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Diffusion bonding of beryllium–copper alloys

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A process has been developed for diffusion-bonding identical beryllium–copper alloy, 1.8 to 2.0 wt% Be, which has produced bond strengths comparable to that of the bulk. Bonding resulted from self-diffusion between two Be–Cu samples, brought into intimate contact and heated in a high vacuum. Metallurgical analyses of the diffusion bonds revealed the bond interface to be a continuous high-angle planar boundary. The analyses also revealed that oxides were present at the interface after bonding. The agreement between the experimental results and a theoretical model for diffusion-bonding of pure copper, derived by Hill and Wallach, was good.

1. Introduction

Beryllium–copper is a high-strength precipitation-hardenable alloy that has many diverse uses, such as springs, diaphragms, electrical contacts, bearings, and various mould inserts for plastic injection moulding and metal die-casting processes [1]. Joining of Be–Cu alloys can be accomplished by using soldering, brazing, and standard fusion welding techniques. Experiments on joining Be–Cu alloys have been successful using a diffusion bonding/brazing technique with an intermediate silver–copper–indium alloy at the interface as a diffusion enhancer [2]. An extensive literature search has indicated that there has not been any work performed on self-diffusion bonding of Be–Cu alloys.

This paper describes the process that was developed for self-diffusion bonding Be–Cu alloys. The integrity of the bond was analysed using various electron microscopy techniques and by standard tensile tests. An attempt was also made to determine the dominant bonding mechanisms in the diffusion bonding of Be–Cu alloys.

2. Theory of diffusion

Solid-state diffusion is the spontaneous random movement of atoms in a solid from one lattice site to another, usually initiated by thermal activation. The diffusion process in a material can be described mathematically using Fick's first and second laws [3–6]

$$J = -D\frac{\partial c}{\partial x} \tag{1}$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

where J is the number of atoms per second or flux crossing unit area at any instant, D is the diffusivity or diffusion coefficient, $\partial c/\partial x$ is the concentration gradient along the axis parallel to the flux direction at the same instant, and $\partial c/\partial t$ is the change in concentration with respect to time.

Fick's first law states that the flux is a function of the concentration gradient and assumes that the material is an ideal solution and that the diffusivity, D, is constant. Fick's second law is used in the experimental study of isothermal diffusion, for determining the diffusivity of an atom in a particular material system. This is accomplished by solving Equation 2 using either the Grube or the Matano–Boltzman method [4, 5]. The former assumes the diffusivity is constant with respect to composition, and the latter (and more difficult) method assumes the diffusivity changes with changing composition. It is believed that the mechanisms for diffusion in a crystal lattice are the vacancy, interstitial, crowdian, interstitialcy, and the Zener ring mechanisms. For face-centred cubic materials (f.c.c.), experimental studies have shown that diffusion predominantly occurs by the vacancy mechanism [3–5], substantiated by the work of Smigelskas and Kirkendall [7]. Solution-annealed Be–Cu has a f.c.c. crystal structure. Diffusion also occurs at defects such as grain boundaries, dislocations and free surfaces.

This study concentrates on diffusion bonding of two identical alloys. The concentration gradient across the interface is zero, therefore the atomic flux defined by Fick's laws will be zero. It is also assumed that the dislocation contribution to diffusion is minimal since the alloys were fully solution-treated, leading to the reduction of the dislocation density to the equilibrium value. Therefore, the three dominant mass transfer mechanisms through which diffusion

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occurs are.

(i) volume diffusion,
(ii) grain boundary diffusion, and
(iii) surface diffusion.

Diffusion occurs more rapidly along free surfaces and grain boundaries, since the mean jump frequencies of the atoms on free surfaces and grain boundaries are much higher than for atoms in the lattice [3–6].

The driving force for surface diffusion is inversely proportional to the radius of curvature of the surface. The driving force for grain boundary diffusion is the chemical potential gradient along the boundary and it depends on the applied pressure and the radius of curvature of the void into which diffusion takes place [8].

