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Low-Temperature Solid-State Bonding of Copper

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Mechanisms associated with low-temperature solid-state bonding of copper were investigated. The low-temperature bonding phenomena was observed to be time/temperature dependent and related to a deformation process. An analytical technique for predicting bond strength and bonding behavior is presented.

1 Introduction

JOINING processes thermally alter any assembly, causing undesirable phase transformations, distortion, and residual stresses. For solid-state bonding to effectively overcome these concerns, bonding at lower temperatures must be attained.

Comprehensive descriptions of high temperature bonding mechanisms have been reviewed by numerous investigators.[1-9] The initial stage has been described as bringing two surfaces together, applying a load sufficient to achieve some degree of intimate contact, and thereby deforming the asperities at the bond interface.[10,11] Heating the assembly will cause these contact areas to increase. Several diffusion-controlled processes may shrink the resulting voids. In the latter stages, bulk diffusion can eliminate the remaining voids, and the interfacial boundary may migrate out of the plane of the original interface to a lower energy configuration.

Long-range diffusion is not an important consideration during the low-temperature bonding process. It is only within a few atom layers of the bonding interface that diffusional processes can effectively improve the joint strength when bonding is completed in a few minutes.[12] Surface diffusion can be beneficial in the early stages of low-temperature bonding.[13] Surface diffusion, driven by the chemical potential dependence on curvature, can produce a short-range decrease in surface roughness.[14] Changes in surface roughness have been reported to obey specific growth laws.[15]

Metallic surfaces have been found to bond at low temperatures immediately on contact.[16-19] The increase in bonding efficiency with rising temperature has been reported to be due to the thermal relaxation of the yield strength and the corresponding increase in ductility.[1,20-22] As ductility of the material increases, the relative ease of deformation of the bonding surface asperities effectively increases the area of metal-to-metal contact. The bond strength has also been reported to increase with increasing processing time.[21,23,24] As the contact area increases with time under load, the effective stress causing deformation at the points of contact is reduced.[15,25] Several mechanistic models that involve highly localized plastic deformation of asperities as the main process in increasing surface contact area have been introduced.[13,15,20,26-30] As the contact surface increases with time under load, the effective stress causing deformation at the points of contact is reduced.[15]

2 Experimental Design and Procedures

2.1 *Preliminary Investigation*

Experiments were designed to determine the time/temperature-dependent mechanisms for bonding at a temperature below the classically accepted range for volume and surface diffusion. A preliminary sequence of bonding tests was performed in the first phase of work to prove the existence of well-behaved time and temperature dependence for low-temperature solid-state joining.

Copper (99.9 wt.%) was selected for this investigation, because it represents a noble metal that has been used in numerous fundamental experiments. Physical and mechanical properties and other useful data for copper are readily available and are needed for fundamental calculations in evaluating the bonding models. Also, noble metals are commonly used as an interlayer material for low-temperature solid-state bonding.

In the preliminary study, 13-mm-diameter copper rod was screw-machined into the form of half-tensile specimens. The specimen interfaces were then analyzed for roughness and waviness in an attempt to hold surface roughness constant. The specimens were ultrasonically cleaned—first in acetone, then in an aqueous detergent, and finally in distilled water.

Table 1 Preliminary Test Parameters and Bonding Conditions

Temperature, °C	Time, sec					
300	300	600	1200	2400	4800	7200
325	300	500	1200	2400	4800	N/A
375	300	600	1200	2400	N/A	N/A
400	300	600	1200	N/A	N/A	N/A

Note: Bonding parameters, pressure = 68.9 MPa (10 ksi) held constant during all tests; sample roughness, 10 to 15 μin. (screw machined). N/A ≡ not applicable due to bulk deformation occurring during bonding.

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In preparation for bonding, the tensile specimens were placed under vacuum (below 2×10^{-6} torr), back-filled with high-purity argon (99.998%) at a pressure of 1×10^{-2} torr and cleaned with a glow discharge plasma.[31,32] A potential of 2000 V and a current of 20 mA were required to sputter off adsorbed gases and surface contaminants from the bonding interface. This process was performed for 3 min. Preliminary work indicated that glow discharge sputtering for periods of time in excess of 4 min could produce surface etching and pitting, thereby changing the desired surface morphology.

Once the bonding surfaces of the tensile specimens were sputter cleaned, the chamber was evacuated (below 2×10^{-6} torr). The halves of the two tensile specimens were then brought together under a load of 68.9 MPa (10 ksi) at various bonding temperatures and times. A summary of the bonding conditions and combinations is given in Table 1.

The bonding coupons were inductively heated to a specified temperature. The temperature of each specimen was measured and controlled by a chromel-alumel thermocouple percussively welded to the specimen near the bond interface. Bonding pressure was held at 68.9 MPa, which is below the bulk yield stress of the material for most bonding temperatures and times. The microdeformation that occurred was restricted to the asperities. Gross deformation associated with bulging or barreling of the specimen was not observed, unless bonding times in excess of 2400 sec or temperatures in excess of 375 °C were used.

The specimens were held at constant temperature and pressure for the specified times during bonding and then cooled to

Table 2 Isothermal Heat Treatment Parameters

Temperature, °C	Time, sec					
200	0	300	600	1200	2400	4800
225	0	300	600	1200	2400	4800
250	0	300	600	1200	2400	4800
275	0	300	600	1200	2400	4800
300	0	300	600	1200	2400	4800
325	0	300	600	1200	2400	4800
350	0	300	600	1200	2400	4800

Note: Bonding parameters, pressure = 68.9 MPa (10 ksi) held constant during all tests; surface roughness, 40 μin. (mill cut). An isothermal time of zero seconds represents the heating cycle of the isothermal heat treatment.

