

Joining of sialon ceramics by Sn–5 at % Ti based ternary active solders

AI-PING XIAN

International Center for Materials Physics, Institute of Metal Research, Academia Sinica, 72 Wenhua Road, Shenyang 110015, Peoples Republic of China

The effect of a third element, such as silver, copper, indium, nickel or aluminium, on the joining of sialon ceramics with tin-5 at % titanium based ternary active solders was investigated. The content of the third element in the Sn-based solders was varied from 5–40% for Cu, from 5–10% for Ag and Al from 5–20% for In and from 1–5% for Ni. The joining was carried out in vacuum at 1100 K for 20 min. The four point bend testing of a butt joint of a ceramic/ceramic structure with dimensions 40 mm long, 3 mm wide and 4 mm high was used to study the bond strength between the ceramic and the Sn-based solders. The results show that the bond strength of the Sn-based solder with the sialon ceramic varied from 54–103 MPa. Small additions of Cu or Ag (about 5–10%), In (about 5–10%), or Ni (about 1–3%) to the solder is beneficial, but too much Ni (more than 5%) or In (more than 10%) is detrimental. On the other hand, Al in the active solder considerably decreased the bond strength of the solders with the ceramic. Suggestions are made for the selection of the third element in order to improve the bond strength of the soft solders with the ceramic. These include a high surface energy, improving the wetting of the solder on the ceramic and strengthening of the solder.

1. Introduction

In the design of an active braze for joining ceramics to metals, there are three criteria [1], namely, excellent wettability, a strong interfacial bond with the ceramic and a good ductility of the solder, that must be satisfied in order to obtain a strong ceramic/metal joint. The last criteria, a high degree of ductility for a brazing filler metal, is of extreme importance for relaxing the interfacial stress in the ceramic/metal joint caused by the mismatch of thermal expansion between the ceramic and the metal. Klomp [2] suggested that in order to avoid harmful thermal stresses, a hard and brittle brazing filler metal cannot be used, therefore, a sufficiently ductile brazing filler metal is necessary. In fact, it is impossible to directly braze a ceramic and a metal unless the braze has enough ductility. For example, since a high residual stress develops during cooling from the brazing temperature [3, 4], the joining of a ceramic and steel by Ni-based brazes without an interlayer is unsuccessful. This is in spite of a strong bond between the brazes and the ceramic. This is the basic reason why Ag-based active brazes [5–14] and Al-based brazes [15, 16], both with relative low yield strength and good ductility, have been rapidly developed.

The recent development of Sn-based active solders [1, 17–20] has enabled the production of metal–ceramic joints with little, or no residual stress. In comparison to Ni and Cu-based brazes, Sn has a very low melting point, (505 K) and the solder does not transfer

stress until it is completely solidified. While Sn has a low yield strength, most of the residual stress, will still be relaxed by yielding of the solder.

Although the operating temperature of a ceramic–metal joint with low melting point Sn solder will be decreased, it is still useful for relatively low temperature applications such as electrical lead-throughs. The use of a low melting point solder with its low residual stress values raises the possibility of producing large ceramic/ceramic or ceramic/metal joints that do not require the use of an interlayer.

In earlier papers [19, 20], it was reported that Sn–Ti based ternary active solders have a good wettability on sialon ceramics at 1100 K. Also the wettability could be further improved by the addition of a third element such as Cu or Ni. Good wettability is the basic criterion that must be satisfied by an active solder, but it is not the only one. Changes in interfacial chemistry by the addition of the third element will influence not only the wetting behaviour but also the interfacial bond strength between the active solder and the ceramic [21]. In spite of the importance of the problem of this bond strength to the development of a practical active solder, little effort appears to be currently invested in understanding this effect. This paper reports work that is focused on the effect of a third element in the Sn-based solders on the interfacial bond strength with a ceramic with the objective of obtaining a new active solder.

2. Experimental

The sintered sialon ceramic was supplied by the Shanghai Institute of Ceramics, Academia Sinica, in the form of bars 3 mm wide, 4 mm high and 20 mm long. The ceramic, with a density of 3.44 g mm^{-3} and a coefficient of thermal expansion of $3.2 \times 10^{-6} \text{ K}^{-1}$ was made by sintering active Si_3N_4 powders with AlN and Y_2O_3 additives at 2073–2123 K for 2 h in nitrogen. The flexural strength of the ceramic bars was about 400 MPa. Full details of the procedure are reported in reference [22].

The Sn-based active solder, Sn–5 at % Ti which has been recently developed, was used as the base alloy in this work. The Ti content in the Sn based active solder remained the same in the ternary Sn-based alloy in order to isolate the effect of the third element. Earlier investigations revealed that most of the Sn based ternary active solders wet the ceramic very well at 1100 K, whilst below this temperature the wettability varies considerably with the added third element. Therefore, in the present work, the joining was carried out at 1100 K for 20 min.