The diffusion bonding mechanisms and their driving forces are explicitly detailed in the work of Hill and Wallach [8], who have developed a model for solid-state diffusion bonding of copper. The use of this model has been implemented in this work in an attempt to determine the dominant diffusion bonding mechanisms for Be–Cu alloys.

2. Experimental procedure

2.1. Material selection

As-received solution-annealed Be–Cu alloy No. 172 was used for the diffusion bonding experiments. The chemical composition of this alloy is 1.8–2.0 wt % Be, 0.23 wt % Co, 0.03 wt % Ni, 0.07 wt % Fe, <0.01 wt % Pb with the remainder being copper. The composition was determined using the inductively coupled argon plasma (ICAP) test which has detectability limits in the p.p.m. range. The as-received properties are shown in Table I.

2.2. Sample preparation and bonding procedures

One-inch (25 mm) long cylinders were machined from 3/8 in (9.5 mm) diameter rods. The bonding surfaces were machined and polished to surface roughness ranging from 2 to 15 μin measured peak to valley.

Prior to bonding, samples were ultrasonically cleaned in trichloroethane for 5 min then chemically cleaned in a bright dip solution to remove surface contaminants. The bright dip solution consisted of 40 ml H_2SO_4, 20 ml HNO_3 and 30 ml deionized H_2O [9]. The samples were held in the solution until the surfaces appeared bright and clean. The samples were immediately rinsed in H_2O, dried, and installed in the bonding fixture and placed under a high vacuum to prevent oxidation of the interfaces at the high bonding temperatures. The fixture was designed to align the samples with a uniaxial compressive stress of 495.2 p.s.i. The fixture was loaded in a vacuum system capable of obtaining vacuum in the 1×10^{-8} torr range. The pressure for all of the bonding experiments ranged from 1×10^{-6} to 2.7×10^{-8} torr. Heat was applied to the diffusion couple with a self-controlled induction heating coil and the temperature was monitored by a thermocouple that was placed in the centre of one of the samples. The heating rate to the bonding temperature (approximately 280 F $\min^{-1}$) or 156 °C $\min^{-1}$) was rapid enough such that diffusional effects could be neglected for the time it took to reach the bonding temperature. The samples were heated to temperatures ranging from 1100 to 1475 °F (593 to 802 °C) and held at the bonding temperature for times ranging from 1 min to 24 h. After the diffusion-bonding process the couples were allowed to cool in a vacuum.

2.3. Bond analyses

The diffusion bonds were analysed using mechanical tensile tests, optical and electron microscopy (SEM and STEM), and Auger surface analyses (AES). The dominant diffusion bonding mechanisms were determined using a theoretical model for diffusion bonding of pure copper, derived by Hill and Wallach [8].

3. Experimental results

3.1. Bond tensile strengths

The bond strengths for the Be–Cu diffusion couples determined by uniaxial tensile test ranged from 27 500 p.s.i. (190 MPa) for couples bonded at 1100 °F (593 °C) for 24 h to 97 600 p.s.i (673 MPa) for couples bonded at 1475 °F (802 °C) for 2 h. Bond strengths of 65 000 p.s.i (448 MPa) were obtained from couples bonded at 1475 °F for 1 min; however, the results were erratic. The bond strengths decreased somewhat for times longer than 2 h at 1475 °F, possibly due to increase in grain size. The strength tends to approach 70 to 75 ksi (483 to 517 MPa) asymptotically as the time is increased from 2 h. The process parameters and their resulting tensile strengths are illustrated in Table II. A plot of the fracture strength as a function of log (time) is illustrated in Fig. 1. This plot shows the temperature dependence of diffusion on the fracture strength for couples bonded at 1475 °F.

