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Solid state bonding of beryllium to copper and vanadium using transition layers

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Abstract

Beryllium is a material under consideration for divertor surfaces in the international thermonuclear experimental reactor (ITER). Since Be itself is not a suitable structural material for constructing the divertor, it needs to be bonded to other materials with sufficiently high thermal conductivity, which at the same time satisfy structural requirements such as adequate strength and fracture toughness. Bonding of Be to other materials is usually accompanied by (a) mismatches in thermal expansion and/or (b) metallurgical incompatibilities. In an attempt to minimize the thermal expansion mismatch we employed Fe or Ni transition layers for the bonding of Be to a copper alloy by hot isostatic pressing. To alleviate the thermodynamic incompatibility between Be and most other metals, thin Ag foil (130 μm) was used as a reaction barrier. Other experiments involved bonding Be (via an Ag reaction barrier) to a V–5Cr–5Ti (wt%) alloy. An Al–Be transition layer for bonding Be to a copper alloy was also explored. The microstructures of the interfaces were examined by optical and scanning electron microscopy. Shear tests carried out with Cu/Fe/Ag/Be and V/Ag/Be specimens indicated average room temperature shear strengths of 52 and 78 MPa, respectively. Fracture occurred usually at the Ag/Be interfaces, which were therefore the weakest link in the bonded specimens. © 1997 Elsevier Science B.V.

1. Introduction

Beryllium is a material under consideration for divertor surfaces in the international thermonuclear experimental reactor (ITER) [1–6]. Among the advantages of Be are its compatibility with plasma environments and its high thermal conductivity. Since Be itself is not a suitable structural material for constructing the divertor, it needs to be bonded to other materials which at the same time satisfy certain requirements such as adequate thermal conductivity, strength and fracture toughness.

The bonding of Be to other materials is often accompanied by mismatches in the thermal expansion and by thermodynamic incompatibilities. These problems have been outlined in a workshop on beryllium technology [5,6], and in a recent review of joining techniques for plasma facing components in fusion reactors [7]. Two important issues are the formation of brittle copper beryllides on the one hand, and, if an Ag reaction barrier layer or Ag-based braze is employed, the transmutation in the reactor of Ag into Cd. In particular, if the Cd finds its way into the plasma, it would exceed the maximum allowable concentration within a few minutes [7]. In an attempt to solve the embrittlement issue, Araki et al. [8] recently deposited thin (15 μm) Cr and Ni layers on copper substrates in order to inhibit diffusion of Cu into the Be tiles brazed onto the substrate. Electron microprobe analysis showed, however, that Cu diffused through the braze into the Be, resulting in brittle Be–Cu intermetallics at the interface between the braze and the Be. Also, although the transmutation of Ag into Cd is a very serious issue, Araki et al. [8] as well as Chaumat et al. [9] use Ag-based brazes for attaching Be or carbon fiber composite tiles, respectively, to Cu. Therefore, since a successful substitute for Ag-based brazes or reaction barriers does not appear to have been found to

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date, the use of Ag in the present work is justified, in spite of the serious limitations of Ag.

In the present work, an attempt has been made to minimize the thermal mismatch by employing Ni or Fe transition layers, while at the same time avoiding the formation of brittle intermetallic compounds by a thin Ag reaction barrier. In additional exploratory experiments, Be was bonded, again with a thin Ag reaction barrier, to a V–5Cr–5Ti (wt%) alloy, and, via a transition Al–Be layer, to Cu.

2. Materials selection

2.1. Thermodynamic considerations

When Be is heated in contact with other metals, brittle intermetallic compounds form in most cases. Al is an exception to this rule, as it forms no intermetallic phases with Be. Ag and Be also form no intermetallic phases as long as the temperature is below 1033 K (above 1033 K, a C15 Laves phase ($AgBe_2$) forms). Therefore, in joining Be to other metals, thin Ag layers may be employed as reaction barriers in order to avoid the formation of brittle beryllides.