Five metals (Ag, Cu, Ni, In and Al) were chosen as the additives in Sn–5 % Ti (at %, is used throughout this paper) solder to improve the bond strength of the solders with the ceramic. The added amounts varied from 5–40% for Cu, from 5–10% for Ag and Al from 5–20% for In and from 1–5% for Ni. The intermetallic alloys X–5 at % Ti (where X is copper, silver, nickel, indium or aluminium) were prepared as the source material for the third element in the solder. The Sn-based active solder was prepared by tungsten arc melting in a protective pure Ar atmosphere, multi-remelting was used to ensure the chemical uniformity of the Sn based solders. The weight loss of the solders during the arc melting was less than 1%. The solders were cold-rolled into a 0.15 mm thick strip, and cut into appropriate sizes for soldering. During the cold rolling, the ductility of the Sn-based solder with high concentrations of Cu (30% or more) was relatively poor. In the cold-rolled product, there were several cracks in the solder strip perpendicular to the rolled direction. Other Sn-based active solders had good ductility allowing them to be cold-rolled to the final thickness. Further details of the solders preparation route is reported in reference [1].

The facing surface of the bars was mechanically polished with diamond paste before soldering, and the surfaces of the Sn-based solders were polished with emery paper (No. 500). Then both the ceramic material and the active solder foils were carefully cleaned in acetone before soldering. The assemblage of the joint, consisting of two ceramic bars with a sheet of active solder, was fixed in an iron jig to ensure the alignment of the joint. The assemblage of the ceramic/ceramic joint was heated in a cold-wall type vacuum brazing furnace to 1100 K at a vacuum of less than 8 mPa and held there for 20 min, then the furnace was cooled to room temperature.

The flexural strength of the joints was measured by a four point bend test in air at room temperature. The span between the two base support points was 27 mm, and the span between both the upper support points

of the cross head was 18 mm. A cross head speed of 0.2 mm min^{-1} was used. The details of the soldering procedures and the strength measurement have been reported in reference [1].

3. Results

3.1. Bond strength

The Sn-based active solders, except in a few cases, wet the ceramic and form fillets very well. The thickness of the soldering seam of the joints was held constant at about 0.1 mm. The fracture surfaces of all the joints joined by the Sn-based solders were along the solder/ceramic interface. A layer of residual solder which was torn out in several pieces remained attached to the fracture surfaces of the joint as is shown in Fig. 1. Similar fracture surfaces were observed in all cases in the present work, which is contrary to the observed behaviour of Ag-based active brazes [11].

Fig. 2 shows the bond strength of the Sn–5Ti–Cu ternary active solders with the sialon ceramic. The addition of 0–20% Cu to the Sn–5Ti solder improved the bond strength between the solder and the ceramic, from 78 MPa for Sn–5Ti to 103 MPa for Sn–5Ti–20Cu. However, the strength changed little with the increase of Cu content. If the Cu addition was more than 30%, the plasticity of the Sn-based ternary solder was itself low, as has been mentioned above and

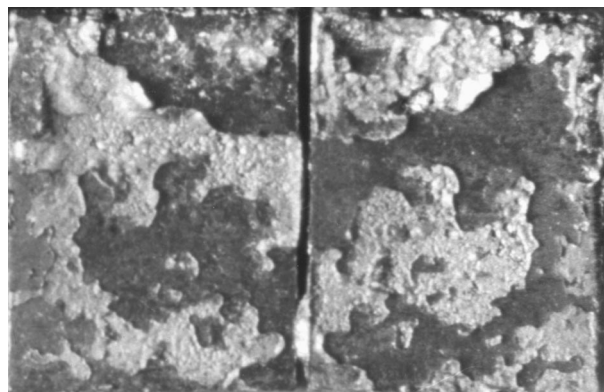


Figure 1 The micrograph of the fracture of Sn–5Ti–1Ni soldering at 1100 K for 20 min, this is a pair of the fracture surfaces, in which the metal solders were peeled off the ceramic surface.

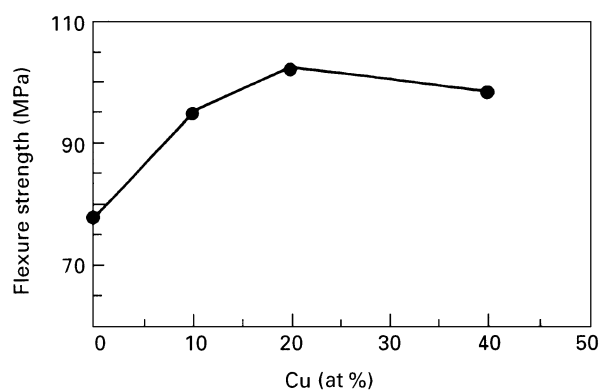


Figure 2 The bond strength of Sn–5Ti–Cu active solders with the sialon ceramic.

