Communication

Effect of Interface Microstructure on Joint Strength of Zirconia/Titanium Alloy Brazed with Amorphous Zr-Ti-Ni-Cu Active Filler Metal

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Received: 12 May 2020; Accepted: 25 May 2020; Published: 28 May 2020

Abstract: Active brazing of zirconia with metallic alloys is a promising method for enhancing the mechanical property of zirconia. However, the brazing process of zirconia and metallic alloys has not been studied in detail because of a limitation in selection of materials and processing conditions. Here, we successfully brazed zirconia with Ti-3Al-2.5V alloy using amorphous Zr_{54}Ti_{22}Ni_{16}Cu_{8} active filler alloy. By manipulating the brazing temperature from 800 °C to 860 °C, a highest strength of ~186 MPa was achieved at 860 °C. Reduced brittle (Zr,Ti)_{2} matrix, ZrO_{2}−X, TiO, and TiO_{2} interlayer play a key role in increasing the joint strength. Our findings will be helpful in developing brazing processes for zirconia and metallic alloys.

Keywords: brazing; active filler metals; zirconia; titanium alloys; Zr-based filler alloys; microstructure

1. Introduction

Zirconia is a very attractive ceramic material because of its high mechanical strength, fracture toughness, corrosion resistance, and biomedical suitability [1]. Despite such excellent advantages, the brittleness of zirconia makes it difficult to fabricate specific shapes or designs for industrial applications. One possible approach for overcoming the brittleness of zirconia is the joining of metals. Among the candidate materials, joining of zirconia with Ti-Al-V metallic alloys is considered an attractive method owing to the potential aerospace applications deriving from the high specific strength and good corrosion resistance of Ti-Al-V alloys [2]. Ti-Al-V alloys also exhibit thermal expansion coefficients (CTE) similar to that of zirconia, enabling joining without interface breakage [3,4].

Brazing using active filler metal is a promising candidate process for heterogeneous ceramic-metal joining, including zirconia and Ti-Al-V alloy joining [5–7]. Active brazing techniques, which use active components such as Zr, Ti, Hf, and Nb show enhanced wettability of filler metal on ceramic and can be used to easily form reaction layers at joining interfaces for high strength [8–10]. Especially, amorphous Zr-Ti-Ni-Cu alloys are emerging as alternative filler metals for the joining of zirconia and Ti-based alloys because of their stability at high temperature and their higher corrosion resistance than those of Al or Ag-based conventional filler alloy [11,12]. In Zr-Ti-Ni-Cu alloys, Ni and Cu act as melting point depressants for low temperature processing; they typically form Ti-based or Zr-based intermetallic compounds (Zr,Ti)_{2}(Cu,Ni), which are brittle phases [13,14]. However, it has only recently
been discovered that the interface reaction of Zr-Ti-Ni-Cu fillers and resulting phases of zirconia and Ti-Al-V alloys allow joining. Investigating the interface microstructure of brazed zirconia and Ti-Al-V is essential because brittle phases exhibit detrimental effects on joint strength.

In this paper, we brazed zirconia with Ti-3Al-2.5V alloy using amorphous Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ filler alloy. Brazing temperature was controlled to manipulating interface microstructure and the effect of microstructure on mechanical strength was evaluated. Especially, the role of diffusive oxygen from zirconia in joining microstructures was systematically studied. To examine the interface microstructure and related diffusion dynamics during brazing, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and element probe micro-analysis (EPMA) were used. Also, the phases formed at the interfaces were revealed by X-ray diffraction (XRD) analysis.

2. Materials and Methods

Zirconia ceramic, partially stabilized by Y$_2$O$_3$, was used and its size was made into a 10 mm $\times$ 10 mm $\times$ 2 mm cube shape. In the case of the Ti-3Al-2.5V alloy, $\Phi$ 20 $\times$ 5 mm Ti alloy plate was produced. Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ atomic percent filler metal was cast into button shapes from 99.9% Zr, Ti, Ni, and Cu by arc-melting under high purity Ar gas (99.99%). To ensure a homogeneous composition of the filler metal, arc re-melting was performed over four times. Using a melt-spinning process, Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ filler metal was made into a thin foil structure of which the dimensions were 70 mm width and 40–50 $\mu$m thickness (Figure 1). XRD analysis clearly demonstrates the amorphous structure of Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ filler alloy fabricated by melt-spinning, indicated by halo pattern. The melting temperature of the filler alloy was characterized using a differential scanning calorimeter (DTA, SDT Q600, TA Instruments, New Castle, DE, USA); results are shown in Table 1.

