SAND99-0758C

TENSILE CREEP PROPERTIES OF THE 50AU-50CU BRAZE ALLOY*

J. J. Stephens
Materials Joining Department (1833)
Sandia National Laboratories
Albuquerque, NM 87185-0367

Abstract

The 50Au-50Cu (wt.%) alloy is a solid-solution strengthened braze alloy used extensively in conventional, hermetic metal/ceramic brazing applications where low vapor pressure is a requirement. Typical metal/ceramic base materials would be Kovar™ alloy and metallized and Ni-plated 94% alumina ceramic. The elevated temperature mechanical properties are important for permitting FEA evaluation of residual stresses in metal/ceramic brazes given specific geometries and braze cooldown profiles. For material with an atomic composition of 76.084 at.% Cu, 23.916 Au (i.e., on the Cu-rich side of Cu_3Au) that was annealed for 2 hr. at 750°C and water quenched, a Garofalo sinh equation was found to adequately characterize the minimum strain rate data over the temperature range 450-850°C. At lower temperatures (250 and 350°C), a conventional power law equation was found to characterize the data. For samples held long periods of time at 375°C (96 hrs.) and slowly cooled to room temperature, a slight strengthening reaction was observed: with the stress necessary to reach the same strain rate increasing by about 15% above the baseline annealed and quenched data. X-ray diffraction indicates that the 96 hr at 375°C + slow cool condition does indeed order. The microhardness of the ordered samples indicates a value of 94.5 VHN, compared to 93.7 VHN for the baseline annealed and quenched (disordered FCC) samples. From a brazing perspective, the relative sluggishness of this ordering reaction does not appear to pose a problem for braze joints cooled at reasonable rates following brazing.

* This work was supported by the US Dept. of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy.

Note: Kovar™ is a registered tradename of Carpenter Technology Corporation.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction

Elevated temperature mechanical properties of braze alloys used in metal/ceramic brazing are of interest because of the role the braze alloy plays in accommodating thermal expansion mismatch between the metal and ceramic sides of the braze joint (refs 1-2). Although it might at first appear unusual, a desirable attribute of alloys used for metal/ceramic brazing is that they have reasonably low creep resistance to facilitate creep deformation and accommodation of the thermal expansion mismatch across the metal/ceramic braze joint during cooldown from the braze process temperature. Avoiding brazing alloys that exhibit significant strengthening increases - and volumetric strains - due to ordering is an important alloy selection consideration. There is extensive evidence in the literature for ordering of 80 wt.%Au-20Cu braze alloy and ternary variations of this alloy which contain Ni. Therefore, these alloys are not recommended for use in brazed metal/ceramic assemblies. Such alloys are very close to equiatomic AuCu composition, which can order relatively rapidly at temperatures of 300°C. Wittenauer (3) demonstrated significant strength increases in the 81.5Au-16.5Cu-2Ni braze alloy (known commercially as Nicoro-80) due to ordering as a result of a 2 hr. age at 300°C. For example, Wittenauer found that the room temperature strength of the Nicoro-80 alloy increases substantially in the ordered condition (annealed + 2 hr. at 300°C), relative to the annealed condition (1 hr at 700°C, water quenched). Those results are shown below (tensile tests run at an engineering strain rate of 1.6×10^{-3} s^{-1}):

Material/ Condition	0.2% Offset Yield Stress (MPa)	Tensile Strength (MPa)	Elongation to Fracture (%)	Microhardness (DPH)
Nicoro-80 Annealed	404.0	751.5	46.	192.
Nicoro-80 Ordered	1027.3	1185.9	12.	304.

Soviet authors (4,5) observed substantial increases in the strength of Au-Cu and Au-Cu-Ni alloys similar to Nicoro-80 following aging treatments at low temperatures. For example, Razuvayeva, et. al. (4) observed that slow cooling at temperatures ≤290°C in a 76.9 wt.%Au-15.4Cu-7.7Ni alloy increased the flow stress at 5% strain from 451 MPa to 931.6 MPa, attributable to AuCu type ordering. Abdulov, et. al. (5) observed an increase in flow stress at 5% strain from 431.5 MPa to 1078.7 MPa due to ordering in the equiatomic AuCu alloy

With the behavior of the above Au-rich alloys in mind, it is perhaps intriguing that the 50wt.% Au-50Cu braze alloy is extensively used for metal/ceramic brazing of vacuum electronic components. In particular, this alloy is used in applications where the metallic side of the braze joint is Kovar™ (54Fe-29Ni-17Co) alloy, and the ceramic side is metallized and Ni-plated 94% alumina ceramic. This braze alloy's nominal composition converts to 75.61 at.%Cu- 24.39 Au, which is very close to the stoichiometric composition Cu_3Au. A number of investigations - dating back to Bain (6) in 1923 - have documented ordering in this composition. More recently, Stoloff and Davies discussed Cu_3Au extensively in their review of mechanical properties of ordered alloys (7). They point out that ordered Cu_3Au has a structure type of $L1_2$, which can be most easily visualized (8) as a simple cubic structure, with four atoms per lattice point. In terms of atom position, place the Au atom at the origin, and three Cu atoms at center cell faces (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2). The references which Stoloff and Davies cite appear to indicate that changes in work hardening rate of ordered Cu_3Au is expected relative to disordered Cu_3Au, and that the exact increase in room temperature strength may depend on precise composition. In particular, Figure 27 of ref. 7 indicates that a minimum in the room temperature yield stress is obtained for the ordered alloy at the stoichiometric composition Cu_3Au.