3.2. Metallurgical analyses

Fig. 2 is a typical micrograph of a diffusion couple that was bonded at 1475 °F (802 °C) for 2 h. In all of the

TABLE I As-received properties for beryllium–copper alloy No. 172

Condition	Yield strength (p.s.i)[a]	Tensile strength (p.s.i)[a]	Elongation (%)	Reduction in area (%)	ASTM grain size No.
Solution-annealed	48 800	75 950	48.4	79.3	9

[a] 1000 p.s.i = 6.895 MPa.

TABLE II Diffusion bonding of beryllium–copper alloy No. 172: process parameters and bond tensile strengths

Bonding temperature (°F)	Holding time (s)	Average tensile strength of bond (p.s.i.)	Maximum/minimum tensile strength of bond (p.s.i.)	ASTM grain size number
1100	86 400	27 500	–	9
1250	14 400	51 950	56 800/47 100	9
1250	21 600	61 650	67 600/55 700	
1250	43 200	51 100	–	8
1250	64 800	54 133	61 900/43 000	8
1250	86 400	60 400	63 000/57 800	7
1350	900	49 900	57 400/42 400	7
1350	7200	61 750	66 900/56 600	7
1350	43 200	43 800	48 000/39 600	6
1350	86 400	67 000	68 100/65 900	6
1475	60	65 000	–	6
1475	300	70 700	–	6
1475	900	65 600	71 000/51 000	5–6
1475	1800	80 160	81 120/79 200	5–6
1475	3600	73 700	77 600/66 100	5–6
1475*	3600	92 300	–	
1475	7200	82 440	97 600/73 360	5–6
1475*	7200	96 300	–	
1475	43 200	78 800	84 800/73 100	5–6
1475*	43 200	88 100	–	
1475	86 400	71 000	82 500/61 500	5
1475*	86 400	97 200	–	
1475	154 800	76 800	–	4

1000 p.s.i. = 6.895 MPa.
*Tensile strength of a solid piece of BeCu exposed to the indicated bonding process.

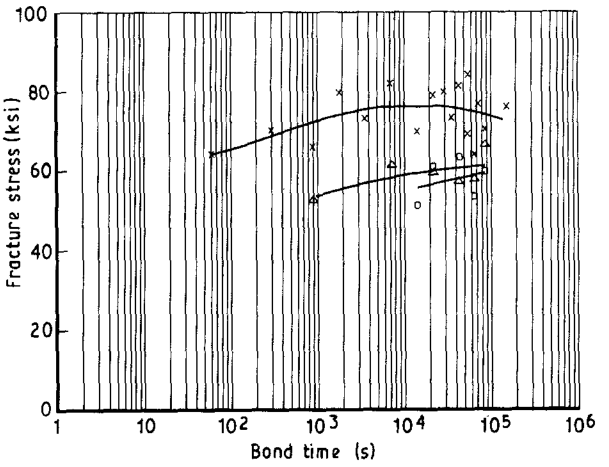

Figure 1 Diffusion bonding of Be–Cu alloy No. 172: bond strength as a function of time at (○) 1250 °F (677 °C), (△) 1350 °F (732 °C), (×) 1475 °F (802 °C). 1 ksi = 6.895 MPa.

diffusion-bonded couples, the bond interface was clearly visible. Coalescence of the grains across the bond interface did occur to a small degree; however, rarely do you see much coalescence. The bond interface appeared to be a continuous planar boundary. The micrographs also showed precipitation along the interface and at the grain boundaries.

The bond interfaces were also analysed using a scanning transmission electron microscope (STEM). The STEM analysis studied the interfaces of samples bonded at 1475 °F (802 °C) for 2, 12, and 24 h and suggests that a random distribution of the Be–Cu precipitate is present at the interface and at the grain boundaries of the grains adjacent to the interface. Fig. 3a is a STEM photograph of the bond interface for the couple bonded at 1475 °F for 2 h. An elemental analysis of particles along the interface, illustrated in Fig. 3, indicated that they were precipitates common to the Be–Cu system.

