Tin-Based Reactive Solders for Ceramic/Metal Joints

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Contact angle measurements on silicon-nitride substrates were conducted on tin-based alloys, containing titanium and zirconium, to determine the suitability of these alloys as filler metals for low-temperature joining of ceramics. Titanium-containing alloys exhibited excellent wettability characterized by contact angles less than 20 deg, whereas the Zr-containing alloys exhibited contact angles around 50 deg. The superior wettability of the Sn-Ti alloys is attributed to the higher activity coefficient of Ti in Sn-Ti alloys. The liquidus temperature of the Sn-Ti alloys is in the 400 °C to 600 °C range. Hence, these alloys are expected to reduce the residual stress problem.

I. INTRODUCTION

RECENT advances in ceramics and the increasing use of ceramic materials have provided an impetus for studying new methods of joining metals and ceramics. Examples of ceramic-metal components include structural ceramic-metal components (such as heat engine components), wear parts, tool materials, electrical feedthroughs, and metal contacts for ceramic superconductors. Among the various joining processes (such as diffusion bonding, plasma spraying, brazing, as well as physical and chemical vapor deposition), brazing is expected to emerge as an important joining technique. The most important step in using brazing for ceramics is the design of the filler metal. Hence, this area has received considerable attention.[1-19]

The critical problem in designing filler metals for brazing and soldering of ceramics is the poor wettability of conventional filler metals on ceramics. To overcome this problem, reactive metals are added to the filler metal.[1-18] These reactive metals promote flow by decomposing a thin layer of the ceramic. Recent efforts in the literature have been directed toward design of suitable filler metals, as well as toward investigating the oxidation behavior of such filler metals.[20] These investigations have centered on designing filler metals for structural ceramics/metal joints that are expected to operate at high temperatures (>600 °C). Hence, the filler metals designed possessed a liquidus temperature that exceeded 800 °C. The brazing temperature was expected to be in the 800 °C to 1000 °C range.

Brazing with fillers that possess a liquidus in the 800 °C to 1000 °C range leads to severe residual stresses from the mismatch in the thermal expansion coefficients of the ceramic and metal.[21,22] These stresses are often severe enough to cause cracking on cooldown from the joining temperature. The popular solution to this problem is the use of interlayer materials such as Mo, Cu, Kovar, and Invar, which possess a thermal expansion coefficient intermediate to the ceramic and the metal.[22] Thus, the final joint is often very complex and possesses several intermediate layers.

There are several ceramic components (including some for ceramic heat engines) where the service temperature of the ceramic-metal joint is much lower than 600 °C. Examples of these would include electrical feedthroughs (expected operating temperature <100 °C) and wear parts in the heat engine, such as ceramic sleeves on rocker arms and ceramic ends on push rods (expected operating temperature 100 °C to 150 °C). For such components, it is preferable to use a lower brazing temperature and thereby minimize the residual stress problem. Lower brazing temperatures would also eliminate the need for interlayers and lead to a simpler joint. Brazing at lower temperatures (or soldering) implies using filler metals that possess a much lower liquidus (400 °C to 600 °C) than the filler metals currently being researched in the literature.

It should be noted that the terms "brazing" and "soldering" are not interchangeable. According to the American Welding Society, the term "soldering" refers to a joining process conducted below 450 °C, whereas the term "brazing" refers to a joining process conducted above 450 °C. In both processes, a filler metal is interposed between the materials to be joined and the entire assembly heated to the joining temperature. During joining, only the filler metal is in the liquid state. Thus, despite being classified as distinct processes, both soldering and brazing are very similar metallurgically.

In this paper, we present the results of our efforts to develop tin-based solders for low-temperature joining of silicon nitride. To our knowledge, this is the first attempt at developing low-temperature filler metals for ceramic-metal joints. It is envisaged that these solders will be used for direct brazing or soldering of ceramics. The term "direct brazing" implies that no surface pretreatment of the ceramic (such as metallizing) will be necessary. The proposed process will be conducted in vacuum or under an argon atmosphere to protect the reactive component of the filler metals from oxidation. Use of fluxes will not be necessary during joining, thereby obviating the need for any flux development. Hence, these solders may be looked upon as "self-fluxing" solders.