The work discussed in the present paper was motivated by two primary objectives (1) to characterize the elevated temperature creep properties of the 50Au-50Cu alloy and (2) determine if this alloy can order under the type of thermal conditions typically observed in the brazing application. We have also quantified the amount of strengthening that can be expected in the ordered condition at room temperature and under creep conditions at lower temperatures.

Materials and Sample Preparation

The 50Au-50Cu (wt.%) material procured used for this study was procured from WESGO Metals, San Carlos, CA in the form of 3.18 mm (1/8 inch) diameter rod. The chemical analysis provided with the material is shown in Table 1. Note that the composition of the material supplied is 49.35 wt.% Au - 50.65 Cu, which converts to an atomic fraction of 76.084 at.% Cu- 23.916Au (i.e., on the Cu-rich side of Cu_3Au).

Table 1. Chemical composition of the material used in this study, purchased as 50Au-50Cu braze alloy from WESGO Metals, San Carlos, CA. (Lot #66219).

Major Analysis (wt.%)	Minor Analysis (wt.%)
49.35 Au, 50.65 Cu	<0.0001 Al, 0.0001 Mg, 0.0200 Ag, 0.0006 Zn, <0.0010 Fe, 0.0010 Mn, <0.0010 Ni, <0.0010 Si.

Mechanical Test Samples

All of the samples used for mechanical testing in this study were machined into miniature threaded (5-40 UNC) tensile samples with a total length of 34.93 mm, a gage diameter of 2.0 mm, and a machined gage length of 19.05 mm. A 3.18 mm radius was used between the gage area and grip region of the sample. Based on room temperature stress-strain tests run with both a clip-on extensometer and the grip-mounted LVDT extensometer (used at higher temperatures), an effective gage length of 20.48 mm (0.8603 inches) was obtained for this alloy/sample geometry. The creep and tensile testing procedures used for this study have been described in detail in a previous paper (9). With the exception of samples tested in the as-received condition at room temperature, all samples were electroplated with 2.5 micron Au to inhibit oxidation. Samples for subsequent testing and microstructural characterization were encapsulated in Quartz ampules with a Ta getter, which were backfilled to a pressure of approximately 100 Torr with high purity Argon.

Annealing and Aging Conditions

In the following sections, a number of annealing and aging treatments were used. The "baseline" annealing condition was 2 hr. at 750°C in a box furnace, followed by removing the quartz ampule from the furnace, and water quenching. In order to obtain a disordered structure at temperatures of 250 and 350°C, baseline annealed samples were heated in the optical testing furnace to 750°C, held for 10^3 seconds, then slow cooled over a period of one hour to the testing temperature. All samples were held at temperature for a period of 1/2 hour prior to testing.

Initial ordered samples for X-ray diffraction were subjected to a 2 hr. anneal at 750°C, then furnace cooled to 375°C over a period of ~3 hrs., followed by an isothermal hold at 375°C for 4 days, and slow cooldown over a period of 8-10 hrs. to room temperature. The 375°C age temperature.was based on close examination of the Au-Cu binary diagram (10). The slow cooldown was achieved by reducing the furnace set point by 50°C increments per hour until a control set point of 25°C was obtained, at which point the furnace power was turned off. The sequence for mechanical test samples was slightly different in that all samples were subjected to the baseline annealing treatment. Thus, the mechanical test samples subjected to the ordering treatment were re-encapsulated in quartz. They were then aged for 4 days at 375°C, followed by the same cooldown to room temperature as described above.

X-ray Diffraction

X-ray diffraction data were obtained on a Siemens θ–2-θ diffractometer equipped with Cu K_{α} radiation equipped with a (diffracted beam) graphite monochromator and a scintillation detector. The start angle (2θ) was 10°, with a maximum angle of 142°, using 0.02° steps. A dwell time of 8 seconds was used during the step scan. An automated peak detection program was used to obtain the precise line location and intensity values.

Experimental Results

Annealing and Aging Study

The baseline 2 hr./750°C anneal followed by water quenching produced a relatively coarse grained microstructure with a significant reduction in microhardness relative to the as-received material – see Table 2. The grain size in the baseline annealed condition was approximately ASTM #3, compared to an as-received grain size number of ASTM #8-9. X-ray diffraction patterns for the baseline annealed and as-received conditions are included in Figure 1 (patterns C and D, respectively). The baseline annealed condition is easily fit to a disordered FCC diffraction pattern, as shown in Table 3. For the case of the as-received material sample, close inspection of Figure 1 indicates that additional broad peaks may exist. However, it should also be noted that the upper two patterns in Figure 1 (patterns A and B) indicate FCC patterns following 3.5 hr. and 24 hr. holds at 375°C, followed by water quenching. These results suggest that the transformation of the alloy to an ordered Cu_3Au structure is fairly sluggish.

Table 2. Vickers microhardness values for the various conditions studied. Indents were obtained using a 300 gm load, and a 15 second indent time.