A primary concern at the beginning and during this study was the removal of the beryllium and copper oxides from the interfaces. Preliminary rough calculations, based on the heat of formation of beryllium and copper oxides, of the temperature required to dissociate these oxides indicated that the alloy would melt before the temperature of dissociation was reached. The chemical composition of the interfaces was analysed by fracturing a few diffusion couples in a high vacuum in a scanning Auger microprobe evacuated to 2.8×10^{-10} torr, and analysed immediately after fracturing. This analysis revealed that there was an oxide present on all of the samples and that the oxide thickness was independent of diffusion time. Fig. 4 shows an Auger depth profile analysis of a couple bonded at 1475 °F (802 °C) for 2 h.

The mode of fracture was determined by scanning electron microscopy of the bond fracture surface. The type of fracture was determined to be primarily ductile, with some areas on the surface having a fracture mode between ductile and brittle. This may have been influenced by the presence of the oxides at the interface. The SEM photograph of the fracture surface for a couple bonded at 1475 °F (802 °C) for 24 h is shown in Fig. 5.

4. Discussion

An attempt was made to determine the dominant bonding mechanism by using the model of Hill and

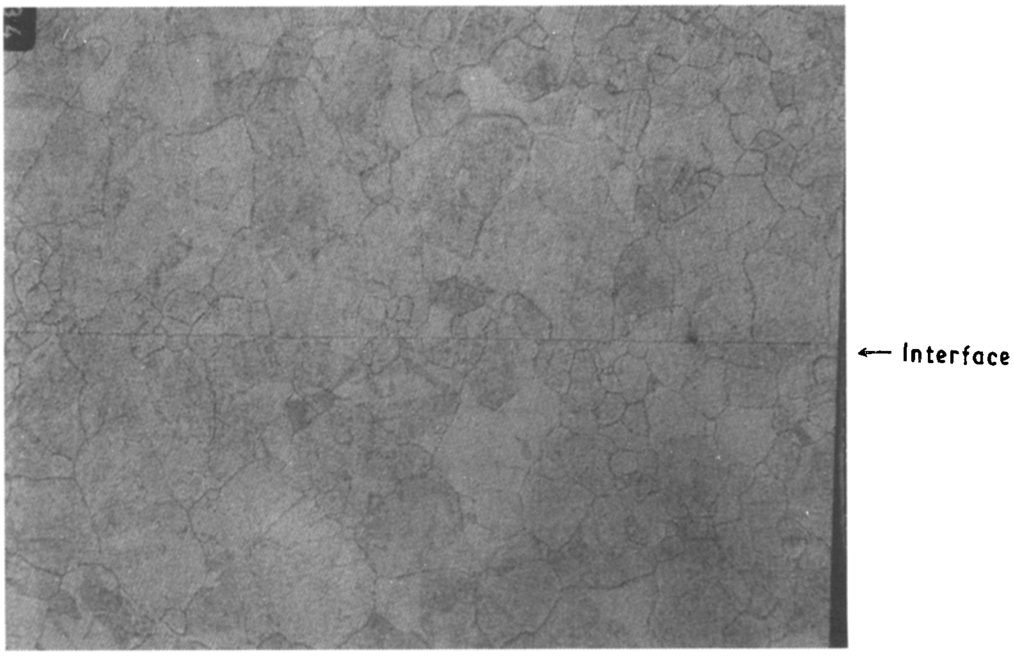

Figure 2 Cross-section of Be–Cu couple diffusion-bonded in a vacuum at 1475 °F (802 °C) for 2 h showing the bond interface (100 ×).