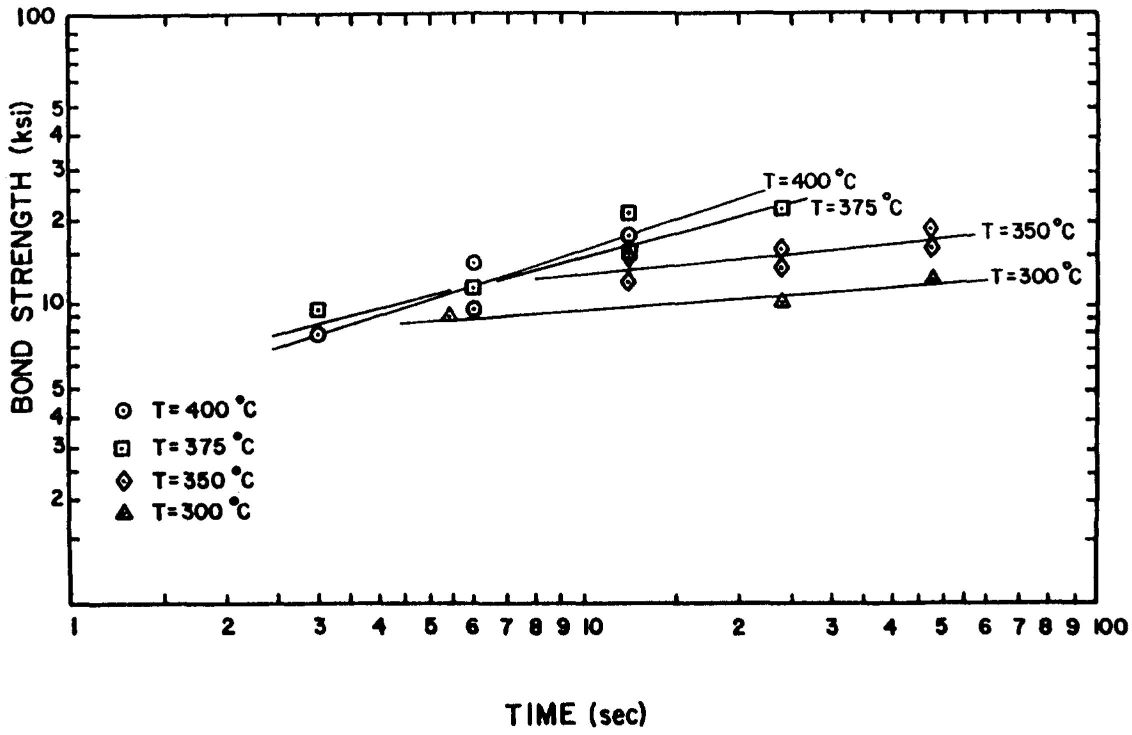

Fig. 1 Preliminary data given as a log-log plot of bond strength as a function of time for various isothermal heat treatments.

ambient temperature while maintaining bonding pressure. This was done to ensure that thermal stresses coupled with elastic stresses did not rupture the bonds created at the interface during rapid cooling.

Bond strengths were obtained by testing the bonded specimens of uniaxial tension to failure. Fractured specimens were analyzed using a scanning electron microscope (SEM). Actual surface contact areas were measured and used in calculating potential bond strengths for comparison with bulk copper properties.

The bond strengths obtained from the preliminary investigation were approximately equal to the yield strength of copper for the various annealing temperatures, but overall ductility of bonded specimens was low. Observations from these results indicated that surface morphology and interface cleanliness affected both the maximum attainable bond strength and ductility. To more clearly distinguish differences in bonding behavior, sample machining and cleaning procedures were changed.

2.2 *Primary Investigation*

In the primary investigation, surface preparation was carefully controlled. At the lower bonding temperatures, surface preparation becomes one of the most important factors determining the repeatability and consistency in bond strengths. Machining details such as cutting speeds were carefully controlled with special attention to the cleanliness and sharpness of the machining cuts.[33]

A systematic test matrix for a given surface preparation, involving the process parameters of bonding temperature, time, and pressure, was designed and followed (Table 2). The range of the test matrix was designed based on observations from hardness-temperature data and preliminary test data that indicated two mechanistic low-temperature bonding regimes.

3 Results and Discussion

The preliminary bonding experiments revealed the existence of a mechanistic change in bond formation for the temperature range studied. The results of the preliminary bonding tests are presented in Fig. 1. These data suggest a thermally activated bonding process where the bond strength, B, is given by:

$$B = [Kt]^n \qquad [1]$$

where t is the bonding time, n is the empirically derived exponent, and K is the rate constant, which is given by:

$$K = K_o \exp[-Q/RT] \qquad [2]$$

The exponent n was determined for the data of the preliminary investigation and found to be 0.2 for the temperature range 250 to 300 °C and 0.5 for the temperature range 375 to 400 °C. The exponent values suggest at least two mechanistic bonding regimes. Numerous other studies have noted dramatic decreases in the hardness of cold worked copper after short times at temperatures near 300 to 350 °C.[34-37] These microstructural

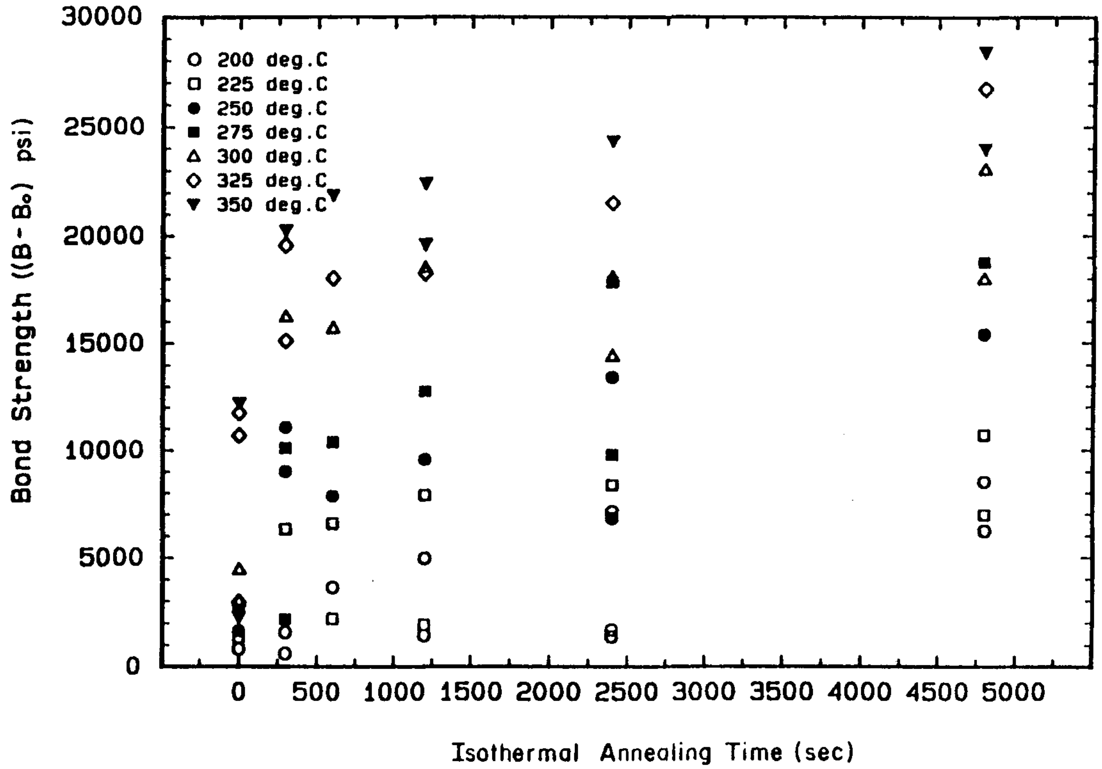

Fig. 2 Fraction of bond strength established during the isothermal annealing time, shown as a function of annealing time, for temperatures from 473 to 623 K (200 to 350 °C).

changes are believed to also be important in explaining the two bonding regimes found in this study.