Our results on contact angle measurements on silicon nitride indicate that it is possible to wet the ceramic using tin-based solders containing titanium. The microstructural observations indicate the presence of an interfacial layer which is rich in the reactive component of

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the filler metal. This confirms that wetting in these systems is controlled by reactive decomposition of the ceramic.

II. EXPERIMENTAL

Experimental alloys were prepared by arc-melting the constituent metals under an argon atmosphere. The weight loss on melting was less than 1 pct for all alloys. A piece of the arc-melted alloy nugget was used for contact angle measurements.

Details of the contact angle setup and the silicon nitride have been published earlier.[20] Samples were heated at 5 °C/min to 950 °C, under a vacuum of 8 mPa, and held there for an hour. Using the contact angle setup, it was possible to obtain the contact angle as a function of temperature, and as a function of time, during the isothermal hold at 950 °C.

Samples from the wetting test were sliced perpendicular to the ceramic-metal interface, prepared metallographically, and examined using a scanning electron microscope equipped with an energy-dispersive X-ray analyzer.

III. RESULTS

Tin was selected as the base metal for these studies. Since pure tin does not wet silicon nitride, it was decided to add incremental amounts of titanium and zirconium to induce wetting on silicon nitride. The choice of titanium and zirconium as reactive metals was based on earlier studies[20] that revealed these two elements to be the only reactive metals capable of lowering the contact angle of the alloy to less than 15 to 20 deg on silicon nitride. Theoretically, a contact angle of less than 90 deg is taken to represent a state of wetting. However, from a practical standpoint, it is necessary to achieve much lower contact angles. A lower contact angle enhances capillary action, ensuring that the filler metal penetrates all joint clearances and thereby eliminates any interfacial voids. Thus, ideally, one would prefer a zero contact angle (such as that obtained during soldering of metals with metallic solders). However, contact angles less than 20 deg usually provide sufficient capillarity for brazing purposes. Hence, in our investigations, alloys exhibiting contact angles less than 15 to 20 deg are judged satisfactory for brazing.

The Sn-Ti and Sn-Zr phase diagrams[23] indicate that Ti and Zr are not soluble in tin in the solid state. Rather, the diagrams comprise several intermetallic compounds, possessing high melting points. The liquidus lines indicate that alloys possessing Ti or Zr contents greater than 10 at. pct have a liquidus temperature that exceeds 500 °C. Hence, it was decided to constrain the maximum addition of Ti or Zr to less than 10 pct.

Three levels of reactive metal (Ti and Zr) additions were tested for wettability on Si_3N_4: (1) 2 pct, (2) 5 pct, and (3) 7 pct (all compositions in atomic percent). During arc-melting, the reactive metal dissolved in the liquid tin matrix; however, on subsequent solidification, the reactive metal precipitated out of solution and formed an intermetallic compound (Ti_6Sn_5 in the Sn-Ti alloys and

$ZrSn_2$ in the Sn-Zr alloys). The intermetallic compound was present as a thin skin covering the as-cast nugget and remained firmly adhered to the nugget even after subsequent sectioning.

A. Contact Angle Data

Figure 1 depicts the variation of the contact angle with temperature during heatup of the sample, while Figure 2 depicts the variation of the contact angle with time during the isothermal hold at 950 °C, for all the seven alloys tested. All alloys bonded to the ceramic. The wetting curves for all alloys, other than the Sn-0.5 pct Ti alloy, show three distinct stages in the wetting process. The temperature range corresponding to each stage depends on the specific alloy composition.

Examination of Figure 1 reveals several distinctive features regarding the three stages observed in the variation of contact angle with temperature. Stage I is the melting stage. On melting, there is a small period of equilibration, following which the molten droplet assumes a fairly large contact angle (which is composition dependent), usually in excess of 100 deg. In stage II, the temperature rise has little effect on the contact angle. Stage III is characterized by a rapid reduction in the contact angle. By the end of stage III, the droplet has equilibrated to a steady contact angle, which remains largely invariant during the subsequent isothermal holding period at 950 °C (Figure 2). As noted earlier, the exact temperatures, demarcating the onset of each stage, vary with the composition of the alloy.