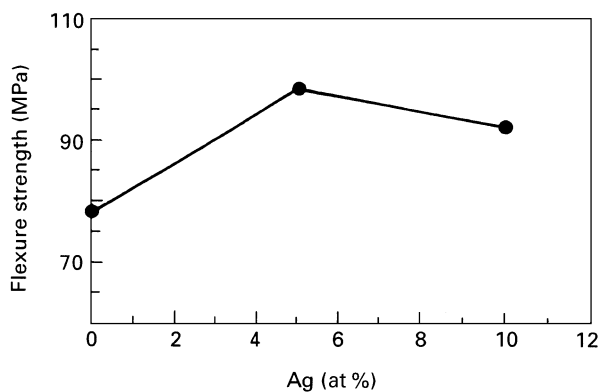


Figure 3 The bond strength of Sn-5Ti-Ag active solders with the sialon ceramic.

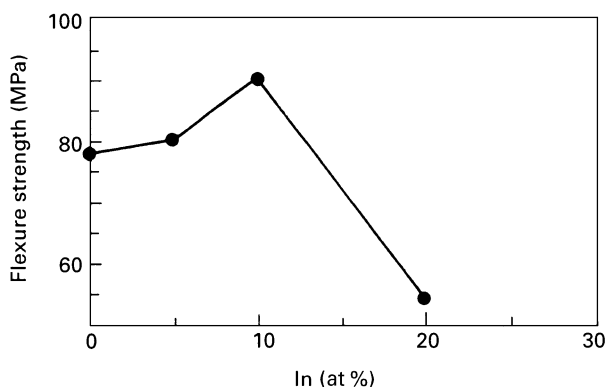


Figure 4 The bond strength of Sn-5Ti-In active solders with the sialon ceramic.

several cold-rolling cracks were present in the active solder sheets.

Fig. 3 shows the bond strength of the Sn-5Ti-Ag active solders with the sialon ceramic. As for Cu, small additions of about 5% Ag in the solder is beneficial to the bond strength, which increased from 78 MPa for Sn-5Ti to 98 MPa for Sn-5Ti-5Ag. After this concentration the bond strength was relatively constant with increasing Ag content. The joints employing the Sn-5Ti-Ag ternary active solders ruptured along the solder/ceramic interface, similar to the behaviour of the Sn-5Ti-Cu solder. However, the addition of too much Ag (40%) in the solders was detrimental to the fluidity of the Sn-5Ti-Ag ternary solder in wetting experiments [20]. We observed the appearance of a spreading droplet on the ceramic in a typical “straw hat” configuration, and that a layer of grey film existed on the top of the hat. Based on these results, it is suggested that a 5% addition of Ag should be suitable in the solder.

Fig. 4 shows the bond strength of the Sn-5Ti-In active solders with the sialon ceramic. Small additions of In were slightly beneficial to the bond strength. However, Indium additions in large concentrations is detrimental to the bond strength. For example, the joint strength decreased from 90 MPa for Sn-5Ti-10 In to only 55 MPa for Sn-5Ti-20 In. Fig. 5 is a set of micrographs of the fracture surface of the joints prepared at 1100 K for 20 min. A tear band

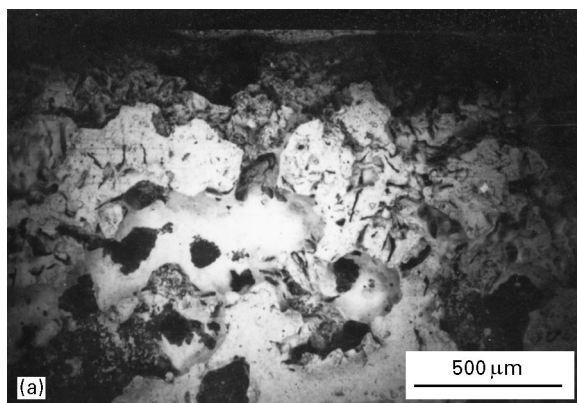


Figure 5 The microstructure of fracture observed by SEM (a) the panorama of the fracture surface (b) the microstructure of the solder peeled off the ceramic.

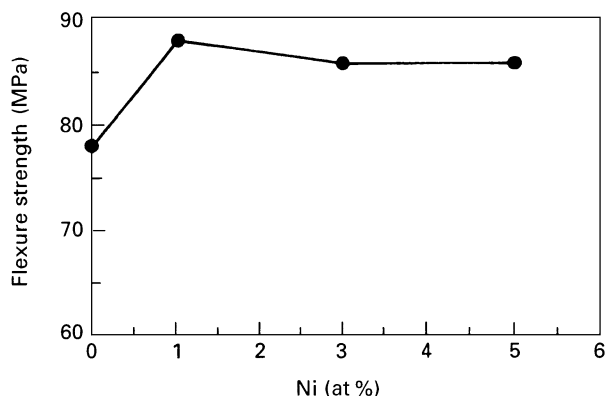


Figure 6 The bond strength of Sn-5Ti-Ni active solders with the sialon ceramic.

with low strength existed on the fracture surfaces. This suggests that greater additions of In decrease the strength of the solder itself, which may be caused by the formation of a low strength phase because of a non-equilibrium solidification. Moreover, when the addition of In in the solders is greater than 30%, similar to the behaviour of Ag in the solder, the fluidity of the Sn-5Ti-In ternary solder is very poor [19].