![X-ray diffraction (XRD) analysis of Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ filler alloy. Inset shows the photograph of the Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ foil.](image)

| Filler Metal (at%) | Chemical Contents (wt%) | Melting Range ($^\circ$C) |
|-------------------|-------------------------|--------------------------|
| Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_8$ | 62.97 | 14.83 | 13.99 | 8.21 | 768 | 786 |

Brazing was performed under $5 \times 10^{-5}$ torr high vacuum pressure by the simple butt joint method, which involves putting the filler alloy between the zirconia and the Ti-3Al-2.5V alloy. To analyze the effect of brazing temperature on the microstructural evolution, processing temperature was verified from 800 $^\circ$C to 860 $^\circ$C, with 20 $^\circ$C steps, and was continuously maintained for 60 min. In the cooling stage, furnace cooling was used to reduce the thermal expansion difference between zirconia and Ti-3Al-2.5V.
To characterize the interface microstructure and the phases after brazing, interface morphology observation was performed via scanning electron microscopy (SEM, JSM5002, JEOL, Tokyo, Japan) and elemental analysis was carried out using energy dispersive X-ray spectroscopy (EDS, JXA-8500F, JEOL, Tokyo, Japan) and an electron probe micro-analyzer (EPMA, JXA-8500F, JEOL, Tokyo, Japan). To measure the joint strength of the brazed specimen, shear stress testing was used with a hydraulic mechanical tester (DTU-900MHN, Daekyung Tech, Incheon, Korea) under 5 × 10⁻⁴/s strain rate. Interface phases after shear stress test was identified via X-ray diffraction (XRD, D8 focus, Bruker, Norfolk, MA, USA) analysis.

3. Results

To optimize the brazing temperature of zirconia and Ti-3Al-2.5V alloy using Zr₅₄Ti₂₂Ni₁₆Cu₈ filler metal, interface microstructures brazed at different temperatures were investigated. Figure 2 shows the back-scattered electron (BSE) images of brazed specimens in the 800 °C to 860 °C temperature range. At low brazing temperature of 800–820 °C, there were three kinds of interface structures formed (Figure 2a,b). At the zirconia side, a ~5 µm thin reaction layer formed, which is shown in dark contrast to the zirconia layer. In the filler metal region, two phases were entwined, divided into bright and dark regions. However, the interface structure brazed at high temperature of 840–860 °C not only shows considerably reduced filler metal region but also a newly formed island-type morphology region (Figure 2c,d). In other words, as brazing temperature increased, the region of the filler metal gradually decreased and the filler alloy phase was differentiated by the changed dissolution and diffusion dynamics of the parent metals and filler alloy.

![Figure 2. Back-scattered electron (BSE) images of ZrO₂/Ti-3Al-2.5V interface microstructures brazed at (a) 800 °C, (b) 820 °C, (c) 840 °C, and (d) 860 °C.](image)

The effect of changed interface microstructure on joint strength was characterized by shear strength measurements. All breakage arose in the zirconia part, not around the brazed region. Figure 3 clearly shows the increased shear strength as the processing temperature increases; the highest shear strength of ~186 MPa is reached at 860 °C. Especially, abrupt increase of shear strength is observed between 840 °C and 860 °C during high temperature brazing. This suggests that the microstructural change observed in Figure 2 is related to the mechanical strength of the brazed joint. To clearly elucidate the effect of microstructural change on the highest mechanical strength, interface phases and diffusion dynamics for the ~860 °C-brazed specimen were further conducted.
Figure 3. Effect of brazing temperature on shear strength of ZrO₂/Ti-3Al-2.5V joints.