In general, all Ti alloys, except the Sn-0.5 pct Ti alloy, exhibited much lower final contact angles than the corresponding Zr alloys. The final contact angle for all the Zr alloys was approximately 50 deg and was insensitive to the Zr content. In contrast, the final contact angle for the Ti alloys varied with the Ti content. For example, the 2 pct Ti alloy exhibited a final angle of 18 deg, whereas the 5 pct Ti alloy exhibited a minimum contact angle of 10 deg. From the data, it is clear that only the Sn-Ti alloys are promising solders, since these alloys alone met the prescribed requirement of a contact angle less than 20 deg. It is also clear that the level of Ti must be in excess of 2 pct, since the Sn-0.5 pct Ti alloy (although
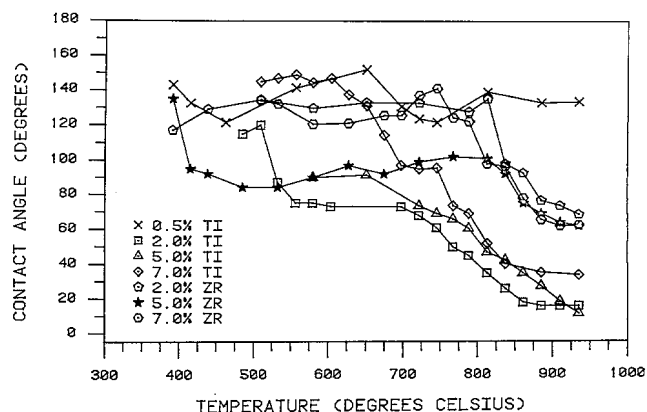

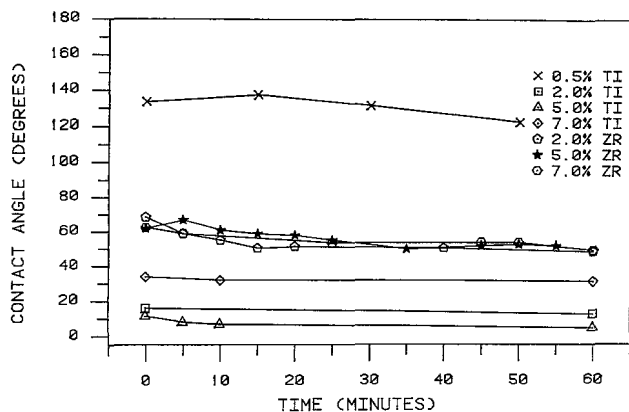Fig. 1—Flow behavior of tin-based alloys on silicon nitride during heatup at 5 °C/min.

Fig. 2—Flow behavior of tin-based alloys on silicon nitride during the isothermal hold at 950 °C following heatup depicted in Fig. 1.

it did bond to the ceramic) exhibited a large final contact angle.

It is clear from the phase diagram and the wetting tests that the liquidus temperature for the Sn-Ti solders lies in the desired range (400 °C to 600 °C). However, in this temperature range, these alloys exhibit high contact angles (80 to 150 deg). To ensure a low contact angle, the joining temperature for these alloys must lie in the 850 °C to 950 °C range. The high temperatures are needed to promote the interfacial reaction that causes wetting. Thus, the proposed tin-based fillers would be similar to the silver- and copper-based brazing alloys, insofar as the joining temperature is concerned. However, during the post-joining cooldown, the copper- and silver-based solders solidify at high temperatures (800 °C), whereas the tin-based fillers would solidify at much lower temperatures (400 °C to 600 °C). Thus, on cooling to room temperature, joints fabricated using tin-based solders would accrue far less residual stress. Evidence of this is obtained on examination of the wetted samples. Wetting test samples for the Ag- and Cu-based brazing alloys often crack on cooling to room temperature. However, no evidence of cracking was seen in the wetted samples for the tin-based solders.