Fig. 6 shows the bond strength of the Sn-5Ti-Ni active solders with the sialon ceramic. Small additions of Ni (about 1%) were slightly beneficial to the joint strength. The addition of more Ni (about 3–5%) in the solder caused the bond strength to reduce slightly. However, when the Ni content was more than 5%, for example a Sn-5Ti-10Ni solder, the bond strength of

the active solder with the sialon ceramic was too low to obtain an acceptable strength. Based on early observations as reported in references [1, 19, 20], the solder has in fact not completely melted because of the formation of a Sn–Ni compound with a high melting point.

Fig. 7 is a set of micrographs of the fracture of soldered joints using Sn–5Ti–5Ni. Obviously, a typical intergranular fracture is present, this implies that a grain-segregation may exist. A little Ni (1–3%) is beneficial to the wetting of the Sn based solder [1, 20] which results from enhanced formation of a wetting precursor film [19]. It is suggested that 1% Ni addition to the Sn based solder should be sufficient. Greater amounts of Ni in the solder may be detrimental to the bonding.

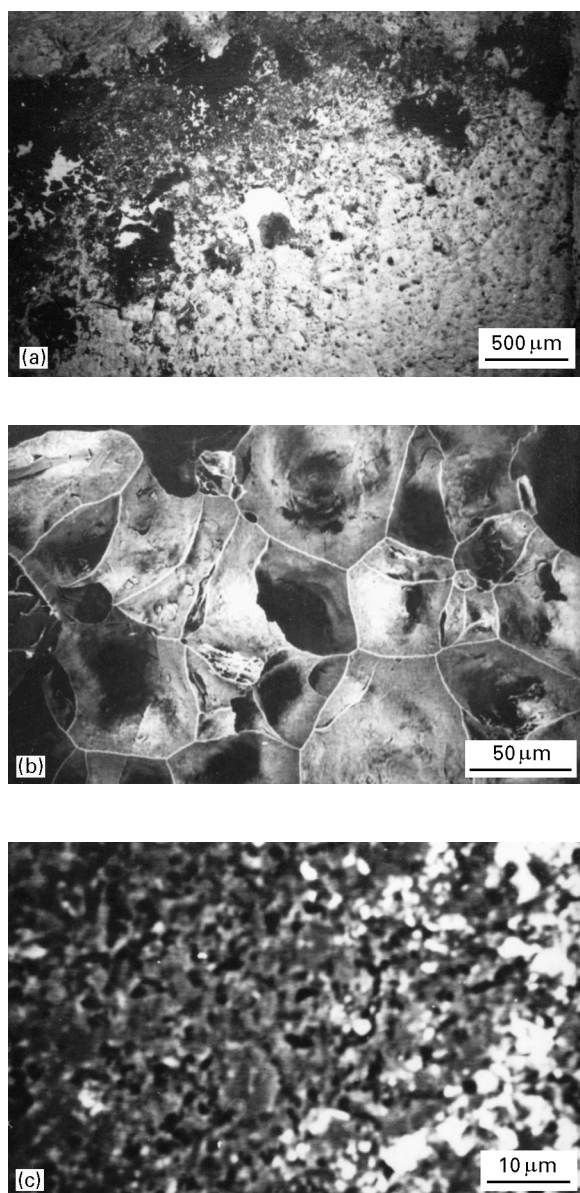


Figure 7 The microstructure of the fracture observed by SEM, typical intergranular fracture. (a) The panorama of the fracture surface, a part of the solder is stuck on the other fracture surface, (b) the intergranular fracture in the solder, corresponds to area marked A in Fig. 7(a), (c) the surface of the ceramic where the solder peeled off, corresponds to area marked B in Fig. 7(a), in which there were many traces of solders with very small sizes.

On the other hand, the addition of Al in the solder is harmful to the bond strength of the solder with the ceramic. When the Al content in the solder was 5%, the bond strength of the active solder decreased from 78 MPa to only 54 MPa, about half the value of the Sn–Ti–Cu ternary solders. It was observed that the solder wetted the ceramic poorly, and after rupture of the joint, a trace metal with a weak yellow colour existed on the fracture face. Moreover, the bond strength rapidly decreased to zero when the Al content in the solder increased to 10%. Hence Al is very harmful to the Sn based solders and it should be avoided in the solder preparation.

3.2. Microstructure

In order to observe the microstructure of the solders after wetting and reaction with the ceramic, an ingot weighing about 50 mg of the Sn based solder was put on the sialon ceramic and subjected to heat treatment. This consisted of being heated in vacuum to 1100 K and held for 20 min followed by furnace cooling to room temperature. The specimen was sectioned by a diamond saw, then carefully polished on a glass plate with fine diamond paste. In order to avoid the formation of a corrosion channel at the solder/ceramic interface, the metallographic section was not etched with a chemical etchant. Hence the image is slightly fuzzy. In spite of this, combined with the result from the X-ray maps, the images are still informative.