3.1 *Time and Temperature Dependence*

The bond strengths measured for samples of the primary low-temperature bonding study are shown in Fig. 2 and 3. Figure 2 gives only values of bond strength that can be attributed to the isothermal annealing time. Depending on temperature, significant bond strength was found to develop during the specimen heating time. The bond strength that developed during the nonisothermal heating time will be referred to as the initial bond strength, B_o. The bond strength obtained for the entire time in which heat was applied to the bond interface will be designated as the maximum bond strength (B).

A complete set of curves depicting maximum bond strength (B) as a function of total heating time is presented in Fig. 3 for easy comparisons among various bonding temperature sets.

Before analysis of the isothermal bonding mechanism can be achieved, results from the initial bond strength (B_o) obtained prior to thermal equilibration (Fig. 4) must be subtracted from the maximum bond strength, B.

A comparison of the results is presented in Fig. 5 and 6 for both the maximum bond strength and that achieved during isothermal conditions. These data are presented for lower (200 °C) and upper (350 °C) temperature regimes. Clearly, at 350 °C, the bond strength established prior to thermal equilibrium can be as much as half the total bond strength. These data can be interpreted by using the following equation:

$$B = B_o + (Kt)^n \qquad [3]$$

where B is the maximum bond strength, t is the isothermal bonding time, and K is the thermally activated rate coefficient. By applying the logarithmic expansion of Eq 3, the value for n of the bonding process for a given temperature was determined. Results of the data plotted in this form are shown in Fig. 7. Careful observation of Fig. 7 reveals that bond strengths established at 300 °C were anomalously high. Numerous researchers[38-40] have observed marked softening of cold worked copper when the material was heated through the temperature range 300 to 350 °C. Depending on exact composition and amount of deformation, recovery or complete recrystallization can occur at these temperatures. During bonding of these copper specimens at 300 °C, material softening increased the interfacial contact area, and greater initial bond strengths resulted. Consequently, the initial bond strength B_o for bonds made at 300 °C and above constituted the major fraction of total bond strength.

Statistical analysis of the seven different isothermal heat treatments resulted in determining a common value for n of 0.25. Figure 8 is the summary for the replotted isothermal bond strength data as a function of $t^{0.25}$. Evaluation of Fig. 8 (when slope equals 0.25) indicates that the rate constant K gradually increases with temperature.

The values for K (see Eq 3) were determined from least-squares analyses of the data shown in Fig. 7 and 8 and plotted as a function of reciprocal temperature in Fig. 9. Figure 9 suggests an apparent activation energy of 11 kcal/mol for low-temperature bonding of copper. In this type of bonding process, and with

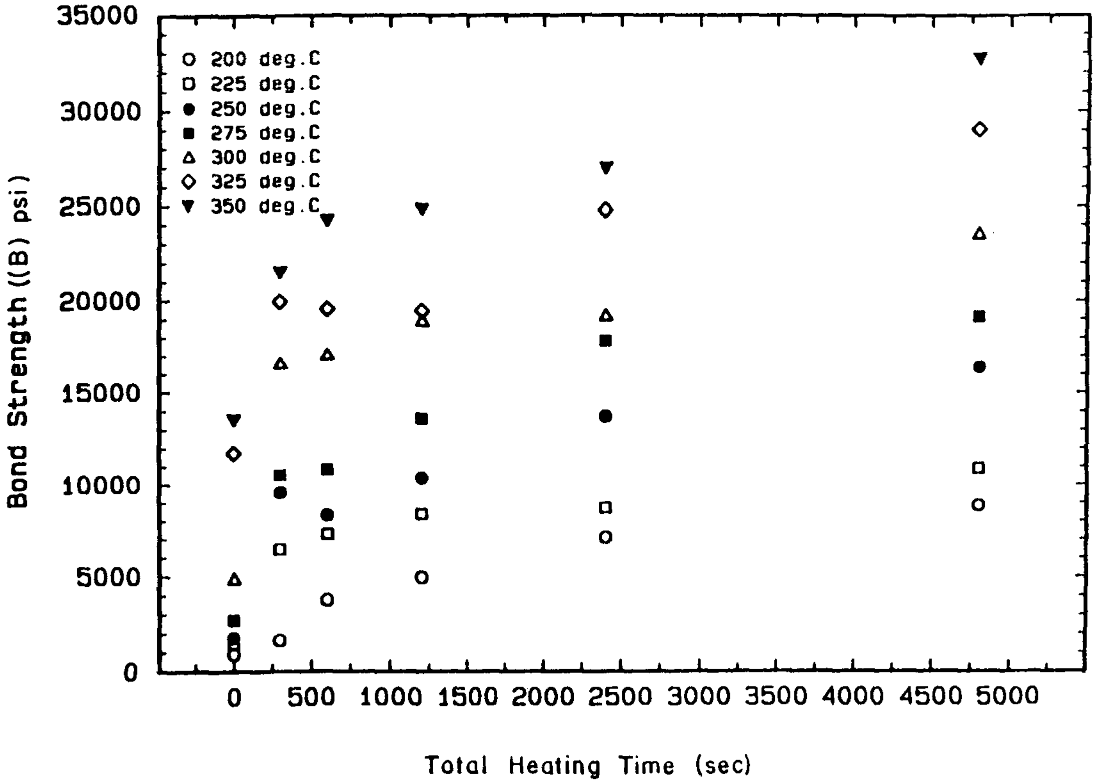

Fig. 3 Maximum bond strength plotted as a function of total heating time for temperatures from 473 to 623 K (200 to 350 °C).