B. *Microstructural Observations*

Figures 3(a) and (b) depict the microstructure of the Sn-5 pct Ti alloy, as seen in the scanning electron microscope, whereas Figures 3(c), (d), and (e) represent the X-ray maps for Sn, Ti, and Si, respectively. The microstructure is comprised of pure tin with second-phase particles interspersed in it. The X-ray maps reveal an absence of Ti in the main body of the alloy. Instead, the Ti appears concentrated in an interfacial layer approximately 3 to 4 μm thick. In addition to the X-ray maps, compositional analysis was also conducted at the locations marked "x" and "y" in Figure 3(a). The composition at location "x" is pure tin, whereas the composition at location "y" corresponds to the composition of the Ti_6Sn_5 intermetallic.

Similarly, Figures 4(a) and (b) depict the microstructure for the Sn-5 pct Zr alloy, whereas Figures 4(c), (d), and (e) represent the X-ray maps for Sn, Zr, and Si, respectively. Compositional analysis at locations "X"

and "Y" in Figure 4(b) reveal that the microstructure comprises a pure tin matrix, containing $ZrSn_2$ intermetallics as a second phase. In addition, a thin discontinuous interfacial layer, rich in Zr and approximately 2 μm thick, is also seen.

Thus, there are similarities in the general features of the microstructures for the Sn-Ti and Sn-Zr alloys. In both cases, the matrix is pure tin and interspersed in it are second-phase particles containing the reactive metal (Ti_6Sn_5 and $ZrSn_2$). Further, in both cases, an intermetallic layer, rich in the reactive metal, is evident. However, in the case of the Zr alloy, the intermetallic layer is thinner and is discontinuous. In addition, the volume fraction of the second phase ($ZrSn_2$) is much greater in the case of the Zr alloy.

IV. THERMODYNAMIC ANALYSIS

Based on the microstructural evidence, the available phase diagrams, and calculated heats of mixing for binary transition metal solutions, it is possible to rationalize the observed differences in wettability between the Zr and Ti alloys. It is known that chemical reaction between the silicon nitride and the reactive metal controls the wetting behavior by formation of new compounds, presumably titanium and zirconium nitrides. Hence, it is logical to examine an Ellingham diagram for nitride stability to investigate the relative stability of titanium and zirconium nitrides with respect to silicon nitride.

The Ellingham diagram[24] reveals that both Ti and Zr possess nitrides that are far more stable than silicon nitride. Further, at unit activity, ZrN is stabler than TiN, although the difference in standard free energies is very small. Hence, if the activity coefficients for Zr and Ti in tin solutions were similar, one would expect Zr alloys to have a similar or stronger tendency to decompose silicon nitride (for solutions of identical composition such as Sn-5 pct Ti and Sn-5 pct Zr). In such a case, the Zr alloys would possess lower contact angles. However, the wetting experiments indicate that the reverse is true. This implies that at identical compositions, the activity coefficient for Zr alloys in Sn-Zr solutions is smaller than the corresponding activity coefficient for Ti in Sn-Ti alloys.

The available phase diagrams and the computed heats of mixing of Sn-X alloys support the conclusion that the activity coefficient of Zr in Sn-Zr alloys is much smaller than the corresponding activity coefficient of Sn-Ti alloys. The calculations of Miedema et al.[25] indicate that at infinite dilution, the heat of mixing for Zr is −172 kJ/gm-atom, whereas that for Ti is −101 kJ/gm-atom. The published phase diagrams indicate that at 950 °C, the solubility of Ti in Sn is 26 pct, whereas that of Zr is 12 pct. Clearly, there is a much greater tendency for compound formation in the Sn-Zr system in comparison with the Sn-Ti system. This leads to a lower activity coefficient of Zr in Sn-Zr alloys and, hence, to a lower Zr activity in Sn-Zr alloys.