2.2. Thermal expansion considerations

Fig. 1 compares the thermal expansions of Be and several other materials [10,11]. Cu exhibits a significantly higher thermal expansion than Be. In joining Be directly to Cu, one faces therefore not only the problem of the formation of brittle beryllides, but also a distinct CTE mismatch. This is particularly problematic since Be is itself a relatively brittle material. In contrast to Cu, the thermal expansions of Fe and Ni are quite similar to those of Be in the temperature range 300–800 K. With respect to the CTE mismatch, Ni and Fe are therefore well suited for bonding to Be. In view of their low thermal conductivities, they may only be used as relatively thin transition layers for bonding to a highly conducting Cu substrate. Also, since both Ni and Fe form brittle intermetallics with Be, some type of reaction barrier would be needed. The bonding of the ductile materials Fe and Ni to Cu is not as difficult a problem as that of bonding Be directly to Cu.

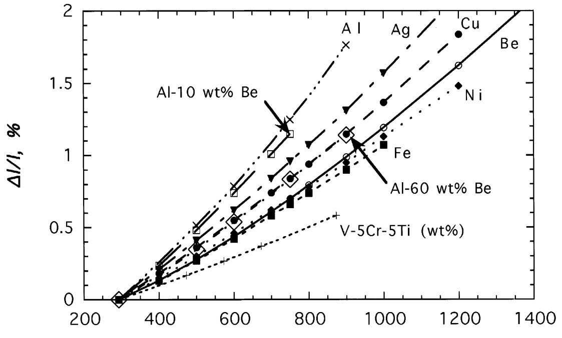

Fig. 1. Thermal expansions of the materials investigated in this study.

Because vanadium alloys are being considered as a structural material for fusion power systems, bonding of Be to V is of interest. Candidate alloys such as V–(4–5)Cr–(4–5)Ti (wt%) have a significantly lower thermal expansion than Be (Fig. 1). In spite of this drawback, an exploratory experiment, in which Be was bonded to a V–5Cr–5Ti alloy via an Ag reaction barrier, was carried out.

By building up, on a Be substrate, Be–Al alloys with continuously increasing Al concentration, one might in principle create graded layers in which the CTE is gradually raised from that of Be to that of Cu or Al. For reference, the thermal expansions of pure Al and several Al–Be alloys are compared to those of pure Al in Fig. 1. The data show that in order to join Be to a Cu substrate, the composition would have to be graded from that of pure Be to Al–60 wt% Be.

3. Experimental procedure

The coupons prepared in this study are shown schematically in Fig. 2. Nominally pure powder-metallurgical Be, as well as nominally pure Ag, Cu–0.65Cr–0.1Zr (wt%)

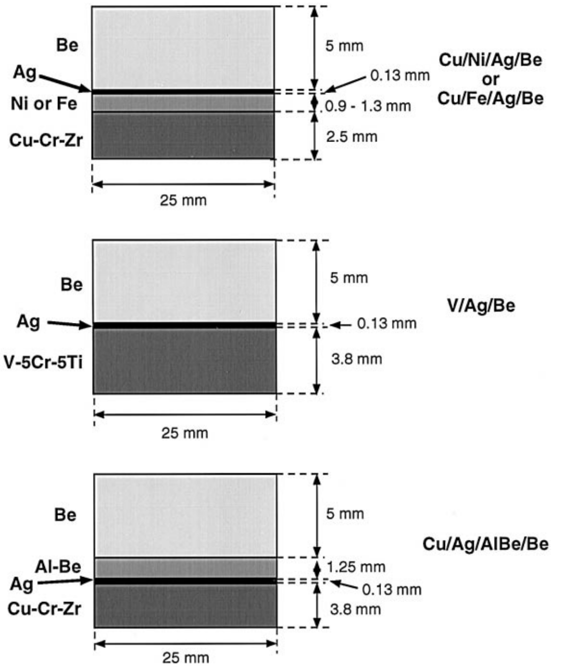

Fig. 2. Schematic diagrams of the fabricated specimens.

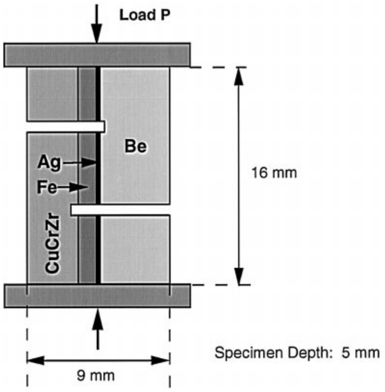

Fig. 3. Schematic of Cu/Fe/Ag/Be simple shear specimen.