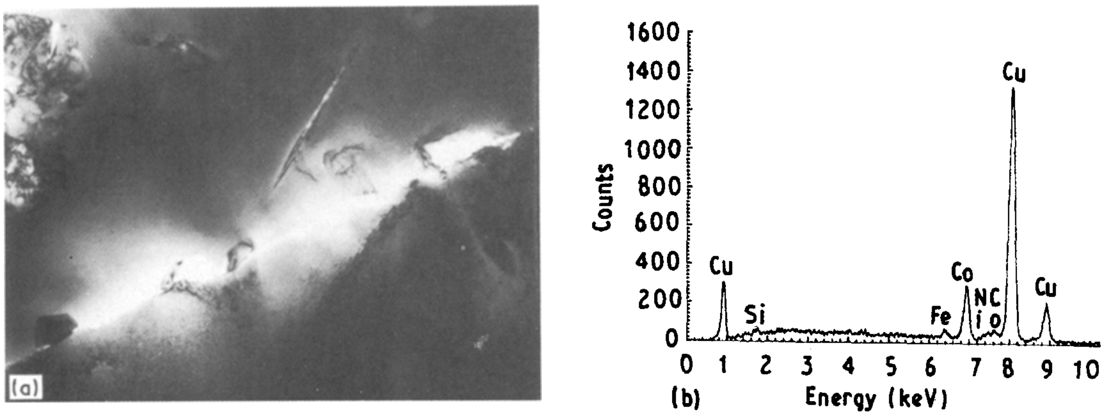

Figure 3 (a) STEM photo of the bond interface for a Be–Cu couple diffusion-bonded in a vacuum at 1475 °F (802 °C) of particles along the interface for 2 h (50 000 ×); (b) elemental analysis.

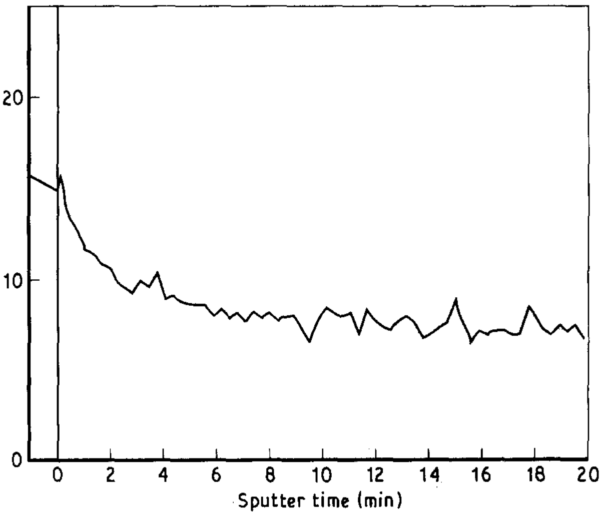

Figure 4 Auger depth profile analysis showing oxygen concentration as a function of sputter time for *in situ* fracture surface of Be–Cu couple bonded in a vacuum at 1475 °F (802 °C) for 2 h. Sputtering energy 4.5 kV, 2 mA; sputter rate for Au approximately 2 nm min^{-1}, with additional sputter at increased rate. 75 × area profile.

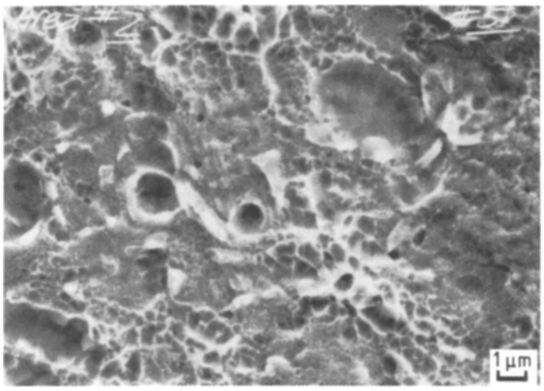

Figure 5 SEM photo of the fracture surface for a Be–Cu sample diffusion-bonded in a vacuum at 1475 °F (802 °C) for 24 h.