The microstructural observations support the above reasoning. A larger volume fraction of the second phase ($ZrSn_2$) is evident in the main body of the Zr alloy, due to the stronger tendency for compound formation.
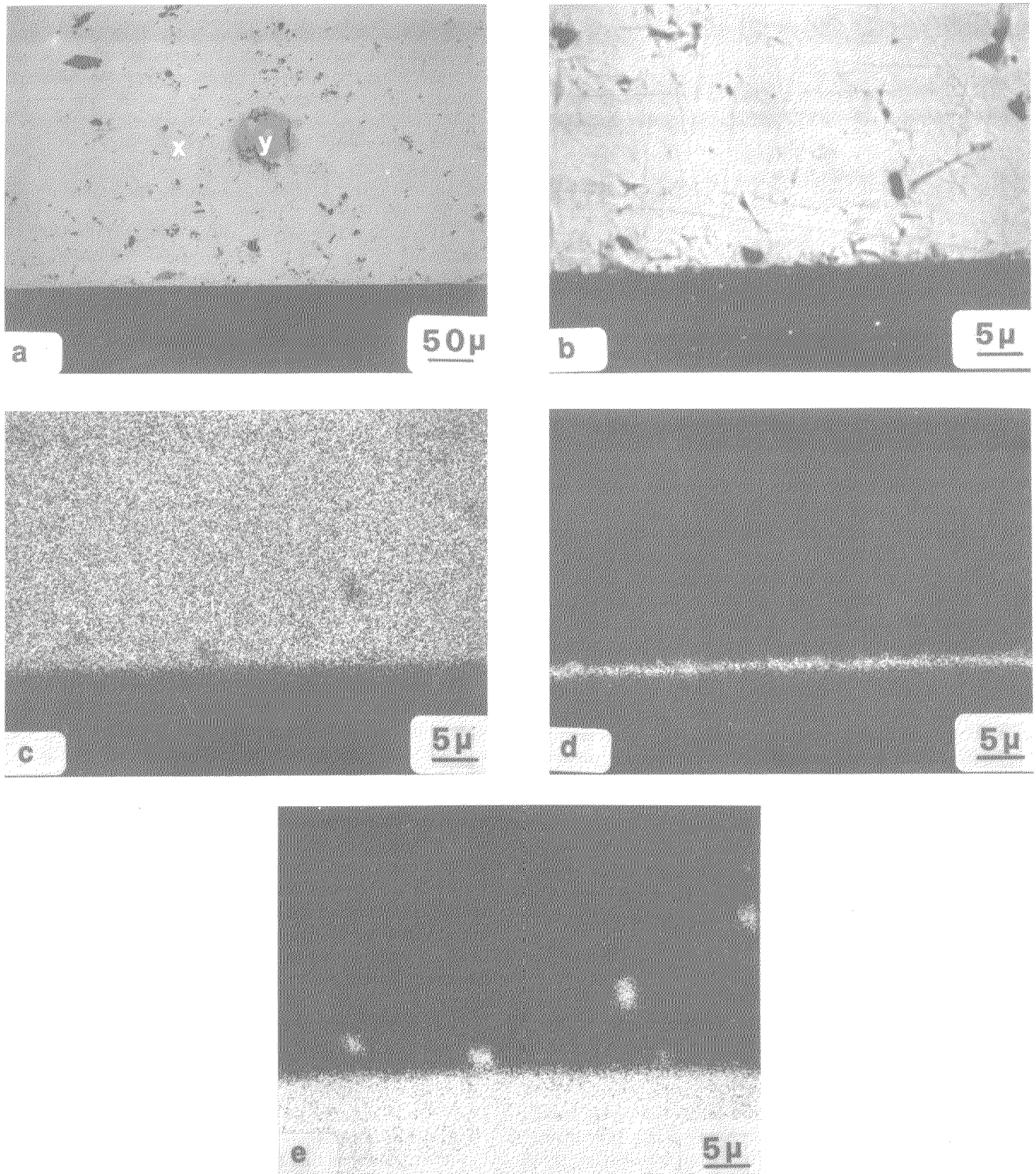
Fig. 3—Microstructures (a, b) and X-ray maps corresponding to (b) for an Sn-5 pct Ti alloy brazed into silicon nitride. (c) Sn X-ray map; (d) Ti X-ray map; (e) Si X-ray map.

Consequently, the activity of Zr in the alloy is lower. Hence, the decomposition reaction in the Sn-Zr alloy proceeds to a lesser extent than the corresponding reaction for the Sn-Ti alloy. This is clearly reflected in the difference in interfacial layer thickness and in the lack of continuity of the interfacial layer in the case of the

Zr alloy. Consequently, the Zr alloys wet the silicon nitride to a lesser degree and exhibit higher contact angles.