(ELBRODUR G, courtesy KM-Kabelmetal America Inc.), Ni, Fe, and V–5Cr–5Ti (wt%), were used as raw materials. The different materials were cut into discs with diameters of 25 mm and degreased. The vanadium was cleaned by etching for 300 s in a solution of 30% HNO_3, 10% HF, and 60% H_2O, by volume. The Be was cleaned with a household cleaner (409) and a soft bristle brush. It was then rinsed in water, further cleaned with a scouring powder (Comet) and a sponge, and rinsed again in water. The discs were then assembled according to the schematic in Fig. 2, and inserted into 304L stainless steel cans. These cans were subsequently evacuated and sealed by welding. Several Be disks were plasma sprayed in argon with a mixture of Be and Al powders up to a deposit thickness of approximately 1.5 mm, assembled according to Fig. 2, and also encapsulated. In this experiment it was attempted to grade the Al–Be layer from pure Be to Al–60wt%Be. However, the compositional control was inadequate and the actual Be concentration turned out to be much lower than 60 wt%, as will be discussed later. The Cu/Fe/Ag/Be, Cu/Ni/Ag/Be, and V/Ag/Be specimens were hot isostatically pressed (HIPed) for approximately 0.5 h at 1035 K and 110 MPa. The Cu/Ag/AlBe/Be specimens (where AlBe indicates the Al–Be transition layer) were HIPed for a similar time and pressure, but at a lower temperature of 800 K. The HIP cans were subsequently machined off. Several coupons were sectioned, polished perpendicular to the bonded interfaces and examined by optical and scanning electron microscopy. Specimens designed for simple shear testing (see Fig. 3) were machined. This technique has been successfully used in the shear testing of lamellar eutectics [12] and NiAl single crystals [13]. The shear specimens were tested in compression between parallel platens at room temperature. The notch depth in each specimen was chosen such that during testing all its interfaces were subject to the same nominal shear stress. The shear strength was calculated from the load at which final fracture occurred, and the area subject to the applied shear stress. The Cu/Ni/Ag/Be and Cu/Ag/AlBe/Be coupons delaminated during machining into shear specimens and could therefore not be mechanically tested. The fracture surfaces of the broken specimens were inspected visually and by scanning electron microscopy (SEM) coupled with energy dispersive analysis (EDS).

4. Experimental results

4.1. Metallography of cross-sections through interfaces

Optical and scanning electron microscopy of the Cu/Ni/Ag/Be and Cu/Fe/Ag/Be specimens did not show evidence of a reaction at the Ag/Be interfaces. This is illustrated by the backscattered electron SEM of a cross-section through Cu/Fe/Ag/Be shown in Fig. 4. Spot analyses in the Be 2 μm away from the interface did not show a significant silver concentration. Likewise, the Ag concentration in the Ag region, 2 μm away from the Ag/Be interface, was identical to that of bulk silver. These findings are consistent with the low mutual solubility of Ag and Be. However, since the HIPing temperature was at the temperature around which the $AgBe_2$ Laves phase forms, the presence of a submicron intermetallic layer cannot be ruled out entirely. In the Cu/Ni/Ag/Be coupon, several cracked regions were found in the Be as illustrated by Fig. 5. These cracked regions probably contributed to the problems encountered during the machining of this material. Although cracks were also found in the Cu/Fe/Ag/Be material, they were far smaller in number.

Consistent with the low mutual solid solubility of Cu and Fe, and the absence of intermetallic compounds in this system, no interfacial diffusion layer was found at the

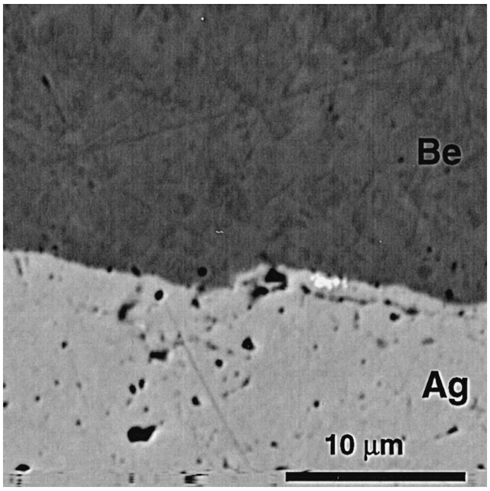

Fig. 4. Backscattered SEM micrograph of metallographic section through Ag/Be interface.