Fig. 8a is the microstructure of the Sn–5Ti–5Cu active solder after wetting on a sialon ceramic, as seen in the scanning electron microscope. Fig. 8(b–d) is a set of X-ray maps for Ti, Cu and Sn, respectively. The microstructure is composed of the pure Sn matrix and second phases which are interspersed in the matrix. The X-ray maps reveal that the second phases are Sn–Ti and Sn–Cu compounds, and that there is no Cu segregation at the interface. Instead, the Cu in the solder can form a Cu–Sn binary compound. A segregation layer of Ti is present at the metal/ceramic interface. This is similar to the behaviour observed for most active brazes wetting a ceramic.

Similarly, Fig. 9a is the microstructure of the Sn–5Ti–5Ag active solder after wetting a sialon ceramic, while Fig. 9(b–d) is a set of X-ray maps for Ti, Ag and Sn, respectively. The microstructure is composed of three parts, there is the pure Sn matrix, with a few blocks and many small particles dispersed in the Sn matrix. The X-ray maps reveal that the block observed in Fig. 9a is a Sn–Ti compound, whereas the small particles are Ag–Sn compounds, which uniformly distribute in the solder matrix. As in the case of Cu, a segregation layer of Ti is present at the metal/ceramic interface, whilst a Ag segregation layer is not observed at the interface.

Thus, there are some similarities in the general features of the microstructure for the Sn-based active solders. In both cases, the matrix is pure Sn, some Ti in the solder segregates at the interface, and the remaining Ti forms a Sn–Ti compound with a block appearance. The third element in the solder forms small Sn–X binary compounds dispersed in the matrix