Previous experiments on Ag- and Cu-based brazing filler metals have consistently revealed a similar trend. The Ti alloys always wet better than the Zr alloys of identical compositions. This trend is seen not only in our
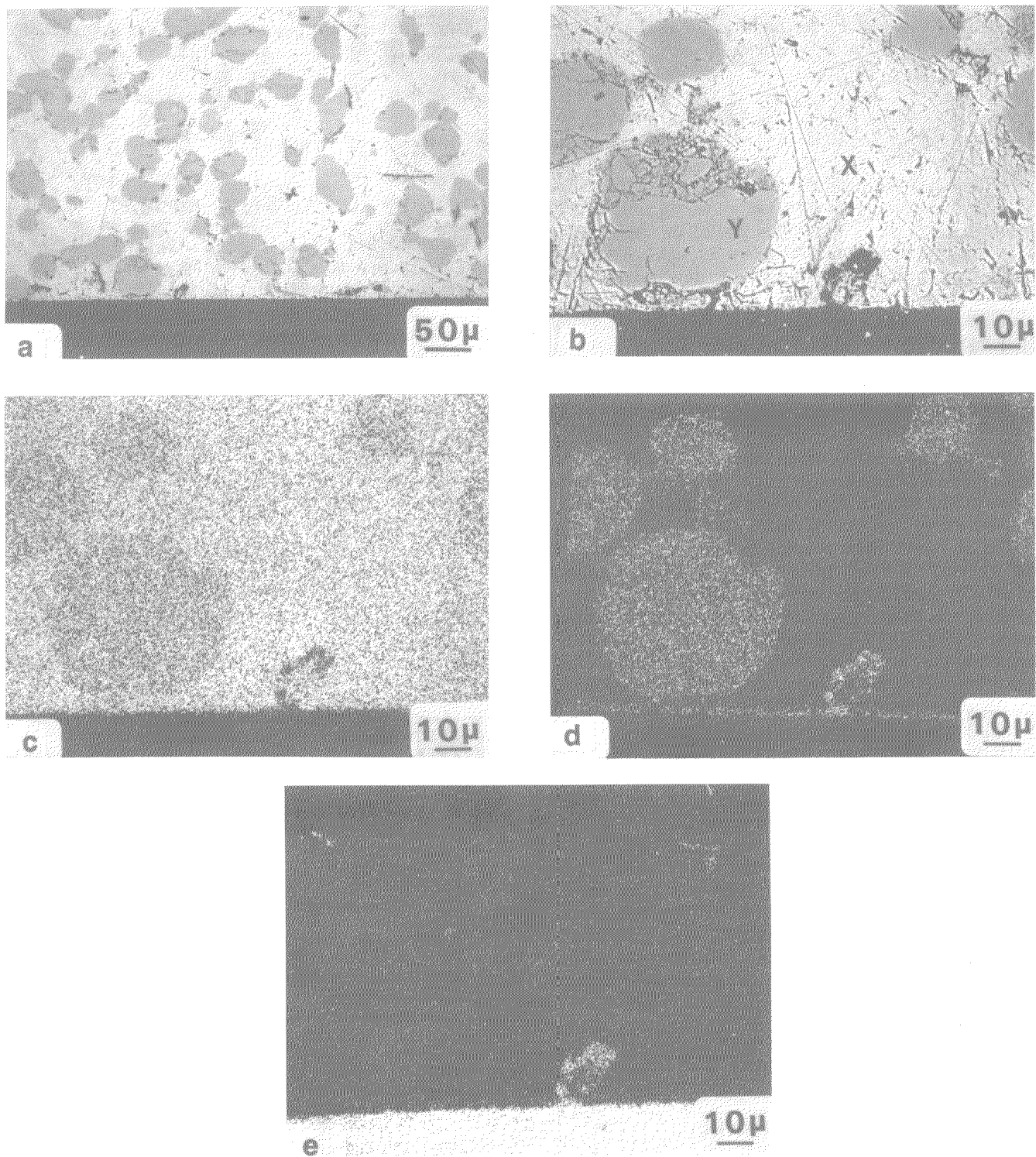
Fig. 4—Microstructures (*a, b*) and X-ray maps corresponding to (b) for an Sn-5 pct Zr alloy brazed into silicon nitride. (*c*) Sn X-ray map; (*d*) Zr X-ray map; (*e*) Si X-ray map.

