperature (at 20°Cmin$^{-1}$). Upon the experiment drop/substrate images were recorded by a high-speed camera at 100 fps. After that, the collected images were used to calculate the wetting kinetic curve (contact angle $\theta$ vs. time) by using dedicated software (Astra2, CNR-ICMATE, Italy [11]) and to compile the movie (Supplementary Material 1). More details on the applied experimental setup, are given elsewhere [12]. The solidified Ni$_{50}$Al$_{50}$/ZrB$_2$ couple was subjected to structural characterization by means of scanning electron microscopy coupled with X-ray energy dispersive spectroscopy (SEM/EDS) by using Hitachi TM3000 microscope and Bruker Quantax 200 analyzer.
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Fig. 1. A schematic drawing of the sessile drop method combined with capillary purification procedure used for the wettability experiment on the Ni$_{50}$Al$_{50}$/ZrB$_2$ system.

3. Results and discussion

The wetting kinetics recorded for the Ni$_{50}$Al$_{50}$/ZrB$_2$ couple is presented in Fig. 2. It is found that just after the drop deposition at 1688°C, molten Ni$_{50}$Al$_{50}$ alloy rapidly wets the surface of ZrB$_2$ ceramic, as it is reflected by contact angle value $\theta$ below 90°. A further holding of the molten drop results in its fast spreading over the ceramics substrate. The contact angle values decreased to $\theta$~25° in around 180 s. In fact, we had to switch to “manual” measurements of contact angle in order to determine very low values obtained after holding time longer than 180 s. Finally, the near zero values of $\theta$, were reached after ~250 s of the experiment. It should be noted that presently obtained contact values at $T=1.02\ T_m$ are definitely lower, while the spreading kinetic is much faster than that reported in the literature [13] for Cu/ZrB$_2$ ($\theta=80°$), Au/ZrB$_2$ ($\theta=34°$) and Ag/ZrB$_2$ ($\theta=153°$) when tested at $T=1.05\ T_m$ for 35-60 minutes.
The results of post-mortem inspections (Fig. 3a) showed that almost whole alloy was infiltrated into the ceramic substrate. The top view SEM/EDS analyzes performed in the vicinity of residual Ni₅₀Al₅₀ alloy (Fig 3b,c) documented the presence of Ni-enriched Ni-Al surface layer and ZrB₂ crystals having hexagonal morphology (Fig. 3c) that we have also identified by using TEM/SAED technique in our previous study on Al/ZrB₂ system [10]. The investigations carried out on the cross-sectioned couple revealed an infiltration zone having a depth of up to 2000 µm (Fig. 4a). The following structural features were recognized: (i) a Ni-enriched surface layer with ZrB₂ needled like crystals (Fig. 4b); and (ii) Al₂O₃ stringers formed along ZrB₂ boundaries and primary pores. Furthermore, we detected a discontinuous interfacial product layer (Fig. 4c, d) in which Al₂O₃, ZrB₂ and another Zr-enriched phase (most probably ZrO₂), were recognized.
Fig. 3. A macroview of the solidified Ni$_{50}$Al$_{50}$/ZrB$_2$ couple (a). The results of top-view SEM/EDS analyzes of the Ni$_{50}$Al$_{50}$/ZrB$_2$ alloy (b, c).

Fig. 4. Low magnification light microscopy image (a) and the results of SEM/EDS studies on the cross-sectioned Ni$_{50}$Al$_{50}$/ZrB$_2$ couple showing identified structural features inside infiltration zone (a); in the residual Ni$_{50}$Al$_{50}$ alloy (b) and at the interface (c).
4. Summary, conclusions and future remarks

The following conclusions are drawn regarding high temperature interfacial phenomena in Ni\textsubscript{50}Al\textsubscript{50}/ZrB\textsubscript{2} system. The Ni\textsubscript{50}Al\textsubscript{50} nickel aluminide shows a very good wetting with hot-sintered ZrB\textsubscript{2} ceramic at temperature of $T=1.02 \ T_m$ (1688°C). The \textit{in-situ} observed contact angles were much lower than that reported for Cu, Ag and Au tested at respective $T=1.05 \ T_m$ temperatures. The presence of ZrB\textsubscript{2} crystals on the surface of solidified alloy and at the alloy/ceramic interface points towards a dissolution/precipitation as the main mechanism of chemical interaction. A primary porosity of ZrB\textsubscript{2} sinter (~6 vol.\%) facilitates a "reactive infiltration" of the melt, that is assisted by a formation of aluminum oxide stringers along grain boundaries (a pre-oxidation of pore walls could be a possible source for oxygen). Consequently, Al is partially "consumed" and Ni-enriched layer is formed on the surface and in the vicinity of Al\textsubscript{2}O\textsubscript{3} particles.

Although a good chemical integrity of Ni\textsubscript{50}Al\textsubscript{50} and ZrB\textsubscript{2} has been observed in the present work, more studies are needed to prove practical usefulness of using Ni\textsubscript{50}Al\textsubscript{50} nickel aluminide as the potential brazing material for UHTCs. In particular, experiments on fully dense ZrB\textsubscript{2} ceramic as well as some joining technological trails ought to be performed and then verified in shear tests.

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