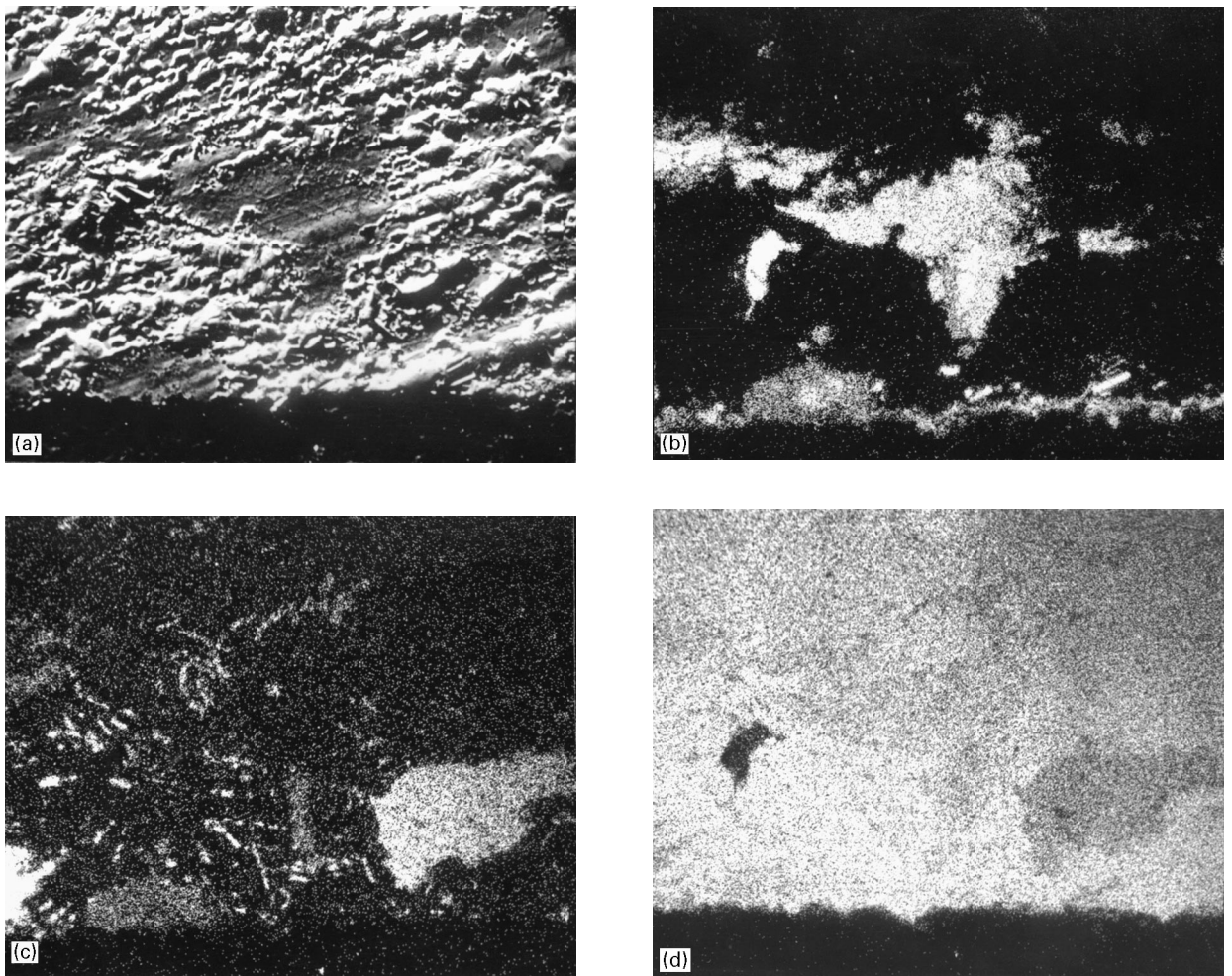


Figure 8 The microstructure and the X-ray map of the Sn-5Ti-5Cu solder wetting on the sialon ceramic at 1100 K for 20 min (without etching). (a) Microstructure, (b) Ti X-ray map, (c) Cu X-ray map, (d) Sn X-ray map.

when its concentration level is small. However, as a comparison, the segregation layer of Ti is relatively thin and discontinuous in the case of the addition of Ag to the solder.

4. Discussion

In a chain-linked system of ceramic-solder-ceramic, the joint strength is only dependent on the weakest link in the series [23]. Because the strength of the solder itself is much less than that of the ceramic, the weakest link should be the solder/ceramic interface or the solder itself. Since all joints tested in the present work ruptured along the solder/ceramic interface, the interface strength is regarded as the weakest link in the system. As a comparison, it was observed that a thick layer of the solder had stuck on the fracture face after soldering with Sn-Hf or Sn-V active solders [1], which corresponded to a higher joint strength.

For the case of no residual stress, the interfacial bond strength of the solder-ceramic is related to the work of adhesion between the metal and ceramic. For an inactive solid-liquid interface, the work of interfacial adhesion can be estimated from the Young-Dupr e equation [24, 25]

$$W_a = \sigma_{lv}(1 + \cos\theta) \quad (1)$$

where W_a is the work of interfacial adhesion between liquid and solid, σ_{lv} is the surface energy of the liquid and θ is the contact angle of the liquid on the solid. Although the relation is deduced from liquid-solid interfacial equilibrium, it is regarded as applicable to a solid-solid interfacial system. Nicholas showed [26] that there is a linear relationship between the bond strength of metal/ceramic interfaces and the value of the work of interfacial adhesion in the systems Al_2O_3 -Ag, Al_2O_3 -Cu, Al_2O_3 -Ni and Al_2O_3 -Fe. In fact, both the interfacial bond strength and the work of interfacial adhesion reflect directly the interaction between the metal and the ceramic. In general, the addition of a high surface energy element will cause an increase of surface energy of the alloy. Although exact data on the surface energies in Sn-5Ti solders with a third element addition is still lacking, it can be predicted that the surface energies of the Sn-based solders with additions of Ag, Cu or Ni will tend to increase due to the higher surface energy of the elements. Also, in the case of chemical wetting in active solder/ceramic systems, the small addition of the third element, such as Cu, is beneficial to the wettability of the Sn based solder on the ceramic as reported in references [19, 20]. The contact angle decreases with the small additions of the elements in certain conditions. Based on the two effects, therefore, the work of adhesion at the interface tends to be increased by the