experiments[26] but also in the data available in the literature.[5] Miedema *et al.*'s data[25] on Cu-*X* and Ag-*X* alloys reveal that *X*-Ti heats of solution are less negative than *X*-Zr heats of mixing (where *X* is Cu, Ag). This trend in enthalpies of solution closely resembles the trend observed in the case of the Sn-Ti and Sn-Zr binary al-

loys. For example, the heat of solution of Zr in Ag is −121 kJ/gm-atom, whereas for Ti in Ag, it is −55 kJ/gm-atom. Similarly, the heat of solution of Zr in Cu is −142 kJ/gm-atom, whereas for Ti, it is −78 kJ/gm-atom. Thus, the lesser effectiveness of Zr as a reactive metal, despite possessing a stabler nitride than Ti, is linked to

its higher affinity for the matrix elements (Cu, Sn, and Ag).

One final experiment was conducted to understand stage II of the wetting process. In the temperature range corresponding to stage II, the contact angle is invariant with temperature. From the wettability experiments (which were conducted by ramping up the temperature), it was not clear whether the invariance of the contact angle with temperature implied a lack of driving force for the interfacial reactions or whether the reaction rate was very slow. To investigate the possibility of slow reaction rates, a piece of Sn-5 pct Ti alloy was placed on the ceramic, heated to 630 °C, and held there for 72 hours. No change in the contact angle was observed in this duration. The droplet bonded to the ceramic and exhibited an equilibrium contact angle of 85 deg. Thus, it is clear that stage II is caused by the lack of sufficient driving force for the interfacial reaction and not by a slow reaction rate. The driving force is large enough to cause bonding and to reduce the contact angle to less than 90 deg but not large enough to cause complete wetting. The possibility of thermal lag could be ruled out, since the thermal lag period was estimated to be a few minutes, whereas the observed duration of stage II was approximately 30 minutes during heatup at 5 °C/min.

The Sn-based fillers provide an interesting contrast to the Ag- and Cu-based filler metals. Silver- and copper-based alloys usually do not exhibit stage II of the wetting process, since the liquidus temperature of these alloys is much higher (800 °C). Hence, interfacial reactions commence almost immediately on melting, thereby eliminating stage II of the wetting process. The Sn-based alloys, on the other hand, melt at a lower temperature and do exhibit stage II of wetting.

Thus, the processing sequence for joining applications must include heating to 950 °C to achieve low contact angles. This poses a minor problem in the classification of these alloys as solders or brazing alloys. The main advantage of the Sn-based fillers is their ability to minimize residual stresses and thereby simplify the joining process. Any residual stresses that may arise are expected to be small due to the low solidifcation temperature of the filler, and it is expected that these will be absorbed by the tin matrix, which is very soft. Since these fillers are intended for low temperature applications, other problems such as oxidation resistance[20] of the filler metal are expected to be far less acute than in the case of fillers designed for operation at high temperatures.

V. CONCLUSIONS

Tin-based alloys containing titanium and zirconium were tested for wettability on silicon nitride. The Ti-containing alloys were shown to possess excellent wettability ($\Theta < 20$ deg), whereas the Zr-containing alloys exhibited contact angles around 50 deg. The Ti-containing alloys wet better due to the higher activity of dissolved Ti in the Sn matrix (for identical levels of Ti and Zr addition to Sn). Thus, Sn-Ti alloys are preferable as solders for ceramic/metal joints.

The liquidus temperature of the Sn-Ti alloys lies in the 400 °C to 600 °C range. Hence, use of these filler alloys is expected to reduce the residual stress problem as compared to active metal brazes. Wetting in these systems is controlled by reactive decomposition of the ceramic. Since the interfacial reactions are favored at high temperatures, it is necessary to braze in the 900 °C range to achieve good wetting.

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