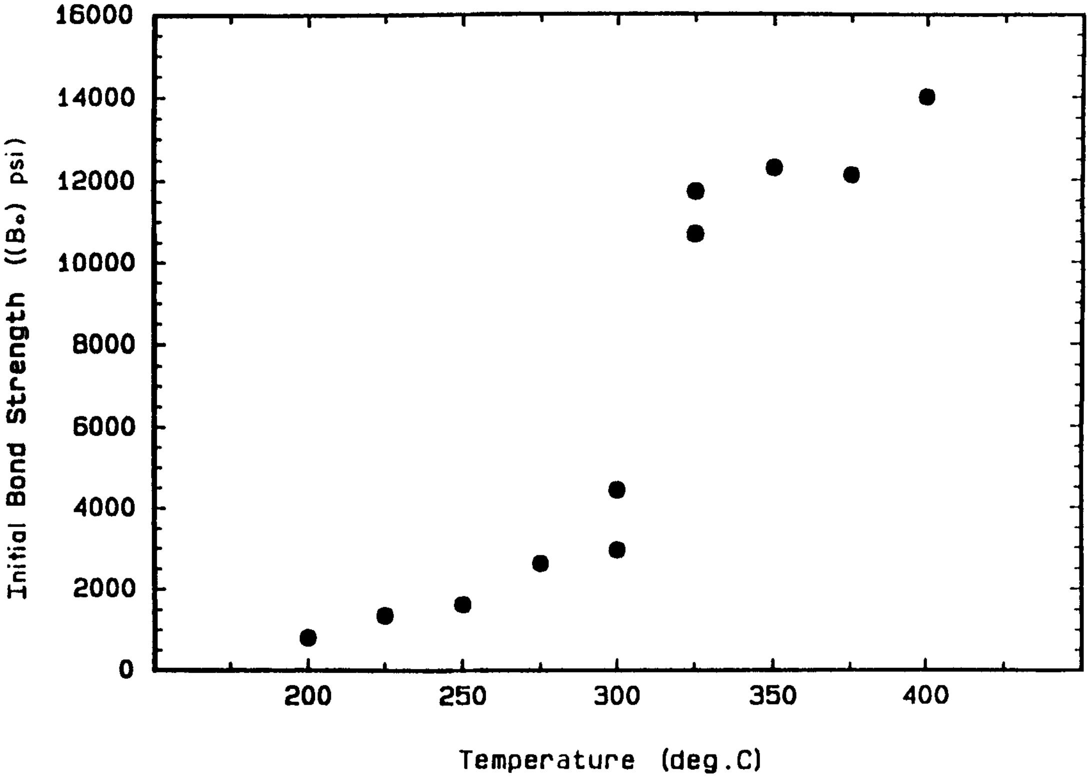

Fig. 4 Bond strengths established during the time required to reach thermal equilibrium, shown as a function of final bonding temperature.

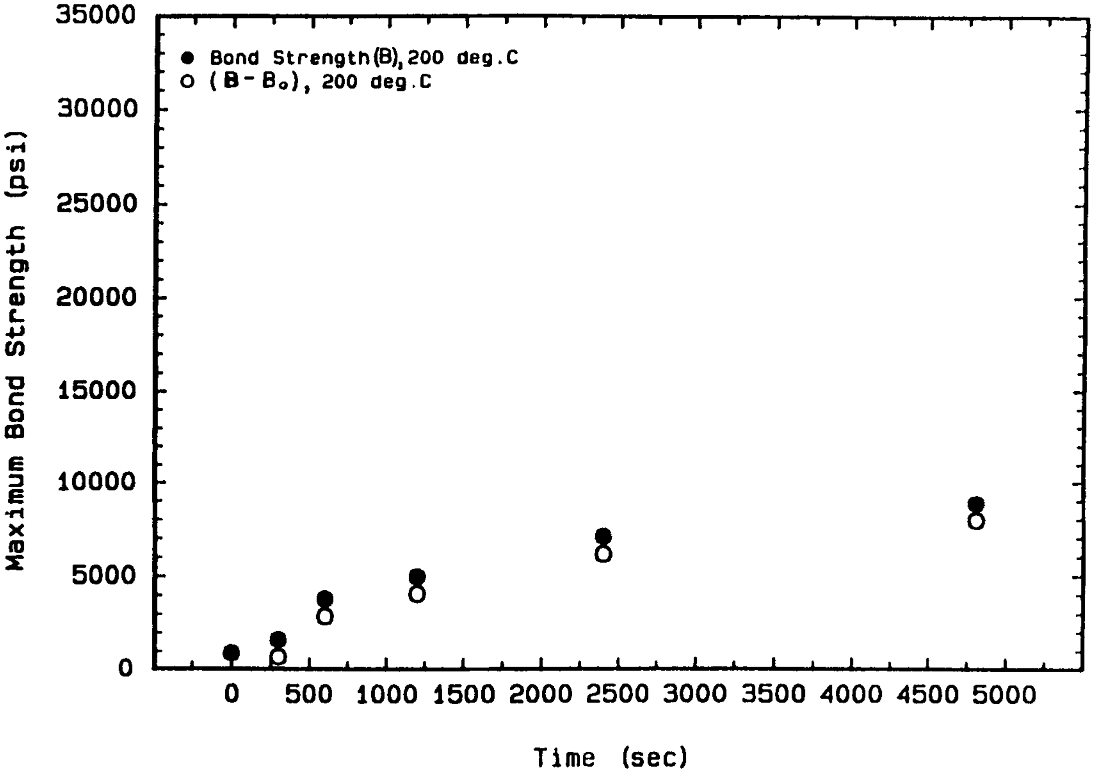

Fig. 5 Comparison of maximum bond strength and the bond strength attributed to the isothermal annealing time, at 473 K (200 °C), shown as a function of isothermal annealing time.

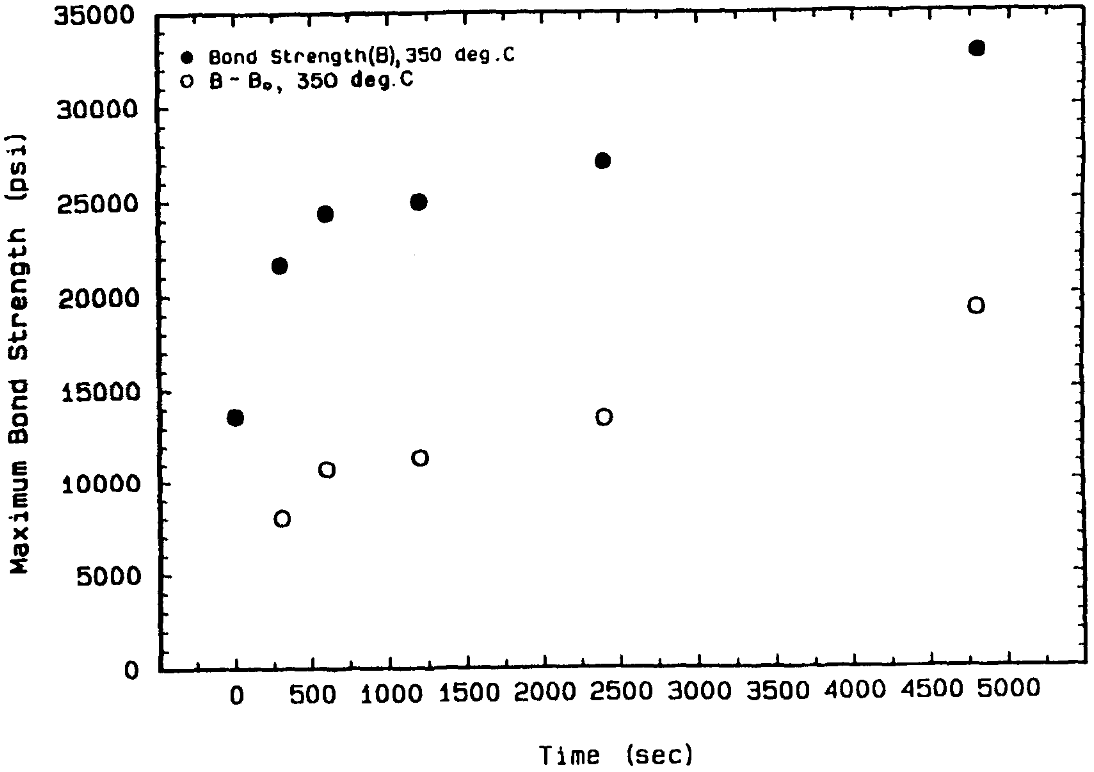

Fig. 6 Comparison of maximum bond strength and the bond strength attributed to the isothermal annealing time, at 623 K (350 °C), shown as a function of isothermal annealing time.