Sample condition	Vickers Microhardness
As-received (cold worked)	129.8 ± 7.8
Baseline (annealed 2 hr. 750°C/ Water Quenched)	93.7 ± 2.5
Baseline anneal + furnace cooled and held 4 days at 375°C/furnace cooled to room temperature.	94.5 ± 2.5

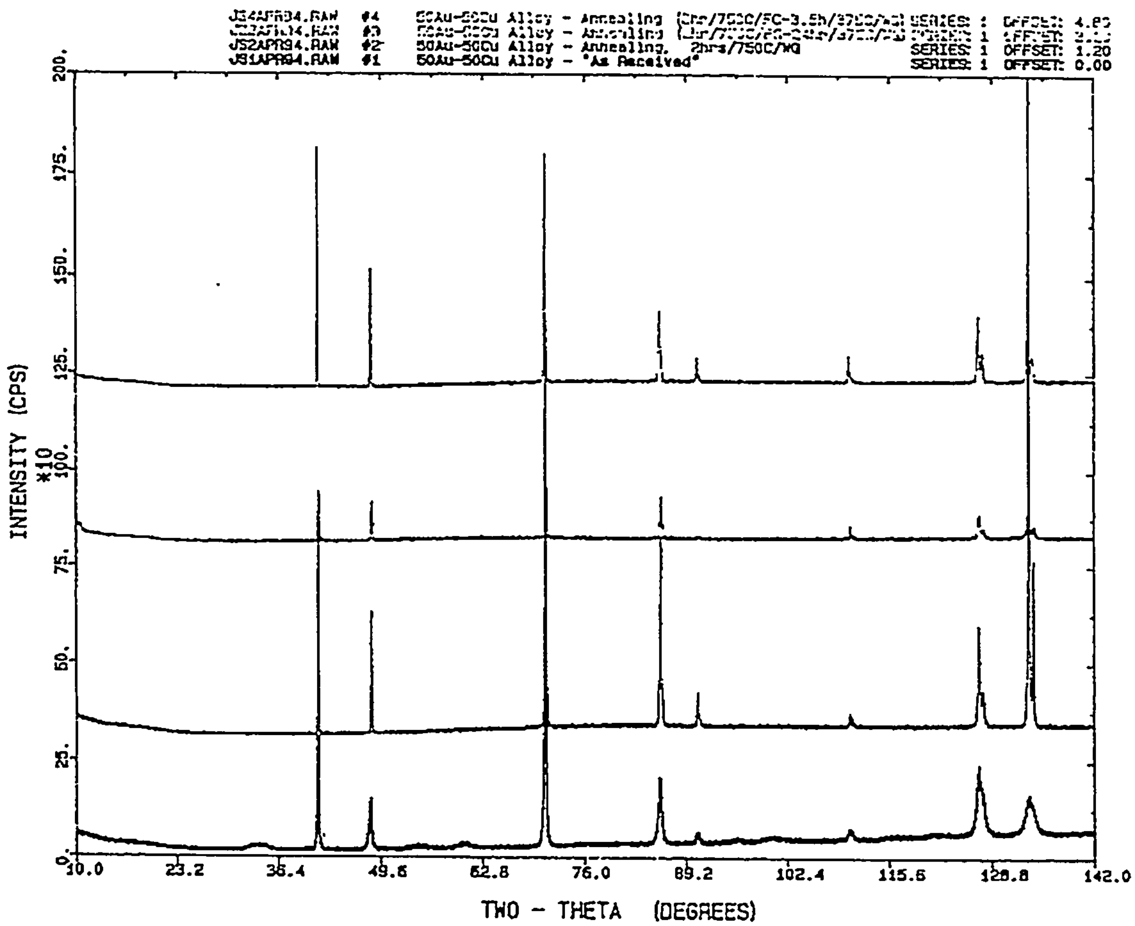

Figure 1. X-ray diffraction patterns of various 50Au-50Cu braze alloy samples. From top to bottom: (A) Annealed 2 hr. at 750°C, then furnace cooled to and held for 3.5 hr. at 375°C, Water Quenched. (B) Annealed 2 hr. at 750°C, then furnace cooled to and held for 24 hr. at 375°C, Water Quenched. (C) Annealed 2 hr. at 750°C, Water Quenched (baseline condition). (D) As-received material.

Ordered diffraction patterns were obtained for the case of samples held for longer periods at either 300 or 375°C. These data are shown in Figure 2. Both patterns index to a simple cubic

Table 3. XRD peak locations and hkl indices for the baseline 50Au-50Cu sample that was annealed for 2 hrs. at 750°C, then water quenched. The FCC lattice parameter corresponding to this pattern was computed as 3.746 Angstroms.

Peak #	2θ (Degrees)	D spacing (Angstroms)	Relative Intensity (%)	*hkl*
1	41.765	2.1609	28.0	111
2	48.566	1.8730	15.3	200
3	71.144	1.3241	43.0	220
4	86.064	1.1288	23.9	311
5	90.864	1.0812	4.2	222
6	110.634	0.9367	1.7	400
7	127.224	0.8599	14.6	331
8	133.614	0.8380	100.00	420

pattern, with the line intensities and angle locations for the 375°C/4 day aged sample shown in Table 4. The 375°C aging treatment was adopted as the aging temperature for the mechanical properties portion of the study.