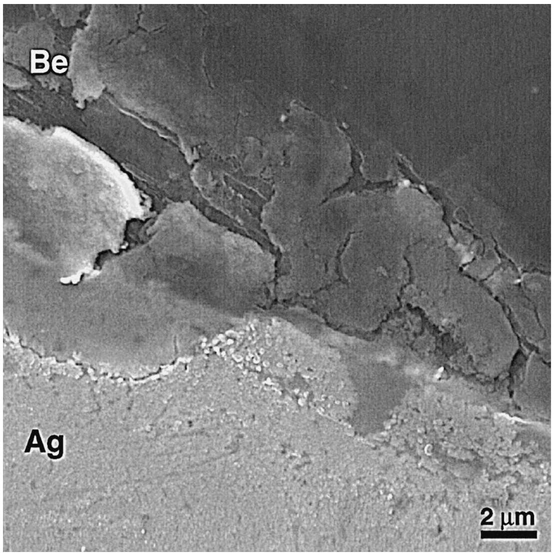

Fig. 5. SEM micrograph of polished cross-section of a Cu/Ni/Ag/Be specimen, showing cracks in the Be at the Ag/Be interface.

Cu/Fe interfaces (within the spatial resolution of the EDS system of approximately 1 µm). The Cu/Ni interfaces, on the other hand, showed an approximately 10 µm wide interdiffusion zone. Such an interdiffusion layer is expected, since Cu and Ni are fully miscible in the solid state.

In the V/Ag/Be specimen, SEM-EDS did not show any evidence (within the spatial resolution of approximately 1 µm) of a reaction between the Ag reaction barrier and the V–5Cr–5Ti alloy, respectively. Again, a few cracks were found in the Be adjacent to the Ag.

In the Cu/Ag/AlBe/Be specimens, the target composition of Al–60wt%Be was not reached. Quantitative image analysis of the Al–Be region showed the volume f

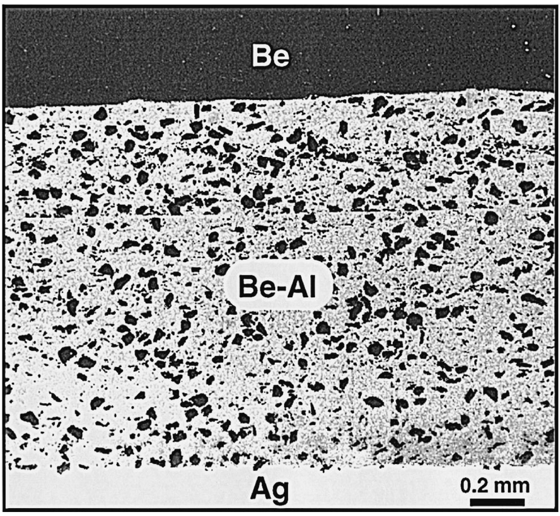

Fig. 6. SEM micrograph of Be–Al transition layer

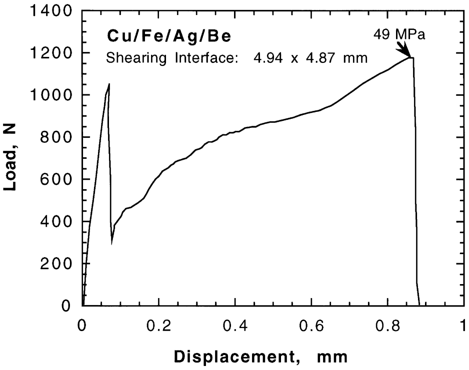

Fig. 7. Load-displacement curve for Cu/Fe/Ag/Be simple shear specimen

graded, but to be almost uniform with an average value of 21 vol% (15 wt%). Fig. 6 depicts the microstructure of the plasma-sprayed and HIPed Al–Be. No reaction zone was found at the Cu/Ag interlayer, since the mutual solid solubility in the Cu–Ag system is small. At the interface between the Ag and the AlBe plasma-sprayed layer, a 30 µm wide Ag–Al interdiffusion layer containing occasional cracks was observed. This interdiffusion layer contained presumably the δ-phase (≈ Al–30at%Ag) and the µ-phase (≈ Al–22at%Ag). The metallographic specimen exhibited a narrow crack at the boundary between the interdiffusion layer and the pure Ag, indicating this interface to be a weak link. As stated before, shear specimens could not be fabricated from the Cu/Ag/AlBe/Be coupons.