4. Discussion

Figure 4 shows a detailed interface phase and schematic illustration of the microstructure formation process for ~860 °C brazing. Generally, phases formed at interfaces are all related with melting, dissolution, and diffusion phenomena between parent materials and filler alloys [15]. Because of the concentration gradient, Zr, Ti, Cu, and Ni diffuse into the parent metal and Ti, Zr, and O from the parent metal reversely penetrate into the filler alloy region. Figure 4a shows the interface layers distinguished from the compositional Z contrast, where five different layers exist. From layers A to E, the composition of each layer was characterized by EDS analysis (Table 2). Based on the compositional differences in the five layers, dissolution and diffusion phenomena are sequentially revealed.

Figure 4. Interface diffusion dynamics between ZrO₂ and Ti-3Al-2.5V during brazing at 860 °C (a) Back-scattered image of interface microstructure after brazing. Schematic illustrations of diffusion processes at (b) initial step, (c) intermediate step, and (d) final step.
Table 2. Chemical compositions (at.%) of various phases shown in Figure 4a.

| Region | Zr  | Ti  | O   | Ni  | Cu  | Al  | V   | Possible Phase                                      |
|--------|-----|-----|-----|-----|-----|-----|-----|---------------------------------------------------|
| A      | 37.66 | 16.54 | 35.36 | 8.45 | 1.82 | 0.17 | -   | ZrO$_{2-x}$, TiO, TiO$_2$, Cu$_2$Ti$_4$O, Ni$_2$Ti$_4$O |
| B      | 40.77 | 25.07 | 8.32 | 17.31 | 7.22 | 0.92 | 0.39 | Zr-Matrix + (Zr, Ti)$_2$(Cu, Ni)                  |
| C      | 41.01 | 48.52 | 6.13 | 1.18 | 2.19 | 0.97 | -   | (Zr, Ti)-Matrix + ZrO$_{2-x}$ + TiO + TiO$_2$        |
| D      | 26.15 | 37.34 | 3.77 | 18.63 | 7.16 | 6.06 | 0.89 | α-Ti-Matrix + (Zr, Ti)$_2$(Cu, Ni)                 |
| E      | 11.97 | 69.74 | 6.14 | 3.66 | 2.61 | 4.54 | 1.35 | acicular Widmanstätten structure                  |

In the first step, the active element Zr from the filler alloy diffused into the zirconia side and reacted with ZrO$_2$ according to the following Equation (1) (Figure 4b).

$$\text{ZrO}_2 + \text{Zr} \rightarrow \text{ZrO}_{2-x} + \text{Zr} (0 < x \leq 0.02),$$

During the forming of non-stoichiometric zirconia, oxygen dissolved into the filler alloy side. Anion defect sites in ZrO$_{2-x}$ lowered the kinetic pathway of oxygen from the parent metal to the filler alloy region [4]. As oxygen dissolved into the Zr-Ti-Ni-Cu filler region, Ti reacted with dissolved oxygen, forming TiO and TiO$_2$ phases. At the same time, in filler alloy region, Ti$_2$Ni or Ti$_2$Cu formed through the eutectoid reaction between Ti and Ni or Cu. In addition, Ti$_2$Ni and Ti$_2$Cu reacted with oxygen, generating oxide phases including Ni$_2$Ti$_4$O and Cu$_2$Ti$_4$O by the following Equations (2) and (3).

$$\text{Ti}_2\text{Ni} + \text{O}_2 \rightarrow \text{Ni}_2\text{Ti}_4\text{O},$$

$$\text{Ti}_2\text{Cu} + \text{O}_2 \rightarrow \text{Cu}_2\text{Ti}_4\text{O}$$

Therefore, layer A comprising ZrO$_{2-x}$, TiO, TiO$_2$, Ni$_2$Ti$_4$O, and Cu$_2$Ti$_4$O was created as a reaction layer on the zirconia side (Figure 4c and Table 2) [16,17]. High resolution SEM analysis supports the formation of several oxide phases in layer A, as shown in Figure 5. Both secondary electron (SE) image and BSE images show contrast difference which could have arisen from compositional difference. In particular, BSE image certainly indicates the compositional Z contrast that existence of several phases are expected. Also, morphological contrast difference observation in SE image implicates non-single phase in layer A.

Figure 5. High resolution scanning electron microscopy (SEM) analysis in reaction layer A. (a) Secondary electron and (b) back-scattered electron images.