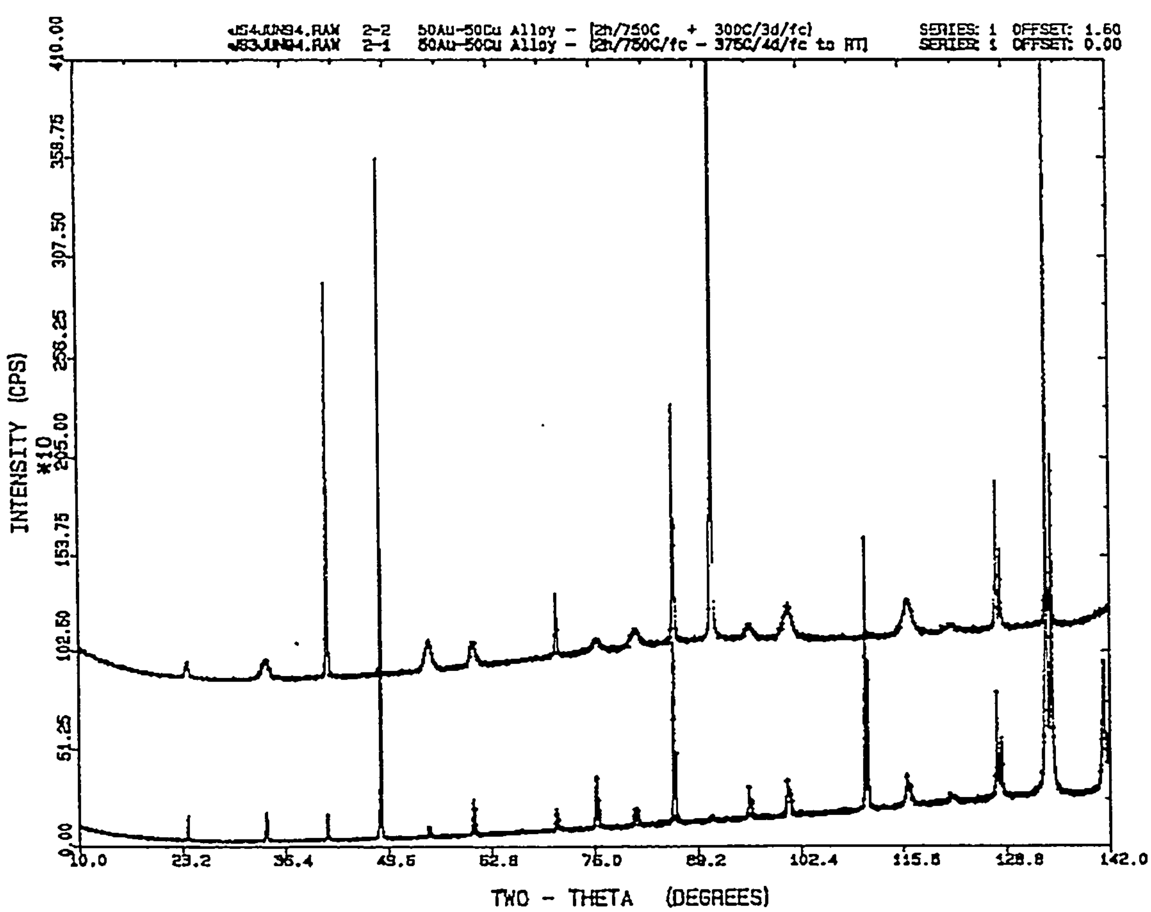

Figure 2. X-ray diffraction patterns of 50Au-50Cu braze alloy samples annealed at 750°C, then aged at lower temperatures to induce ordering. From top to bottom: (A) Annealed 2 hr. at 750°C, then furnace cooled to and held for 3 days at 300°C, furnace cooled to room temperature. (B) Annealed 2 hr. at 750°C, then furnace cooled to and held for 4 days at 375°C, furnace cooled to room temperature.

Table 4. XRD peak locations and hkl indices for the ordered 50Au-50Cu sample that was annealed for 2 hrs. at 750°C, furnace cooled to and held at 375°C for 4 days, followed by slow furnace cool to room temperature. The simple cubic lattice parameter corresponding to this pattern was computed as 3.742 Angstroms.

Peak #	2θ (Degrees)	D spacing (Angstroms)	Relative Intensity (%)	*hkl*
1	23.911	3.7184	2.7	100
2	34.016	2.6334	3.3	110
3	41.902	2.1542	3.4	111
4	48.740	1.8668	85.0	200
5	54.913	1.6706	1.4	210
6	60.666	1.5252	4.7	211
7	71.319	1.3213	2.9	220
8	76.379	1.2459	7.1	300
9	81.311	1.1823	4.4	310
10	86.228	1.1270	21.8	311
11	95.913	1.0372	4.4	320
12	100.802	0.9997	4.9	321
13	110.788	0.9359	34.3	400
14	116.143	0.9076	3.9	410
15	121.608	0.8824	1.2	330
16	127.655	0.8583	15.0	331
17	134.047	0.8367	100.0	420
18	141.274	0.8165	19.3	421

Mechanical Properties

A. Room temperature tensile properties

Room temperature stress-strain curves were obtained for both the baseline annealed and 375°C-aged condition. These data are shown in Figure 3. Note that the yield strength of the annealed sample is slightly higher than that of the ordered sample. However, the work hardening slope is higher for the ordered sample is higher than that of the annealed sample. These stress-strain curves are similar in shape and magnitude to the engineering stress-strain curves shown in Figure 47 of Stoloff and Davies (7).