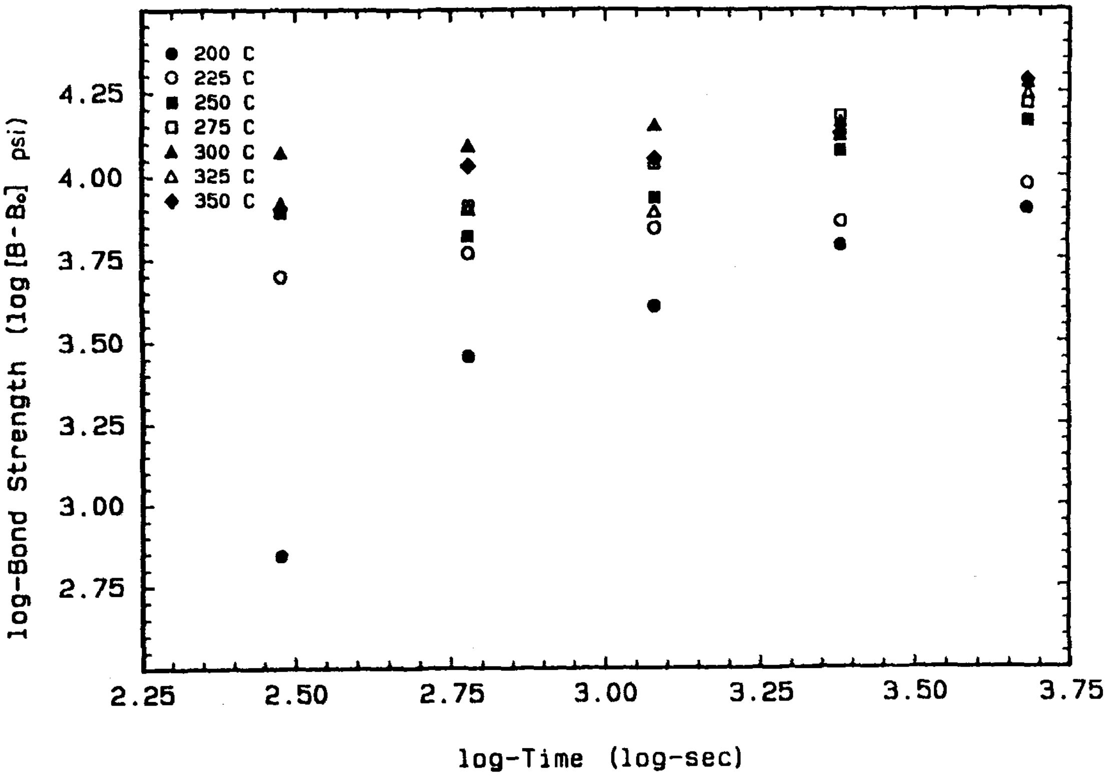

Fig. 7 Isothermal annealing bond strength (B–B_0), shown as a function of isothermal annealing time. Scales are in common logarithm form. Temperatures range from 473 to 623 K (200 to 350 °C).

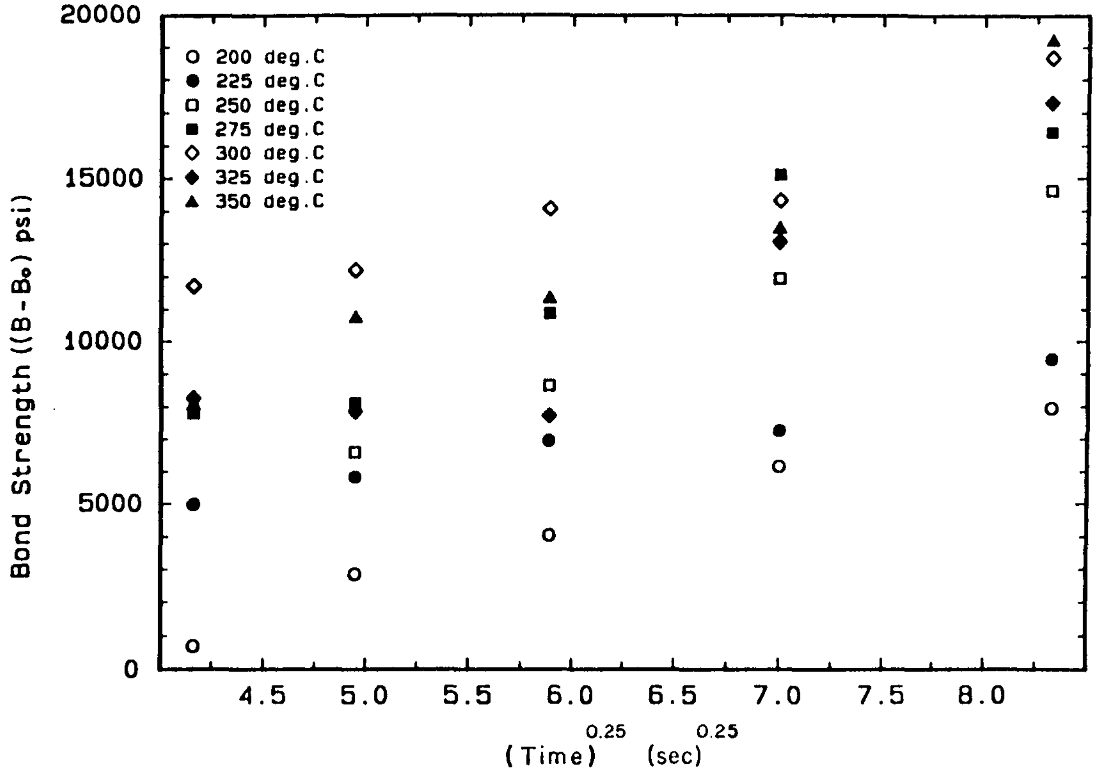

Fig. 8 Isothermal annealing bond strength, plotted as a function of isothermal annealing time taken to $n = 0.25$. Temperatures range from 473 to 623 K (200 to 350 °C).

others, it is difficult to achieve a mechanistic understanding of the rate-controlling process. Difficulty in the mechanistic interpretation results from the continuous change in microstructural details controlling the bonding process (a decrease in real stress at the bonding interface occurs, even though the bonding load is constant). To achieve a physical interpretation of the apparent activation energy, an experiment that maintained constant stress and constant material conditions at the bonding interface would be required.