4.2. Shear strengths

The load-displacement curves of the shear specimens typically reached a maximum, after which the load fell suddenly and substantially. In most cases, the load increased again during further deformation, as illustrated in Fig. 7. Prior to reaching the first load drop, a small amount of yielding (corresponding to a crosshead displacement on the order of 10 to 20 µm) was usually observed. This indicates a small amount of ductility prior to the beginning of interfacial fracture. The measured shear strengths were evaluated from that load after which a substantial drop occurred and are summarized in Table 1.

Table 1
Room temperature shear strengths

Specimen	Shear strength (MPa)
Cu/Fe/Ag/Be	49
Cu/Fe/Ag/Be	55
V/Ag/Be	77
V/Ag/Be	78

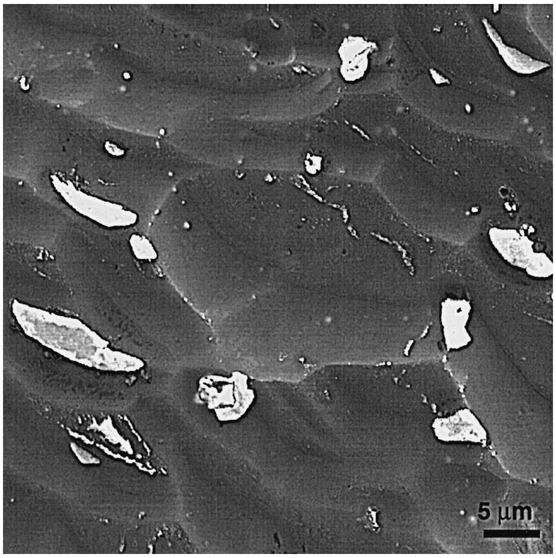

Fig. 8. SEM micrograph of Be fracture surface of Cu/Fe/Ag/Be specimen.

4.3. Fractography

The Cu/Ni/Ag/Be, Cu/Fe/Ag/Be, and V/Ag/Be specimens all fractured along the Ag/Be interfaces. Fig. 8 gives an example of the Be side of the fracture surface of a Cu/Fe/Ag/Be specimen. The ridge-like features on this fracture surface correspond presumably to the grain boundaries of the Be. Small silver particles adhered to the Be. The corresponding Ag fracture surface was essentially a replica of the Be surface.

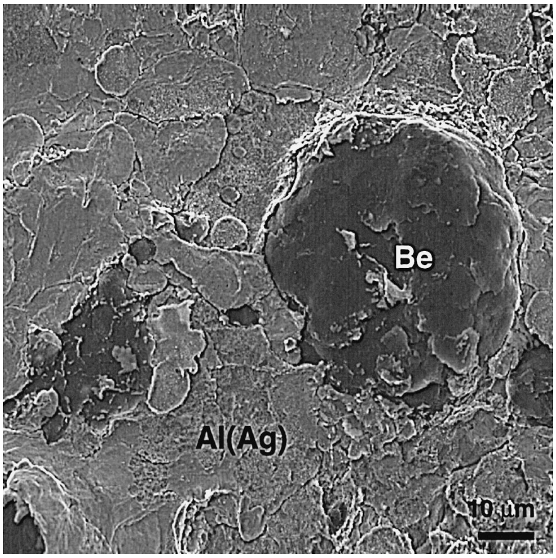

Fig. 9. SEM micrograph of fracture surface of Cu/Ag/AlBe/Be specimen. Fracture occurred along the Ag–AlBe interface, and the AlBe side is shown.

The Cu/Ag/AlBe/Be specimens fractured at the interface between the Ag and the AgAl interdiffusion layer, which formed between the Ag and the plasma-sprayed Al–Be. The fracture surface shown in Fig. 9 consists primarily of Al with Al–Mg intermetallic precipitates (which are not visible at the magnification of Fig. 9). Embedded Be particles protrude from the AgAl fracture surface. Among the reasons for the poor mechanical integrity of the Cu/Ag/AlBe/Be coupons are the presumably brittle AgAl intermetallic precipitates and the high internal stresses expected because of the insufficient Be content (approximately 15 wt%) of the Al–Be transition layer (compare Fig. 1).