After the formation of reaction layer A, oxygen from zirconia side is able to continuously diffuse into the liquid phase of the filler alloy and dissolved. Typically, diffusion length is proportional to...
processing temperature and diffusion coefficient \( D \) is governed by the Arrhenius Equation, indicated by Equations (4) and (5) [18].

\[
D = D_0 \exp \left( \frac{q}{kT} \right), \quad (4)
\]

\[
L \sim \sqrt{Dt} \quad (5)
\]

Accordingly, high temperature brazing of \( \sim 860 \, ^\circ C \) enables oxygen diffusion and oxygen vacancies of \( \text{ZrO}_2-x \) to also cooperate with oxygen diffusion from the zirconia side to the filler alloy. During the cooling stage, dissolved oxygen in the \( \text{Zr-Ti-Ni-Cu} \) filler alloy formed oxide phases mainly composed of \( \text{ZrO}_2-x \) and Ti-based oxide \( \text{TiO} \) or \( \text{TiO}_2 \), shown as layer C (Figure 4d and Table 2).

Owing to the oxygen affinities of Zr and Ti, which are higher than those of Ni and Cu, with values of \( \sim 30 \) at \% solubility at \( \sim 860 \, ^\circ C \), dissolved oxygen selectively reacted with elemental Zr or Ti upon cooling. Meanwhile, remaining liquid phase filler alloy matrix composed of Zr, Ti, Ni, and Cu transformed into brittle (Zr,Ti)_2(Ni,Cu) phases, indicated as layers B and D, through ternary eutectic reaction [19]. Consequently, brittle (Zr,Ti)_2(Ni,Cu) phases were separated into regions B and D by island-type oxide phase formation such as \( \text{ZrO}_2-x \), \( \text{TiO} \), and \( \text{TiO}_2 \) in interlayer C.

At the same time, diffusion phenomena from Ti-3Al-2.5V arises, but not significantly affects the interface phases or reaction owing to the pre-existence of Ti element in the \( \text{Zr}_5 \text{Ti}_{22} \text{Ni}_{16} \text{Cu}_4 \) filler alloy. Because of the Ti diffusion from Ti alloy side, compositional gradient generates between layer B and D, presenting high Ti content in layer D than that of layer B. In addition, diffusion and dissolution of Al and V elements occur from Ti alloy side to filler region, but the amount of diffused elements is too little to form new interface phases or reaction. Exceptionally, Al content of \( \sim 6 \) at \% is observed in layer D, but \( \alpha \)-Ti-Matrix could dissolve \( \sim 10 \) at \% of Al that new phase or reaction is not expected.

Except for oxides and brittle phases, layer E, known as an acicular Widmanstätten structure, also formed as a result of the \( \beta \)-Ti transformation into acicular \( \alpha \)-Ti from dissolution of \( \beta \)-Ti stabilizer Ni or Cu in Ti-alloy during high temperature heat treatment [20]. However, the E layer was found to have similar aspects during both low temperature and high temperature brazing, as shown in Figure 2; thus, it is considered as not affecting the mechanical strength of the joints.

The possible phase candidates expected by EDS analysis were confirmed by XRD analysis in both the zirconia and Ti-alloy sides, which were separated after the mechanical tests. Figure 6a shows the phases formed at the zirconia side, where \( \text{ZrO}_2-x \) from reaction layer A, other oxides and brittle phases were produced. It was expected that \( \text{TiO} \), \( \text{TiO}_2 \), \( \text{Ni}_2 \text{Ti}_4 \text{O} \), and \( \text{Cu}_2 \text{Ti}_4 \text{O} \) phases would be detected from reaction layer A on the zirconia side. Brittle (Zr,Ti)_2(Ni,Cu) phase is confirmed on both the zirconia and Ti-alloy sides (Figure 6b). Oxide phases such as \( \text{ZrO}_2-x \) and \( \text{TiO}_2 \) shown on the Ti-alloy side may be from the island-type layer C. Small portions of \( \text{Ni}_2 \text{Ti}_4 \text{O} \) and \( \text{Cu}_2 \text{Ti}_4 \text{O} \) on the Ti-alloy side may have appeared from layer A. In other words, all interface phases from layers A to E, resulting from brazing at \( \sim 860 \, ^\circ C \), were identified.