3.2 *Interpretation of Results*

The initial bond strengths established during the time required to reach thermal equilibrium were shown in Fig. 4 to abruptly increase as the target bonding temperature was increased through the 300 to 325 °C temperature range. Although a distinct step or discontinuous increase in the bond strength was observed, the slope or rate at which the initial bond strength, B_o, increased with temperature appeared relatively constant in both the high- and low-temperature regimes, as shown in Fig. 4.

The initial bond strength for these temperature regimes can be empirically represented by the following equations:

$$B_o = 31T - 14{,}151 \quad \text{for } T < 573\text{ K} \qquad [4]$$

$$B_o = 31T - 7351 \quad \text{for } T > 573\text{ K} \qquad [5]$$

where T is the absolute temperature, and B_o is given in units of pounds per square inch (psi). The temperature coefficient for the initial bond strength is identical in both equations. The second terms in the two equations are the constants that contain information about the discontinuity relationship and the instantaneous bond strength value for the specified temperature range.

If Eq 4 is set equal to zero, then the temperature at which the initial bond strength B_o becomes greater than zero can be determined. By performing the calculation for this boundary condition, a temperature of 184 °C can be determined. The 184 °C temperature value represents the temperature for the initial measurable bond strength under this particular set of bonding conditions. It is anticipated that with an increasing applied load used during bonding, the minimal bonding temperature can be lowered further.

Comparing these bonding results to copper annealing data,[38-40] several similarities can be observed. Clarebrough *et al.*[40] reported the importance of deformation in influencing the recrystallization temperature of copper. The recrystallization temperature range observed by Clarebrough *et al.*[40] (325 to 350 °C) was similar to the temperature range observed in this investigation for a finite change in bonding mechanism. Bonding mechanism changes were observed at ~325 °C for both the preliminary tests (see Fig. 1) and for the more extensive primary bonding studies that followed (see Fig. 4). This comparison between the present investigation and the work of Clarebrough *et al.*[38-40] suggests that low-temperature bond strength in copper can be greatly influenced by *dynamic recrystallization.*

Understanding the processes that occur along the bonding interface prior to and during heating is important to further improvements in low-temperature solid-state bonding. In general, the morphology of the bond interface may be used to promote an

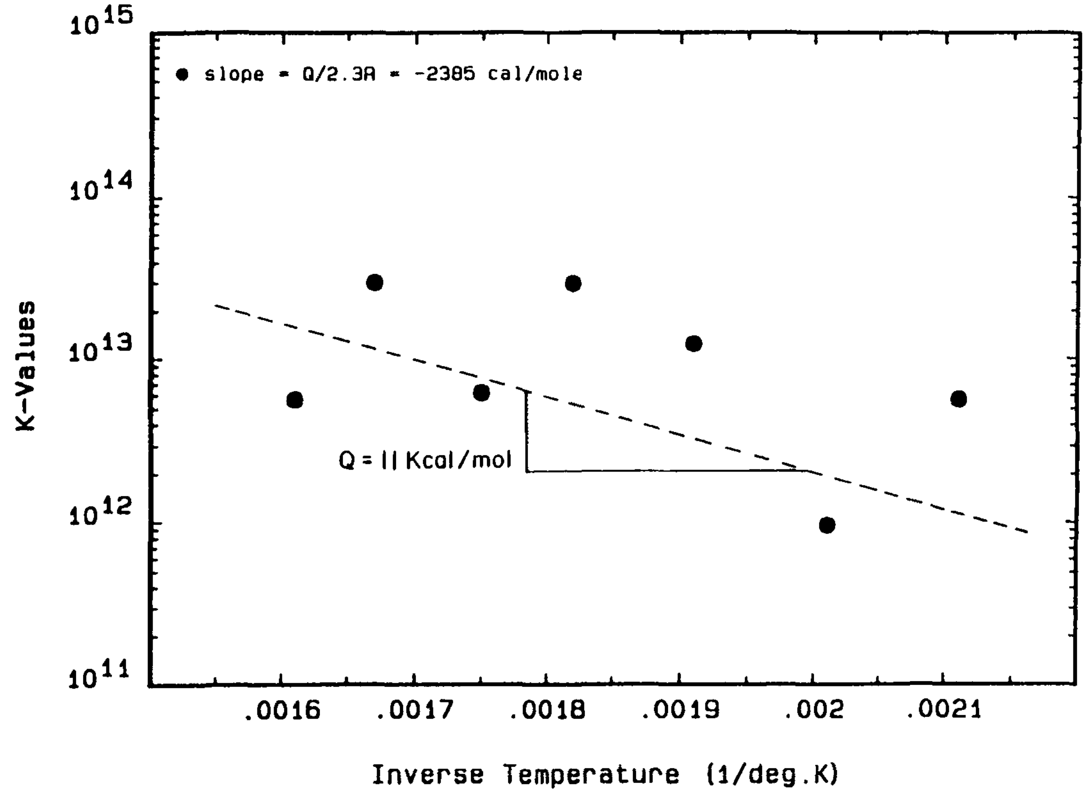

Fig. 9 Logarithmic rate constant K (see Eq 3) as a function of reciprocal absolute temperature, revealing the apparent activation energy for the bonding of copper.

increase in contact area through the process of strain and deformation. The area of true interfacial contact is very small initially, and the concentrated stress at the contacting asperities is greater than the yield stress. These asperities plastically deform on contact, and the contact area increases until the local stresses decrease to a value below that of the yield strength.

To understand the limits of the low-temperature bonding process and to assist in bond strength predictions, it is desirable to develop an empirical expression. This expression must allow for the prediction of bond strength through the complete bonding thermal cycle, encompassing both heating and isothermal segments. In considering the functional relationship of the initial bond strength, B_o, it is assumed that the minimum temperature at which bonding has been determined to occur is 457 K (184 °C).

The initial bond strengths are given by Eq 4 and 5 for the two distinct isothermal bonding temperature ranges. By incorporating the heating rate into these equations, a time-dependent equation for the bonding process can be expressed.

The expression for the determination of the initial bond strength in the temperature range 457 to 573 K for this specific heating rate (0.26 K/sec where $T > 573$ K) becomes:

$$B_o = 8.06\,t - 1708 \quad T < 573\ \text{K} \qquad [6]$$

Similarly, the initial bond strength for the upper temperature range 573 to 673 K can be determined by considering the discrete increase in bond strength, ΔB_o, that occurs over the temperature range of 573 to 623 K. This high-temperature initial bond strength equation becomes:

$$B_o = 8.06\,t + 5092 \quad T > 573\ \text{K} \qquad [7]$$

A comparison of the calculated results for the initial bond strength to the experimental data is shown in Fig. 10, where the empirical expressions represent the data quite well.