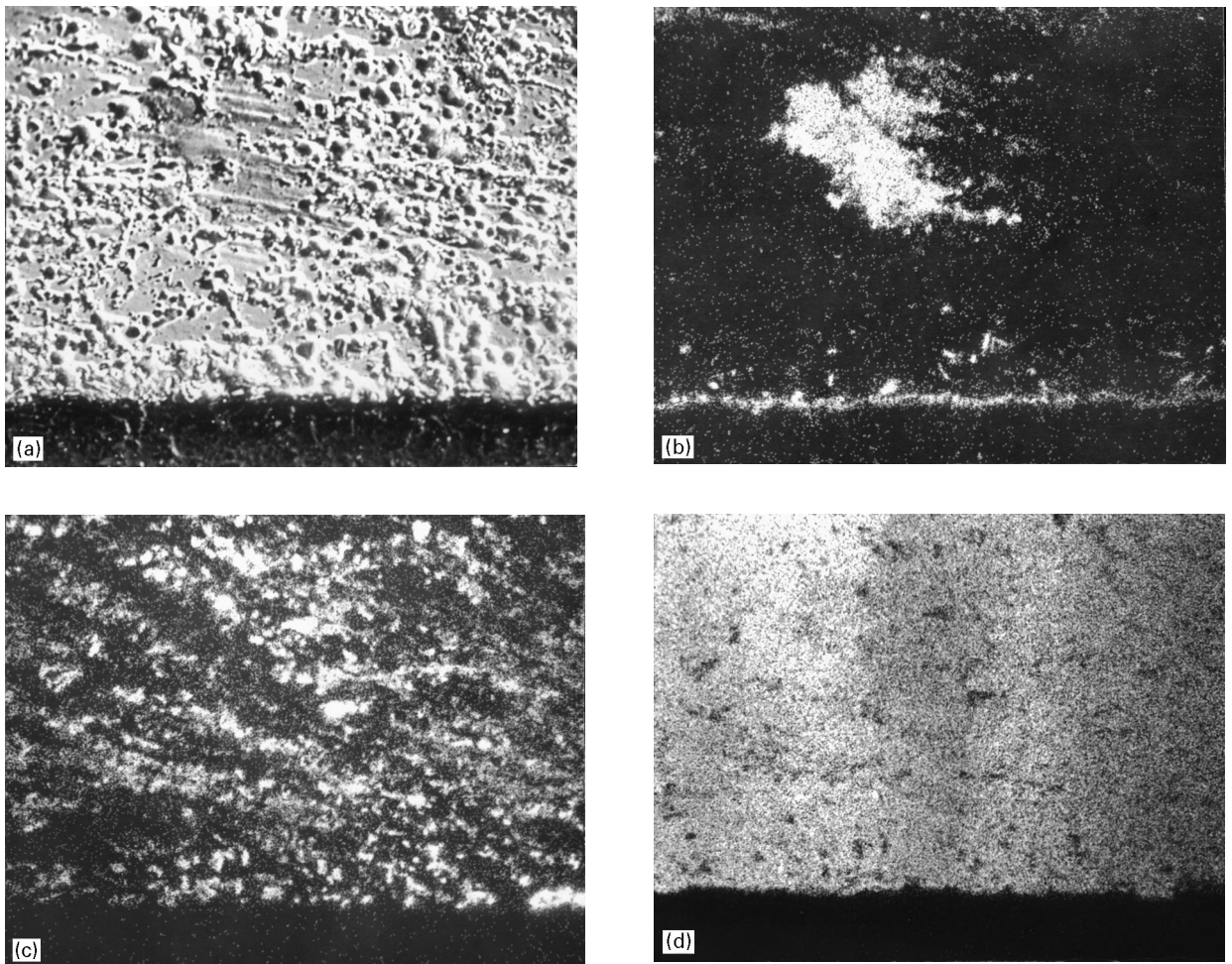


Figure 9 The microstructure and the X-ray map of the Sn-5Ti-5Ag solder wetting on the sialon ceramic at 1100 K for 20 min (without etching). (a) Microstructure, (b) Ti X-ray map, (c) Ag X-ray map, (d) Sn X-ray map.

addition of the third element. This results in the increase in bond strength between the active solder and ceramic. Based on the same reasoning, because Al in the Sn-based active solders can strongly decrease the wettability of the solders on the ceramic [20], the bond strength between the sialon ceramic and the Sn-5Ti-Al ternary active solders was very poor.

On the other hand, the strength of pure Sn is only 13MPa [27], which is far less than the strength of the joints (about 80–100 MPa) soldered with the Sn-based active solders. Although the soft soldering seam may be strengthened by the constraint of the hard ceramic on both sides and alloying with other elements, the large difference in strength implies that it is quite possible, that the fracture of the joint can partly take place in the soft solder. Hence it is helpful to strengthen the Sn-based solder itself in order to increase the joint strength. From this view point, the small additions of Ag or Cu are beneficial. Based on the binary phase diagram of Sn–Ag and Sn–Cu [28], Ag or Cu show only a small solubility in Sn, in fact, the element forms many small second phase particles with Sn, such as the intermetallic compound Ag_3Sn (melting point 753 K) or Cu_3Sn_2 (melting point 688 K), which are dispersed in the solder matrix. This resulted in the increase of the strength of the solder alloy. On the other hand, based on the binary phase

diagram of Sn–In [28], there is a δ -solid-solution zone of Sn if the In content is less than about 7% at room temperature, and an intermetallic compound of τ -phase if the In content is about 9% at 476 K or from 15–22% at room temperature. When the In content is more than about 22% and less than about 60%, there is a eutectic reaction at 388 K to form the intermetallic compounds of the τ and β phase, the last one having a very low melting point. As a result, when the In content is less than about 10%, the strength of the Sn–In alloy would be increased by the effects of the solid-solution and the intermetallic compound with a relatively high melting point. However, when the In content is more than 10%, the intermetallic compound of the β -phase with a low melting point should form because of a non-equilibrium solidification. The strength of the intermetallic compound with more than 60% In may be very low, which will tend to decrease the alloy strength. This is the reason why the joint strength drops rapidly at 20% In content in the experiments.

As has been mentioned previously, it is suggested that, when the third element is selected to add into a soft active solder for improving the interfacial bond strength between the solder and the ceramic, the following three selection criteria should be observed; (1) a high surface energy, in general, corresponding to

a metal whose melting point is higher than that of the matrix metal; (2) an improved wettability of the solder on the ceramic and (3) strengthening the solder alloy itself.