**Figure 6.** X-ray diffraction (XRD) analysis of (a) \( \text{ZrO}_2 \) side and (b) Ti-3Al-2.5V.
To verify the diffusion dynamics shown in the interface microstructure brazed at ~860 °C, elemental mapping by EPMA was additionally carried out (Figure 7). EPMA data clearly show the resulting elemental distribution by diffusion. As shown in Figure 4, oxide layers from reaction layer A and interstitial island layer C are both present in the oxygen element mapping. Island type layer C is mainly composed of Ti, Zr, and O, but Ni and Cu are excluded. However, the brittle (Zr,Ti)$_2$(Ni,Cu) layers B and D mostly do not contain oxygen components. This distinctive elemental distribution and morphology demonstrates the (Zr,Ti) matrix, ZrO$_{2-x}$, TiO, and TiO$_2$ phase segregation from the (Zr,Ti)$_2$(Ni,Cu) matrix and implies the areal reduction of brittle (Zr,Ti)$_2$(Ni,Cu) phase. As can be seen in Figure 2, because of the long diffusion length of oxygen at high temperature, only high temperature brazing from 840~860 °C leads to island phases of oxide layer C. Thus, it is considered that high joint strength of ~186 MPa results from island-type oxide phase formation at high temperature brazing, induced by reduction of (Zr,Ti)$_2$(Ni,Cu) brittle phases.

![Elemental mapping](image)

**Figure 7.** Two-dimensional elemental mapping of ZrO$_2$/Ti-3Al-2.5V interface microstructure after brazing at 860 °C.

5. Conclusions

We successfully brazed zirconia and Ti-3Al-2.5V using Zr$_{54}$Ti$_{22}$Ni$_{16}$Cu$_{6.8}$ filler alloy. By investigating the effects of the brazing temperature on the interface microstructure and mechanical strength of the joints, the relationship between the highest ~186 MPa shear strength of the joints and the microstructure phases brazed at 860 °C was demonstrated. From dissolution and diffusion of oxygen from the zirconia side, ZrO$_{2-x}$, TiO, TiO$_2$, Ni$_2$Ti$_4$O, and Cu$_2$Ti$_4$O oxide phases initially formed as a reaction layer on the zirconia side. Furthermore, continuously diffused oxygen produced island-type (Zr, Ti) matrix, ZrO$_{2-x}$, TiO, and TiO$_2$ phases in the brittle (Zr,Ti)$_2$(Ni,Cu) matrix. As a result, the thickness of the brittle (Zr,Ti)$_2$(Ni,Cu) phase was significantly reduced and high joint strength was
obtained. Our findings suggest key information for controlling the interface microstructure in brazing of zirconia and Ti-3Al-2.5V using Zr-Ti-Ni-Cu active filler alloys.