Substitution of Eq 6 and 7 into Eq 3 will quantify the bond strength for each temperature regime. However, the appropriate time intervals to be used must be considered carefully. The time in Eq 6 and 7 begins at the moment when the two specimen halves are brought together and the heating cycle begins. The end of the heating time occurs when the isothermal temperature is reached, or when the value dT/dt becomes zero. The time in Eq 3 begins when the heating cycle ends and continues at constant temperatures until cooling is initiated. Thus, the total time (t_t) of the bonding cycle is the sum of the heating segment (t_h) and the isothermal segment (t_l). The final form of the bond strength equation can be written for two temperature ranges:

$$B = (8.06\,t_h - 1708) + [Kt_l]^{0.25} \quad T < 573\ \text{K} \qquad [8]$$

$$B = (8.06\,t_h + 5092) + [Kt_l]^{0.25} \quad T > 573\ \text{K} \qquad [9]$$

where K is an exponential expression (see Eq 2) with the apparent activation energy of 11 kcal/mol. Equations 8 and 9 are plotted in Fig. 11 for bonding temperatures of 475 and 623 K, respectively. The model represents the data reasonably well. The experimental bond strength data for seven temperatures between 473 and 623 K are also shown in Fig. 11.

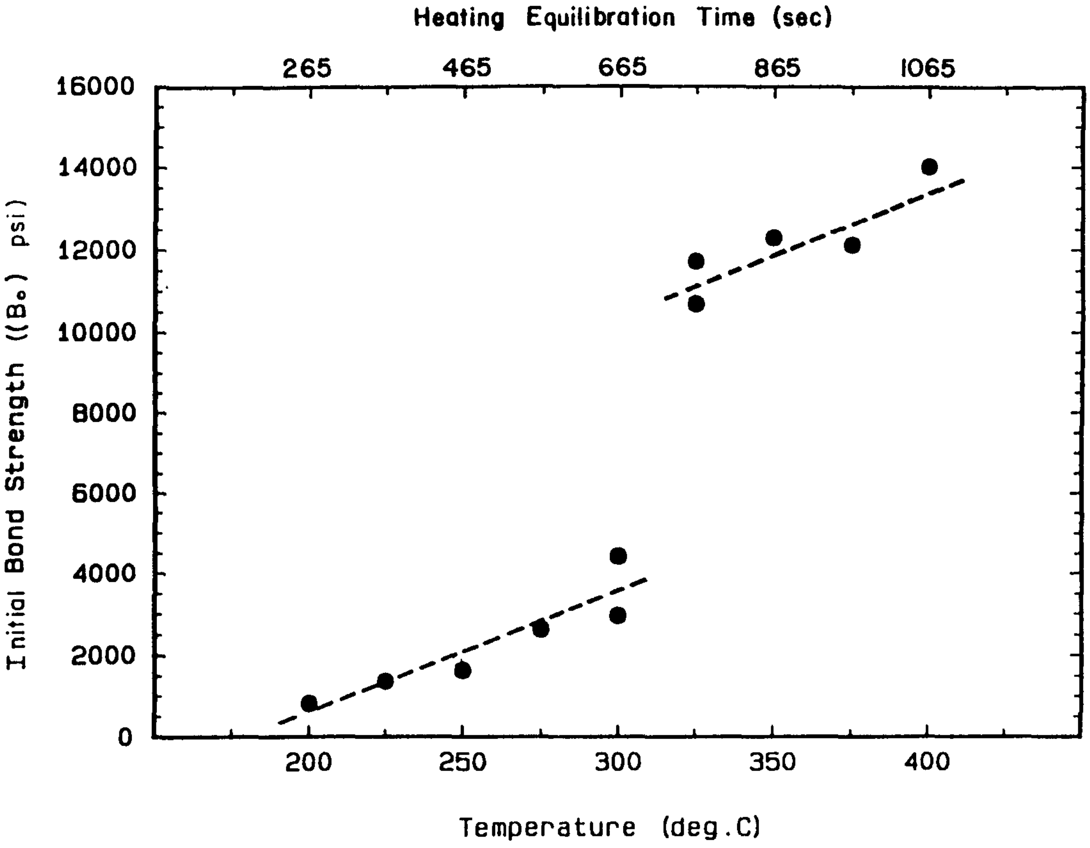

Fig. 10 Initial bond strength data of tough pitch copper for temperatures and equilibration time indicated. Solid lines are the empirical equations given in the text (Eq 6 and 7).

4 Conclusions

Bond strengths of low-temperature copper bonds have been characterized in copper for the temperature regime of 473 to 623 K. Low-temperature solid-state bonding of copper is a time/temperature-dependent process that is primarily controlled by deformation. A time-dependent exponent of 0.25 and an apparent activation energy of approximately 11 kcal/mol were determined.

Separation of the various stages in the bonding cycle—initial contact, nonequilibrium heating, and the isothermal anneal—are essential in determining an understanding of the mechanistic nature of low-temperature solid-state bonding. An empirical equation for predicting low-temperature solid-state bond strength for copper as a function of bonding time and temperature was determined.

Acknowledgments

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References

1. R.F. Tylecote, *The Solid Phase Welding of Metals*, St. Martins Press, New York (1968).
2. D.R. Milner and G.W. Rowe, *Metall. Rev.*, *7*(28), 433-480 (1962).
3. N. Bay, *Weld. J*, *62*(5), 137s-142s (1983).
4. N. Bay, *Brit. Weld. J. Met. Const.*, *18*(6), 369-372 (1986).
5. N. Bay, *Brit. Weld. J. Met. Const.*, *18*(8), 486-490 (1986).
6. C. Clemensen, O. Juelstorp, and N. Bay, *Brit. Weld. J. Met. Const.*, *18*(10), 625-629 (1986).
7. C.H. Hamilton, *Titanium Science and Technology*, Proc. 2nd Int. Conf., R.I. Jaffee and H.M. Burte, Ed., Vol. 1, Plenum Press, New York, 625 (1973).
8. R.A. Nichting, G.R. Edwards, D.L. Olson, and B.B. Rath, "Theories of Low Temperature Solid State Bonding," Proc. Int. Conf. on Trends in Welding Research, Gatlinburg, TN, May 19-22, 733-738, ASM, Metals Park (1986).
9. D.L. Olson and A.L. Liby, Joining III: Diffusion Bonding, in *Beryllium Science and Technology*, Vol. 2, Plenum Press, New York, 275-296 (1979).
10. W.H. King and W.A. Owczarski, *Weld. J.*, *47*(10), 444s-450s (1968).
11. J.M. Gerken and W.A. Owczarski, "A Review of Diffusion Welding," Welding Research Council, Bull. 109, Oct (1965).
12. V.D. Taran, *Svar Proizv*, *11*, 12-14 (1958).
13. B. Derby and E.R. Wallach, *Met. Sci.*, *16*(1), 49-56 (1982).
14. E. Elliott, E.R. Wallach, and I.A. Bucklow, *J. Mater. Sci.*, *15*, 2823 (1980).