Wallach [8] model for solid-state diffusion bonding. The model assumes that the mechanisms that occur in pressure sintering may also occur in diffusion bonding. Through the use of an iterative computer program, the model produces two forms of graphical output. One form produces diffusion-bonding mechanism maps (Fig. 6) similar in nature to the deformation mechanism maps produced by Frost and Ashby [10]. The maps show the various bonding mechanisms which may occur for a particular material and for a set of process conditions. Each area outlined on the maps indicates a dominant mechanism. The second output (Fig. 7) is a plot of the rate of contribution from each group of mechanism sources (grain boundary, surface and creep). The map by itself will indicate the dominant mechanism; however, it will not indicate how this mechanism contributes relative to the other mechanisms that may be occurring. By using the second output, the relative contribution of the various mechanisms can be determined and thus the most dominant mechanism can also be interpreted [8]. The model is applicable to any single-phase similar-to-similar metal bond. The limitations in the model are the assumptions that the interfaces are free of oxides and other contaminants, the couples do not form intermetallic phases, and the appropriate materials data are available.

The process parameters for diffusion-bonding Be–Cu and materials data were sent to Dr E. R. Wallach in Cambridge, England, and he ran the model for diffusion-bonding Be–Cu. He also provided the diffusion-bonding mechanism map shown in Fig. 6 and the plot showing the relative contribution to bonding from the mechanism sources, which is illustrated in Fig. 7. The assumption made for this paper was that the model could use certain materials data published for pure copper, not Be–Cu, which should be applicable since the Be–Cu alloy No. 172 is approximately 98 wt % copper so that the majority of the diffusing species would be copper. A map generated according to Hill and Wallach's theory for a Be–Cu couple diffusion-bonded at 1475 °F (802 °C) for 1 and 2 h is illustrated in Fig. 6. Fig. 7 is a plot generated from Hill and Wallach's model showing the relative contributions to bonding from the mechanism sources for couples bonded at 1475 °F.

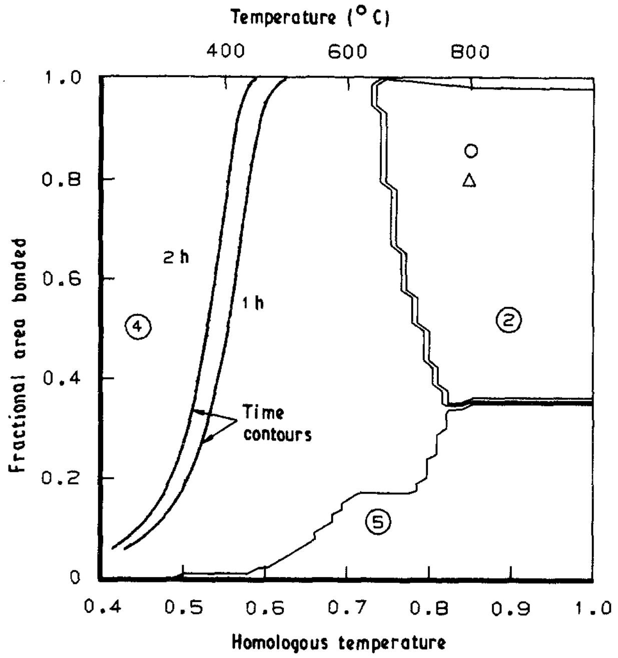

Figure 6 Diffusion-bond mechanism map for Be–Cu showing the fractional area bonded as a function of bonding temperature: (△) 1 h, (○) 2 h. Possible mechanisms (1) surface diffusion–surface source; (2) volume diffusion–surface source; (3) evaporation–condensation; (4) grain-boundary diffusion–grain-boundary source; (5) volume diffusion–grain-boundary source; (b) power-law creep–grain-boundary source; (○) plastic flow. Pressure 3.4 MN m^{-2}, grain size 16 µm, roughness wavelength 69 µm, roughness height 0.1275 µm.