5. Conclusions

The bond strength of the Sn based ternary active solders, Sn–5Ti with various contents of Ag, Cu, In, Ni, or Al, with sialon ceramic has been reported. The main results are:

(1) The bond strength of Sn–5Ti solder with the sialon ceramic after soldering at 1100 K for 20 min is about 80 MPa, it can be increased to 90–100 MPa by small additions of Ag or Cu (about 5–10%).

(2) Small concentrations of Ni (about 1–3%) in the solder is slightly beneficial to the bond strength, however beyond about 5% it becomes harmful.

(3) Small additions of In (less than 10%) are beneficial to the bond strength, but too much In strongly decreases the bond strength.

(4) Small additions of Al in the active solder are harmful to the bond strength of the Sn-based solders, which is decreased from 78 MPa for Sn–5Ti to only 54 MPa for Sn–5Ti–5Al.

We have suggested that in order to increase the bond strength of the soft solders with the ceramic then the solder should have a high surface energy, excellent wetting characteristics and show good strength properties.

Acknowledgments

This research was supported by the National HTDP Science Foundation for Young Scientists Grant No 863-715-YF25-9308, and Liaoning Province Science and Technique Foundation for Postdoctoral Scientists. The sialon ceramic was supplied by the Shanghai Institute of Ceramics, Academia Sinica. The author would like to thank Prof. Zhong-Yao Si for his encouragement in this research, and Mr. Zhu-Tao Mao for his assistance in preparing the Sn based active solder.

References

1. A. P. XIAN, Ph.D. Thesis, Institute of Metal Research, Academia Sinica, Shenyang 110015, China, (1991).
2. J. T. KLOMP, *Weld. J.* **50** (1971), 88s–90s.
3. A. P. XIAN and Z. Y. SI, *J. Amer. Ceram. Soc.* **73** (1990) 3462.
4. K. SUGANUMA, Y. MIYAMOTO and M. KOIZUMI, *Ann. Rev. Mater. Sci.* **18** (1988) 47.
5. W. WEISE, in *Designing Ceramic Interfaces*, Proceedings of the Second European Colloquium, Petten 11–13 Nov. 1991, Ed. by S. D. Peteves, (JRC, Institute for Advanced Materials, PO Box 2, NL-1755 ZG Petten, The Netherlands), pp. 221.
6. M. HOWARD, EP 0135603 Al, (1985).
7. H. MIZUHARA and K. MALLY, *Weld. J.* **64** (1985) 27.
8. H. MIZUHARA and E. HUEBEL, *ibid* **65**, (1986) 43.
9. H. MIZUHARA, US Pat. No. 4591535, 1986.
10. R. R. KAPOOR and T. W. EAGER, *J. Amer. Ceram. Soc.* **72** (1989) 448.
11. A. P. XIAN and Z. Y. SI, *J. Mater. Sci.* **25** (1990) 4483.
12. *idem. ibid.* **27** (1992) 1560.
13. A. P. XIAN, Z. Y. SI, L. J. ZHOU, J. N. SHEN and T. F. LI, *Mater. Lett.* **12** (1991) 84.
14. A. P. XIAN and Z. Y. SI, *J. Mater. Sci. Lett.* **10** (1991) 1381.
15. X. S. NING, K. SUGANUMA et al., *J. Mater. Sci.* **24** (1989) 2865.
16. X. S. NING, T. OKAMOTO et al., *ibid.* **24** (1989) 2879.
17. R. R. KAPOOR and T. W. EAGER, *Metall. Trans.* **20B** (1989) 919.
18. A. P. XIAN and Z. Y. SI, *J. Mater. Sci. Lett.* **10** (1991) 1315.
19. A. P. XIAN, *J. Mater. Sci.* **28** (1993) 1019.
20. *idem*, *Mater. Sci. Engng* **B25** (1994) 39.
21. M. G. NICHOLAS, T. M. VALENTINE and M. J. WAITE, *J. Mater. Sci.* **15** (1980) 2197.
22. L. P. HUANG, Z. K. HUANG, Y. R. QU and X. R. FU, *J. Inorganic Mater.* **1** (1986) 123. (in Chinese).
23. A. P. XIAN and Z. Y. SI, *J. Mater. Sci.* **27** (1992) 1560.
24. F. DELANNAY, L. FROYEN and A. DERUYTTERE, *ibid.* **22** (1987) 1.
25. J. G. LI, in *Designing Ceramic Interfaces*, Proceedings of the Second European Colloquium, Petten 11–13 Nov. 1991, Ed. by S. D. Peteves, (JRC, Institute for Advanced Materials, PO Box 2, NL-1755 ZG Petten, The Netherlands) pp. 481–98.
26. M. G. NICHOLAS, *Mater. Sci. Forum* **29** (1988) 127.
27. *Soldering Manual* (Second Edition, Revised), American Welding Society Committee on Brazing and Soldering, American Welding Society, Inc., (1978).
28. C. J. SMITHELLS, "Metals Reference Book" (fifth edition), (Butterworths, London & Boston) (1976).

Received 10 March 1995
and accepted January 1996