B. High temperature (450-850°C) Creep Properties – Annealed Material

In general, most of the elevated temperature creep tests exhibited an inverted-type behavior. This is illustrated in Figure 4, where the strain-time curves obtained at 750°C are shown. This behavior is characteristic of class I solid-solution alloys and is expected in binary Au-Cu alloys due to atomic size mismatch (11). The minimum strain rate for all tests run in the temperature range 450-850°C are shown in Figure 5. Note the increase in apparent stress exponent at 450°C relative to the other temperatures. This feature in the data set suggests the use of the Garofalo sinh equation (12) to fit the minimum creep rate data as a function of stress and temperature. Using multivariable regression analysis, the following fit was obtained to the high temperature data set:

$$\dot{\varepsilon}_{min}\,(s^{-1}) = 9.92 \times 10^{7}\,(\sinh[0.00866\,\sigma(MPa)])^{3.47}\,\exp(-187{,}972/RT) \qquad (1)$$

where T is in Kelvin and R is given as 8.314 Joules/mole-Kelvin. A correlation coefficient (r^2) of 0.948 was obtained from the statistical analysis. The quality of fit to eq. (1) is better illustrated by replotting using the Zener-Holloman parameter (i.e., plotting temperature-compensated minimum strain rate vs. True Stress), as shown in Figure 6.

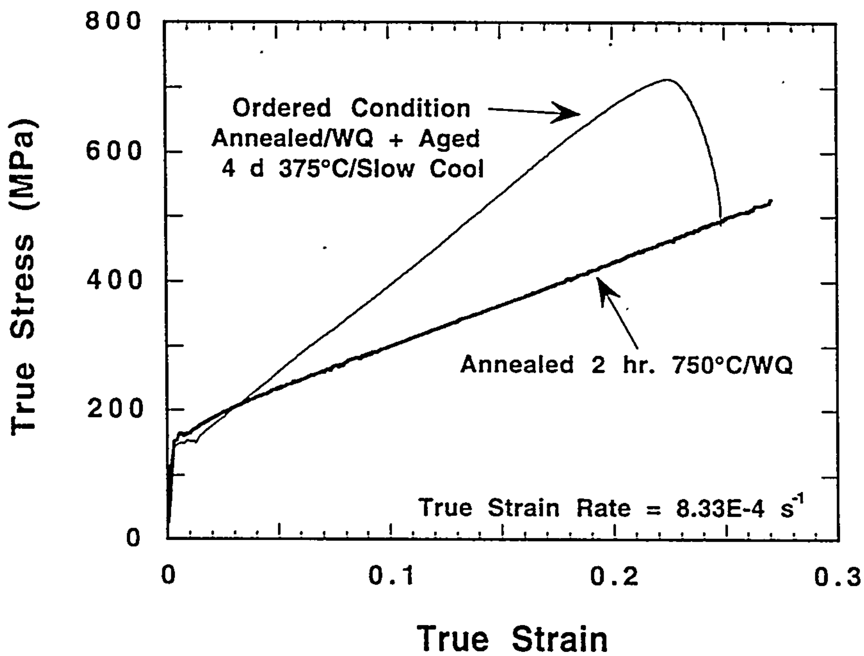

Figure 3. Room temperature stress strain curves for 50Au-50Cu braze alloy. The conditions run were: (A) annealed condition, and (B) ordered condition, i.e., annealed 2 hr. at 750°C, then furnace cooled to and held for 4 days at 375°C, furnace cooled to room temperature.

C. Lower Temperature (250-350°C) Creep Behavior - Baseline Annealed Condition

Significantly different creep kinetics were observed at the lower temperatures of 250 and 350°C. The strain-time curves for the baseline annealed and temp. cycled samples tested at 250°C are shown in Figure 7. Note that the primary strain at this lower temperature is a strong function of applied stress; this is consistent with the behavior observed in the 62Cu-35Au-3Ni alloy (9). The minimum strain rate at 250 and 350°C are shown in Figure 8. The trends in the data suggested use of a power law creep equation, and the following fit was obtained to the data:

$$\dot{\varepsilon}_{min}\,(s^{-1}) = 6.87 \times 10^{-30}\,(\sigma(MPa))^{16.3}\,\exp(-145{,}407/RT) \qquad (2)$$

Clearly, a rather high stress exponent was obtained. It is not clear why power-law breakdown behavior is not observed at these lower temperatures. Longer term tests (beyond the scope of this study) could perhaps illustrate whether the high stress exponent is sustained at lower values of applied stress in this regime.

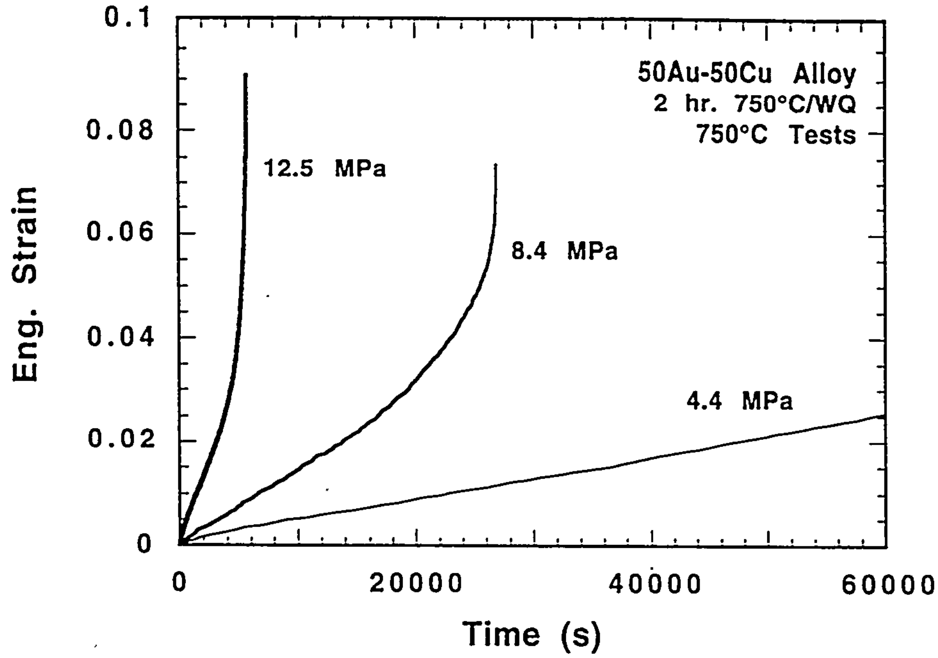

Figure 4. Strain-time curves for baseline (annealed 2 hr. 750°C/WQ) 50Au-50Cu braze alloy run at 750°C.