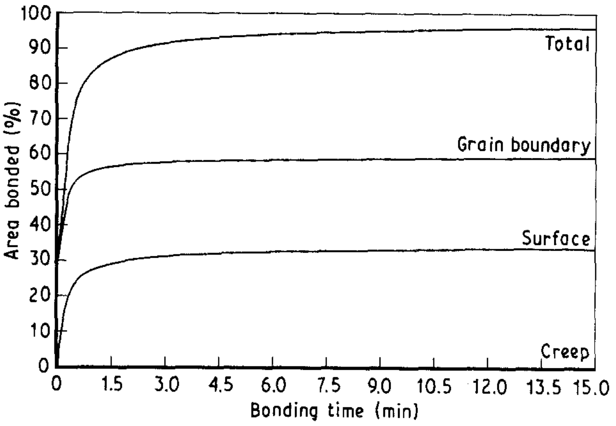

Figure 7 Contributions from the three mechanism sources to the Be–Cu diffusion bond at 1475 °F (802 °C). Process conditions as for Fig. 6.

Attempts were made to compare experimental results with the predictions made by Hill and Wallach's model, by determining the fractional area bonded. The experimental fractional area bonded was determined by comparing the tensile strengths of bonded couples to that of a solid piece heat-treated similarly to the bonded ones.

In general, the theoretical predictions from the model agreed with the experimental results. At 1475 °F for 2 h, the model predicted that there would be 100% bonding while the experimental results showed appoximately 86% bonding. This difference may be attributed to (i) the method used to determine the experimental fractional area bonded; (ii) the couple's cross-section at the interface being a continuous planar boundary with varying degrees of oxide contamination, thus creating an inherent weakness in the couple; (iii) the use in the model of some of the materials data published for pure copper; and (iv) the fact that oxide was present during and after the bonding process.

The diffusion-bonding map illustrated in Fig. 6 indicated that with the process variables set at 3.4 MPa, grain size of 16 μm, roughness wavelength of 69 μm and roughness height of 0.1275 μm the dominant diffusion-bonding mechanism was volume diffusion from a surface source, when bonded at 1475 °F for 2 h. The map also indicated that, at 1475 °F, volume diffusion from a grain boundary source was an important mechanism for bonding. The plot illustrated in Fig. 7 indicates that diffusion from grain-boundary sources contributes the most towards bonding; however, the plot also indicates that diffusion from surface sources also contribute a great deal towards bonding.

5. Conclusions

1. Beryllium–copper alloy No. 172 can be diffusion-bonded in a high vacuum at temperatures ranging from 1100 to 1475 °F (593 to 802 °C) at times ranging from 5 min to 24 h. Bond strengths of up to 97 600 p.s.i. (673 MPa) were obtained; however, on average, strengths up to 86% of the bulk were obtained for couples bonded at 1475 °F for 2 h.

2. Metallurgical analysis of the Be–Cu diffusion bond revealed the bond to be a continuous high-angle planar boundary with a random distribution of the Be–Cu precipitate. Analysis of the diffusion-bonded fracture surface revealed primarily a ductile fracture throughout the interface; however, in many of the fracture surfaces the fracture mode was between a ductile and brittle fracture. This may have been influenced by the presence of an oxide at the interface.

3. As a result of the high bonding temperatures, the grain size increased substantially from that of the as-received bulk material. The average ASTM grain size number for the as-received material was 9. For couples bonded at 1475 °F for 2 h, the average grain size number was 5. Hoffman *et al.* [2] studied the effect of holding time at elevated temperatures on grain growth and showed that the grains grew very large after short bonding times at 1475 °F. A grain size number of 5 was also found in the work by Hoffman *et al.* for Be–Cu heated to 1475 °F for 2 h.

4. Agreement between the experimental results and a theoretical model for diffusion-bonding pure copper produced by Hill and Wallach [8] was good. The method used to determine the fractional area bonded from the experimental results and the presence of oxides at the interface introduced some error into the fractional area bonded calculations. The diffusion-bonding map produced by the model indicated that volume diffusion from a surface source was the dominant mechanism. Volume diffusion from a grain-boundary source was also indicated in the map as an important bonding mechanism. The model produced a plot that indicated that mechanisms with grain-boundary sources contributed the most towards bonding.

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