Author Contributions: Conceptualization, S.W.P. and H.L.; performance of brazing, microstructure and XRD analysis, S.W.P.; mechanical test and analysis, K.I.K.; data curation, B.H.L and T.H.K.; writing—original draft preparation, H.L.; writing—review and editing, H.L.; visualization, S.A.H. and M.K.; supervision and funding acquisition, K.T.K.; project administration, S.-K.H., G.H.R., and K.T.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Ansan-Si hidden champion fostering and supporting funded by Ansan city.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Hanson, W.; Ironside, K.; Fernie, J. Active metal brazing of zirconia. Acta Mater. 2000, 48, 4673–4676. [CrossRef]
2. Alhazaa, A.; Khan, T. Diffusion bonding of Al7075 to Ti-6Al-4V using Cu coatings and Sn-3.6 Ag-1Cu interlayers. J. Alloys Compd. 2010, 494, 351–358. [CrossRef]
3. Pimenta, J.S.; Buschinelli, A.J.; do Nascimento, R.M.; Martinelli, A.E.; Remmel, J. Brazing of metals to zirconia mechanically metallized with titanium. J. Braz. Soc. Mech. Sci. Eng. 2010, 32, 468–474. [CrossRef]
4. Singh, M.; Shpargel, T.; Asthana, R. Brazing of stainless steel to yttria-stabilized zirconia using gold-based brazes for solid oxide fuel cell applications. Int. J. Appl. Ceram. Technol. 2007, 4, 119–133. [CrossRef]
5. Fiorentini, V.; Gulleri, G. Theoretical evaluation of zirconia and hafnia as gate oxides for Si microelectronics. Phys. Rev. Lett. 2002, 89, 266101. [CrossRef] [PubMed]
6. Pimenta, J.S.; Buschinelli, A.J.; Nascimento, R.M.d.; Martinelli, A.E.; Remmel, J. Brazing of zirconia to titanium using Ag-Cu and Au-Ni filler alloys. Soldag. & Insp. 2013, 18, 349–357.
7. Liu, Y.; Hu, J.; Shen, P.; Guo, Z.; Liu, H. Effects of fabrication parameters on interface of zirconia and Ti-6Al-4V joints using Zr 55 Cu 30 Al 10 Ni 5 amorphous filler. J. Mater. Eng. Perform. 2013, 22, 2602–2609. [CrossRef]
8. Smorygo, O.; Kim, J.; Kim, M.; Eom, T. Evolution of the interlayer microstructure and the fracture modes of the zirconia/Cu–Ag–Ti filler/Ti active brazing joints. Mater. Lett. 2007, 61, 613–616. [CrossRef]
9. Durov, A.; Naidich, Y.V.; Kostyk, B. Investigation of interaction of metal melts and zirconia. J. Mater. Sci. 2005, 40, 2173–2178. [CrossRef]
10. Guedes, A.; Pinto, A.M.P. Active metal brazing of machinable aluminum nitride-based ceramic to stainless steel. J. Mater. Eng. Perform. 2012, 21, 671–677. [CrossRef]
11. Singh, M.; Asthana, R.; Shpargel, T. Brazing of ceramic-matrix composites to Ti and Hastealloy using Ni-base metallic glass interlayers. Mater. Sci. Eng. A 2008, 498, 19–30. [CrossRef]
12. Singh, M.; Asthana, R. Joining of zirconium diboride-based ultra high-temperature ceramic composites using metallic glass interlayers. Mater. Sci. Eng. A 2007, 460, 15–162. [CrossRef]
13. Sun, J.-H.; Lee, D.-M.; Lee, C.-H.; Hong, J.-W.; Shin, S.-Y. A novel Zr-Ti-Ni-Cu eutectic system with low melting temperature for the brazing of titanium alloys near 800 °C. J. Mater. Res. 2010, 25, 296–302. [CrossRef]
14. Lee, D.; Sun, J.; Kang, D.; Shin, S.; Hong, J. Microstructural evolution of the Interface between pure titanium and low melting point Zr-Ti-Ni (Cu) filler metals. Metall. Mater. Trans. A 2014, 45, 5914–5922. [CrossRef]
15. Zhang, X.; Shi, Y. A dissolution model of base metal in liquid brazing filler metal during high temperature brazing. Scr. Mater. 2004, 50, 1003–1006. [CrossRef]
16. Botstein, O.; Rabinkin, A. Brazing of titanium-based alloys with amorphous 25wt.% Ti-25wt.% Zr-50wt.% Cu filler metal. Mater. Sci. Eng. A 1994, 188, 305–315. [CrossRef]
17. Liu, Y.; Hu, J.; Zhang, Y.; Guo, Z. Interface microstructure of the brazed zirconia and Ti-6Al-4V using Ti-based amorphous filler. Sci. Sinter. 2013, 45, 313–321. [CrossRef]
18. Song, J.; Yu, J.; Lee, T. Effects of reactive diffusion on stress evolution in Cu-Sn films. Scr. Mater. 2004, 51, 167–170. [CrossRef]
19. Yang, M.; Lin, T.; He, P.; Huang, Y. In situ synthesis of TiB whisker reinforcements in the joints of Al2O3/TC4 during brazing. *Mater. Sci. Eng. A* **2011**, *528*, 3520–3525. [CrossRef]

20. Chang, C.; Yeh, T.; Shiue, R.; Chang, C. Microstructural Evolution of Infrared Brazed CP-Ti Using Ti-Cu-Ni Brazes. *J. Mater. Sci. Technol.* **2011**, *27*, 131–138. [CrossRef]

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