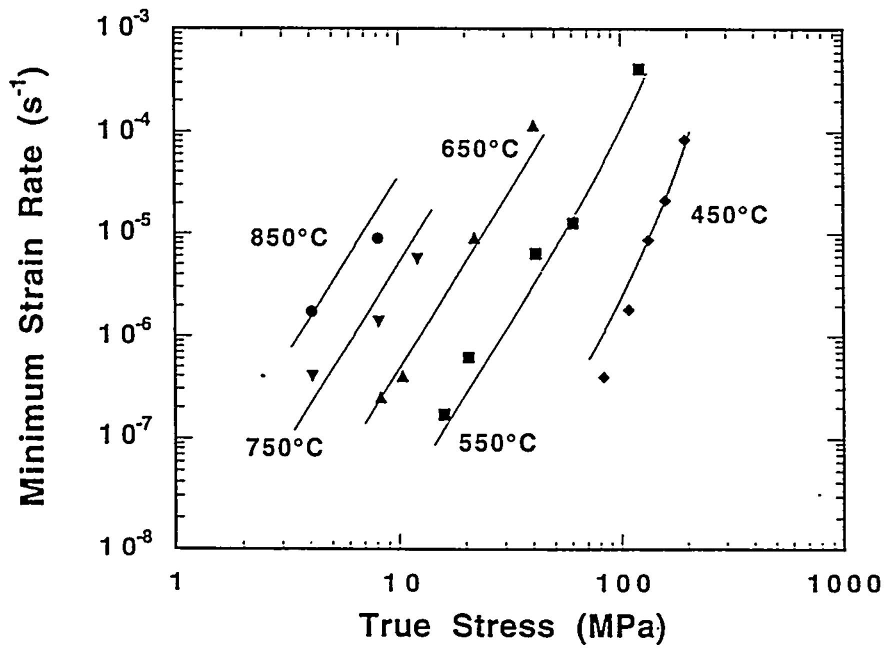

Figure 5. Minimum creep rate as a function of stress and temperature for annealed 50Au-50Cu braze alloy over the temperature range 450-850°C.

D. Lower Temperature (250-350°C) Creep Behavior - Ordered Condition

Finally, a limited number of baseline annealed samples were subjected to the 375°C aging treatment described in the previous sections, and were creep tested at 250 and 350°C. The

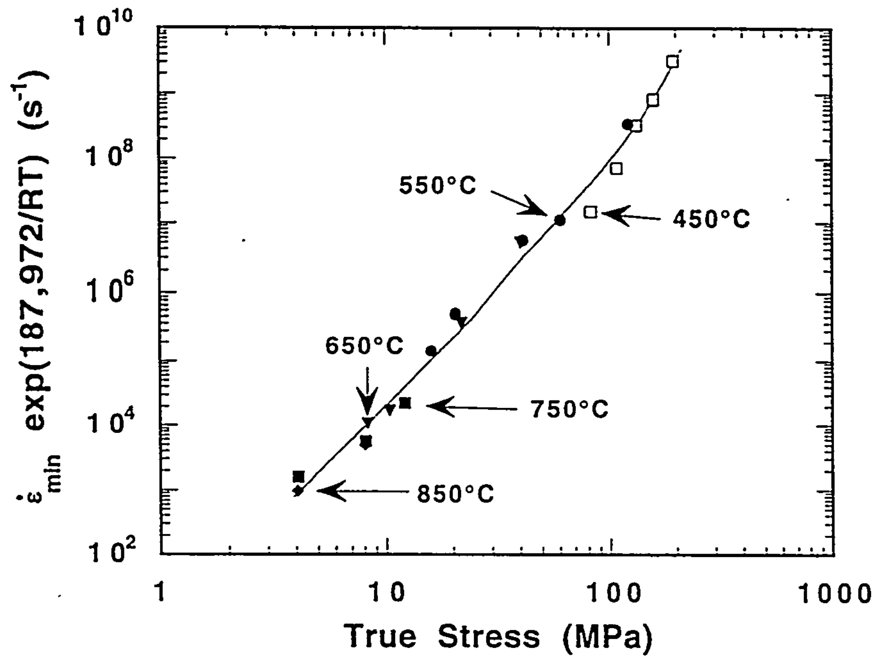

Figure 6. Zener-Holloman plot showing temperature compensated strain rate as a function of stress for annealed 50Au-50Cu braze alloy over the temperature range 450-850°C.