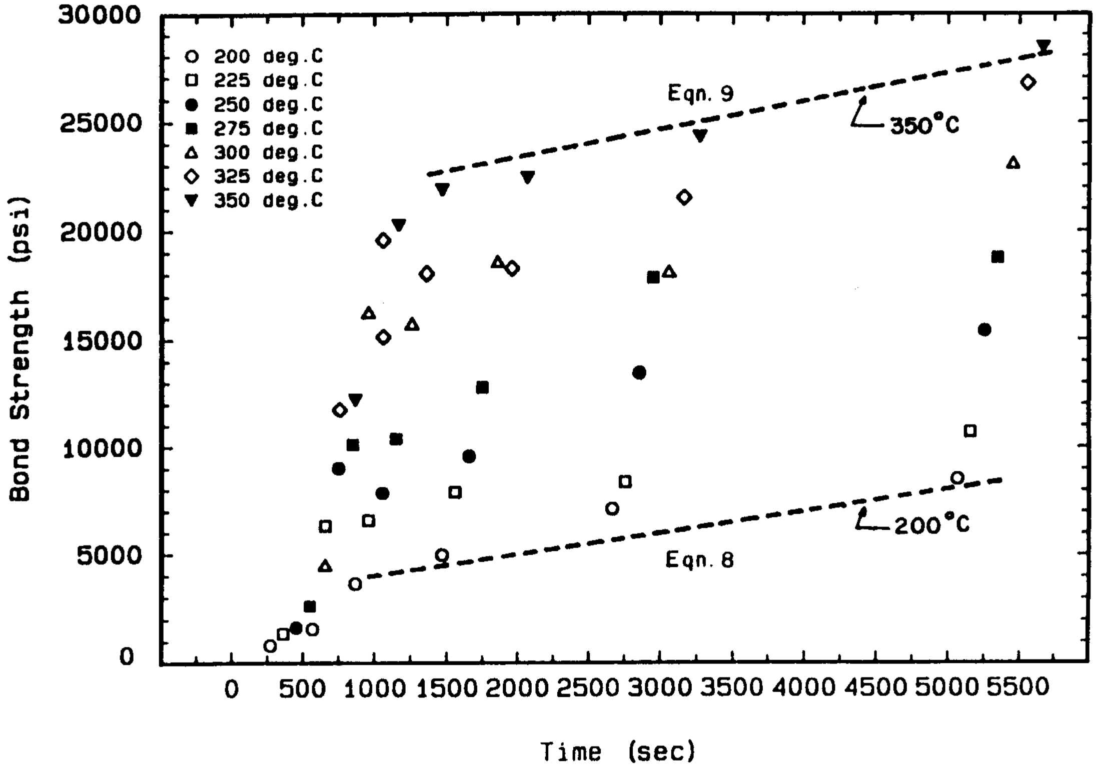

Fig. 11 Comparison among experimental data and the empirical equations given in the text (Eq 8 and 9).

15. D.J. Allen and A.A.L. White, Sintering Processes in Diffusion Bonding, in *The Joining of Metals: Practice and Performance*, 96-103, The Institution of Metallurgists, London, (1980).
16. A.C. Moore and D. Tabor, *Brit. J. Appl. Phys.*, *3*, 299-301 (1952).
17. S.B. Ainbinder and E.F. Klokova, *Latvijas psr Zinatnu Akad Vestis*, *10*(87), 113-128; Brutcher Translation No. 3755, *Mechanism of Bonding in Cold Welding* (1954).
18. F.P. Bowden and G.W. Rowe, *Proc. Roy. Soc.*, *233A*, 429-442 (1956).
19. T. Spalvins and D.V. Keller, *Trans. Vac. Met. Conf. 1962*, R.F. Bunshah, Ed., American Vacuum Soc., Boston, 149-155 (1963).
20. W.H. King and W.A. Owczarski, *Weld. J.*, *46*, 289s-298s (1967).
21. M.G. Nicholas and D.R. Milner, *Brit. Weld. J.*, *9*(8), 469-475 (1962).
22. K.J.B. McEwan and D.R. Milner, *Brit. Weld. J.*, *9*(7), 406-420 (1962).
23. J.S. McFarlane and D. Tabor, *Proc. Roy. Soc. London, Ser. A*, *202*(1069), 224-243 (1950).
24. G. Schoeck, Theories of Creep, in *Mechanical Behavior of Materials at Elevated Temperatures*, J.E. Dorn, Ed., McGraw Hill, New York, 79-107 (1961).
25. P.H. Kammer, R.E. Monroe, and D.C. Martin, *Weld. J.*, *48*(3), 116s-124s (1969).
26. A.A.L. White and D.J. Allen, Elimination of Voids and Oxide in Diffusion Bonding, in *Advances in Welding Processes*, Vol. 1, Harrogate, England (1975).
27. H.A. Mohamed and J. Washburn, *Weld. J.*, *54*(9), 302s-310s (1975).
28. B. Derby and E.R. Wallach, *Met. Sci.*, *18*(9), 427-431 (1984).
29. H. Kellerer and L.H. Milacek, *Weld. J.*, *49*, 219s (1970).
30. B. Derby and E.R. Wallach, *The Joining of Metals: Practice and Performance*, 96-103, The Institution of Metallurgists, London, (1981).
31. B.N. Chapman, *J. Vac. Sci. Technol.*, *11*(1), 106-113 (1974).
32. D.M. Mattox, *J. Vac. Sci. Technol.*, *10*(1), 47-52 (1973).
33. J. Ayers, private communication, EG & G Rocky Flats Plant, Golden, CO (1989).
34. J. Engl and G. Heidtkamp, *Zeit. Physik.*, *95*, 30 (1935).
35. P. Ludwik, *Zeit. Physik. Chem.*, *91*, 232 (1916).
36. E. Hart, *Acta Metall.*, *5*, 597 (1957).
37. N.H. Nachtrieb and G.S. Handler, *Acta Metall.*, *2*, 797 (1954).
38. L.M. Clarebrough, M.E. Hargreaves, D. Michell, and G.W. West, *Proc. Roy. Soc. (London)*, *215A*, 507 (1952).
39. L.M. Clarebrough, M.E. Hargreaves, and G.W. West, *Proc. Roy. Soc. (London)*, *232A*, 252 (1955).
40. L.M. Clarebrough, M.E. Hargreaves, and G.W. West, *Philos. Mag. Ser. 7*, *44*(355) (1953).