5. Discussion

In the following, we compare our results to several recent reports on joining Be to various substrates. Franconi et al. [1] joined Be to AISI 316 stainless steel or copper by brazing with an Ag–Cu eutectic alloy. They also investigated a hot-pressing technique in which a Cu substrate was coated with a 10 μm Ag layer. Ultrasonic testing demonstrated that sound joints could be obtained. However, no mechanical properties were determined. Barabash et al. [2] produced direct Cu/Be bonds by diffusion bonding in vacuum at 1073–1123 K and 30–50 MPa. During the holding time of 5 min at 1073–1123 K, a 250 μm thick interdiffusion layer consisting of 4 distinct transition zones developed. In particular, a 10 μm thick layer of copper beryllides with a high hardness formed. By tensile testing of Be strips bonded together over part of their length, the ultimate shear strength of these bonds was determined to be 50 MPa. The interface at which fracture occurred was not identified. Gervash et al. [14] explored several techniques for bonding Be to Cu or Cu alloys. One of these techniques was direct (i.e., without a reaction barrier or compliant layer) diffusion bonding between Be and a CuCrZr alloy. They tested two specimens, which had shear strengths of 43 and 103 MPa, respectively. Although there was a $\cong 10$ μm thick intermetallic layer, fracture occurred in both cases in the Be itself. Joints fabricated by brazing with an Ag-based braze reached shear strengths of 115 MPa, and Cu/Be joints fabricated by joint rolling exhibited a shear strength of 130 MPa. Bartlett and Castro [4] employed plasma spraying to first put down a thin (50–100 μm) reaction barrier layer of W, V, or Ti, and then about 10 mm of Be. They measured interfacial fracture toughness ranging from 3 to 4 MPa $m^{1/2}$. They presented, however, no shear strength data.

In our work with Cu/Fe/Ag/Be and V/Ag/Be we obtain shear strengths that are in line with previously published work. A small amount of plastic deformation was observed prior to the first load drop during deformation. Since the yield strengths of the CuCrZr alloy and of the V–5Cr–5Ti alloy are ≥ 270 MPa[15] and 430 MPa [16], the plastic deformation occurred most likely in the Ag and/or Fe, which exhibit yield strengths around 50 MPa [17]. Further analysis of shear specimens would be required to substantiate this claim. The formation of brittle Be–Cu intermetallic phases was successfully avoided by a thin Ag reaction barrier. Fracture occurred usually at the Ag–Be interface. Several reasons may be responsible for this fracture location. First, the maximum HIPing temperature was in the vicinity of 1033 K, above which the brittle Laves phase $AgBe_2$ forms. SEM analysis did not show any evidence for this phase, but the presence of a submicron layer cannot be ruled out. Second, interfacial oxides of Be cannot be completely ruled out. Third, although the CTE mismatch between Be and Ni, or Be and Fe, respectively, is low, Ag has a much higher CTE than any of these materials. Therefore, it must have undergone significant tensile deformation during cool down from the HIPing temperature. A much thinner Ag layer might alleviate this problem and might result in shear strengths closer to those obtained by Gervash et al. for brazed joints. Fourth, the presence of segregants at the Ag/Be interfaces leading to embrittlement cannot be ruled out from the present experiments.

It is also not clear why the Cu/Fe/Ag/Be coupons, as well as the Cu/Ni/Ag/Be coupons (which disintegrated during machining), exhibited cracks in the Be adjacent to the Ag reaction barrier. During the HIPing operation, the pressure was increased as the specimens were heated up. Possibly, the Be was pressed against the substrate at a temperature too low for the Be to be sufficiently ductile to survive this processing step. More careful control of the HIPing process might alleviate this problem.

It is interesting to note that the V/Ag/Be specimens showed a higher shear stress than the Cu/Fe/Ag/Be specimens, although the CTE mismatch between the V alloy and the Be is much higher than that between Fe and Be. This means that there are other parameters besides the thermal expansion mismatch that need to be controlled. In thermal cycling conditions, CTE matching may however be more important than in the present work, in which only static strengths were measured.