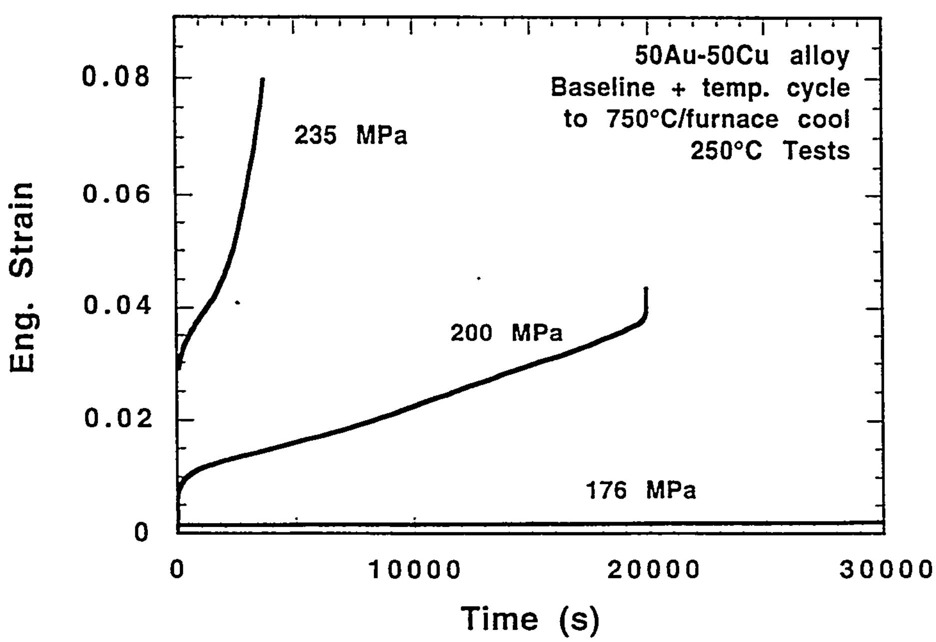

Figure 7. Strain-time curves (short time plot) for annealed and furnace cycled 50Au-50Cu alloy at 250°C. Note that the amount of primary strain is a strong function of applied stress.

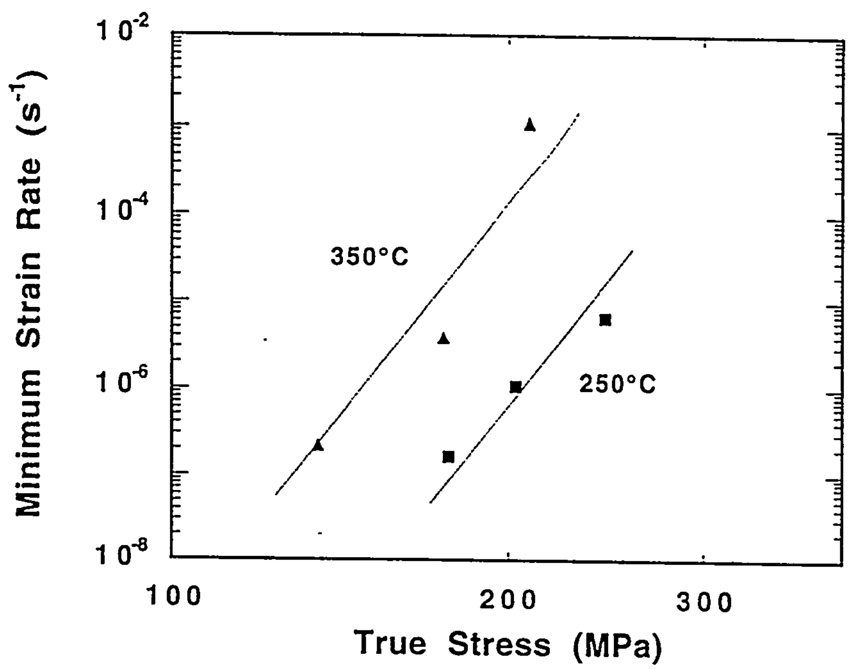

Figure 8. Power-law creep correlation for annealed and furnace cycled 50Au-50Cu alloy at 250 and 350°C.

minimum strain rate for those tests are shown in Figure 9, along with the results for the baseline annealed samples. The results of these tests on ordered samples indicates that there is a measurable (~15 percent) increase in True Stress needed to achieve the same minimum strain rate relative to the baseline (disordered) condition.

Discussion – Implications for Metal/Ceramic Brazing

Two important points must be kept in mind regarding the ordered Cu_3Au structure with respect to metal/ceramic brazing with the 50Au-50Cu alloy: (1) very long hold times (e.g., 3-4 days at 375°C) are required to obtain the ordered Cu_3Au structure, and (2) the strength differential (ordered vs. disordered structures) is not very substantial. The results of this study suggest that ordering of the 50Au-50Cu braze alloy should not occur in practice. This is because the longest braze process cooldown cycles which may be expected in practice are overnight (~16 hours), and are thus substantially shorter than the times needed to obtain the ordered Cu_3Au structure.

There is another effect which may need to be considered for the actual brazing application: namely, the effect of base metal alloying on the final composition of the braze. While this behavior has been well characterized for Kovar™/metallized alumina braze joints made with Cu braze material, it has not been performed for the case of the 50Au-50Cu alloy. However, it would be expected that small amounts of Fe, Ni, or Co which may dissolve into the braze joint as a result of erosion of the Kovar™ base metal should substitute as Cu, and would not be expected to accelerate ordering behavior.

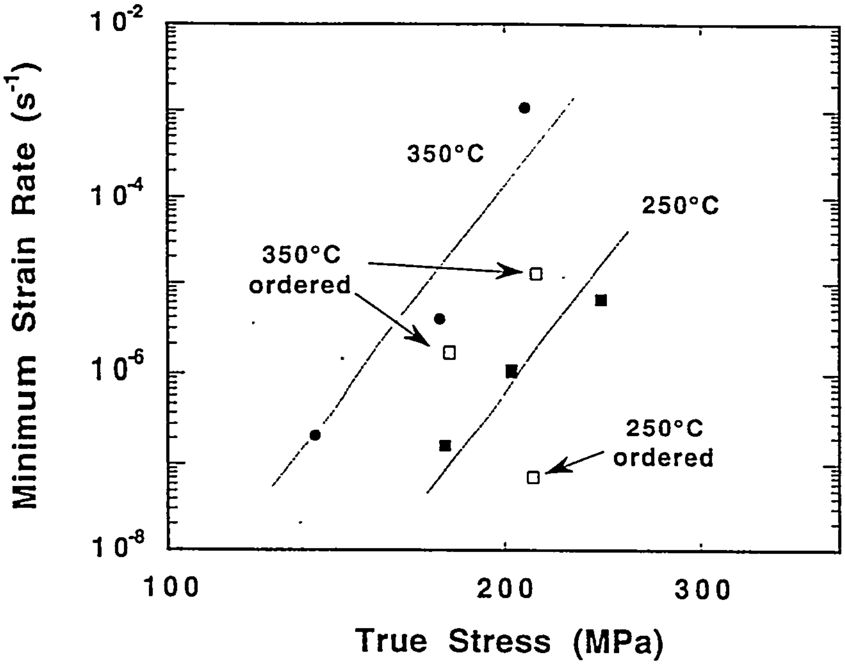

Figure 9. Creep data for (a) annealed and furnace cycled 50Au-50Cu alloy and (b) ordered 50Au-50Cu alloy at 250 and 350°C.

Summary

(1) Relatively long hold times (~3-4 days) at intermediate temperatures (300-375°C) are required in order to obtain an ordered Cu_3Au structure in the 50Au-50Cu alloy.

(2) The elevated temperature (450-850°C) creep properties of annealed 50Au-50Cu braze alloy are well characterized by the Garofalo sinh equation, with an apparent stress exponent of 3.47, and an activation energy of 187.97 kJ/mole.

(3) The lower temperature (250-350°C) creep properties of baseline annealed and temperature cycled 50Au-50Cu braze alloy are well fit by a power law creep equation with a stress exponent of 16.3 and an activation energy of 145.41 kJ/mole.

(4) There is an increase in creep strength for the case of the ordered Cu_3Au structure. Based on the limited amount of data collected, it appear to be a strength increase of 15%.

(5) Based on the long amount of time needed to trigger the Cu_3Au ordering transformation, it is expected that ordered 50Au-50Cu braze alloy will not be encountered under realistic use conditions.

Acknowledgements

The expert assistance of the following personnel are gratefully acknowledged: D. T. Schmale and K. D. Hamann (mechanical testing), M. Gonzalez (X-ray diffraction), and M. J. Meade (miniature tensile sample machining). The help of J. T. Cutchen and G. W. Smith for securing internal project funding for this study are acknowledged. I would also like to express my appreciation to P. T. Vianco for review of this manuscript. This work was performed at Sandia National Laboratories, Albuquerque, New Mexico, under DOE contract number Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy.

References

1. J. J. Stephens, S. N. Burchett and F. M. Hosking, "Residual Stresses in Metal/Ceramic Brazes: Effect of Creep on Finite Element Analysis Results," in Metal/Ceramic Joining ed. P. Kumar and V. A. Greenhut (Warrendale, PA: TMS, 1991), 23-41.

2. J. J. Stephens, S. N. Burchett and W. B. Jones, "Stress Relaxation of Braze Joints," in Advances in Electronic Packaging 1992 ed. W. T. Chen and H. Abe (New York, NY: ASME, 1992), 363-372.

3. J. Wittenauer, Lockheed Missiles and Space Co., Inc., private communication with author, 11 June 1990.

4. B. D. Razuvayeva et al., "Influence of Phase Transformations on Mechanical Properties of Gold-Copper Alloy With Additions of Nickel and Zinc," Fiz. Metal. Metalloved., 42 (1976), 132-139.

5. R. Z. Abdulov, et al., "Phase Precipitation on Domain Boundaries of Ordered Alloy CuAu With Additions of Nickel and Silver," ," Fiz. Metal. Metalloved., 45 (1978), 118-124.

6. E. C. Bain, "Crystal Structure of Solid Solutions," Trans. AIME, 68 (1923), 625-639.

7. N. S. Stoloff and R. G. Davies, "The Mechanical Properties of Ordered Alloys," Progress in Materials Science, 13 (1968), 1-84.

8. D. B. Cullity, Elements of X-Ray Diffraction, 1978 (Reading, Mass: Addison-Wesley Publishing Co.), 383-389.

9. J. J. Stephens and F. A. Greulich, "Elevated Temperature Creep and Fracture Properties of the 62Cu-35Au-3Ni Braze Alloy," Metallurgical Transactions A, 26 (1995), 1471-1482.

10. Phase Diagrams of Binary Gold Alloys, H. Okamoto and T. B. Massalski, eds., ASM International, Metals Park, OH, 1987, pp. 76-81.

11. W. R. Cannon and O. D. Sherby, Metallurgical Transactions, 1, (1970), 1030-32.

12. F. A. Garofalo, Fundamentals of Creep and Creep-Rupture in Metals, 1965 (New York, NY: The MacMillan Company), 51-53.