The poor mechanical properties of the Cu/Ag/AlBe/Be coupon are not surprising in view of the lower than planned Be content of the AlBe transition layer and the severe reaction between the Al and the Ag. Better results might be obtained with continuously graded Be contents reaching 60 wt%.

If small amounts of Ag are considered tolerable in divertor applications, the present experiments suggest that future work should focus on the strength and chemical composition of the Ag/Be interfaces, as well as elimination of cracking in the Be. Much higher shear strengths than those found in this work may then be possible. Alternatively, the Cu/AlBe/Be system could be examined more closely.

6. Conclusions

In this work we have shown that shear strengths as high as 78 MPa may be achieved when bonding Be to other materials in the solid state. Attempts have been made to minimize the CTE mismatch between Be and the other materials, and to avoid thermodynamic incompatibilities by employing Ag reaction barrier layers. Shear strength measurements suggested that minimum CTE mismatch is not necessarily associated with maximum interfacial shear strength. It was found that the Ag/Be interfaces were usually the weakest link in fracture. Further research should focus on the Ag/Be interfaces or, alternatively, on graded AlBe layers.

Acknowledgements

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References

[1] E. Franconi, G.C. Ceccotti, L. Magnoli, J. Nucl. Mater. 191–194 (1992) 493.
[2] V.R. Barabash, L.S. Gitarsky, G.S. Ignakovskaya, Yu.G. Prokofiev, J. Nucl. Mater. 212–215 (1994) 1604.
[3] R.G. Castro, P.W. Stanek, K.E. Elliott, J.D. Cotton, R.D. Watson, J. Nucl. Mater. 226 (1995) 170.
[4] A.H. Bartlett, R.G. Castro, in: C. Briant, C. B. Carter, E. Hall (Eds.), Interfacial Engineering for Optimized Properties, Proceedings of MRS Fall Meeting 1996, vol. 458, MRS, Pittsburgh, PA, to be published.
[5] G.L. Longhurst, A. Gervash, M. Dalle Donne, J.E. Hanafee, R.D. Watson, H. Kawamura, D.M. Dombrowski, Fusion Technol. 29 (1996) 409.
[6] G.R. Longhurst (Ed.), Proceedings 2nd IEA International Workshop on Beryllium Technology for Fusion, September 6–8, 1995, Jackson Lake Lodge, Wyoming, Lockheed Martin Idaho Technologies, Idaho Falls, CONF-9509218.
[7] B.C. Odegard, B.A. Kalin, J. Nucl. Mater. 233–237 (1996) 44.
[8] M. Araki, D.L. Youchison, M. Akiba, R.D. Watson, K. Sato, S. Suzuki, J. Nucl. Mater. 233–237 (1996) 632.
[9] G. Chaumat, P. Le Gallo, G. Le Marois, F. Moret, P. Deschamp, J. Nucl. Mater. 233–237 (1996) 932.
[10] Y.S. Touloukian, R.K. Kirby, R.E. Taylor, P.D. Desai, Thermophysical Properties of Matter, vol. 12, Plenum Press, New York, 1975.
[11] W.D. Porter, R.B. Dinwiddie, M.L. Grossbeck, Fusion Materials, Semiannual Progress Report for Period ending March 31, 1994, DOE/ER-0313/16.

[12] M. Ignat, S. Kaddour, M. Dupeux, J. Phys. 46 (1985) 651.

[13] A.J. Duncan, M.J. Kaufman, J.H. Schneibel, Scr. Metall. Mater. 31 (1994) 105.

[14] A.A. Gervash, R.N. Giniatouline, I.V. Mazul, A.A. Ganenko, L.S. Gitarskij, V.S. Sizenev, D.A. Davydov, in: G.R. Longhurst (Ed.), Proceedings 2nd IEA International Workshop on Beryllium Technology for Fusion, September 6–8, 1995, Jackson Lake Lodge, Wyoming, Lockheed Martin Idaho Technologies, Idaho Falls, CONF-9509218, pp. 364–380.

[15] Manufacturer’s information, KM-Kabelmetal America Inc., Oak Brook, IL.

[16] B.A. Loomis, L.J. Nowicki, D.L. Smith, J. Nucl. Mater. 215 (1994) 790.

[17] M.F. Ashby, D.R.H. Jones, Engineering Materials, Pergamon, Oxford, UK, 1980.