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Active Soldering of Indium Tin Oxide (ITO) With Cu in Air Using an Sn3.5Ag4Ti(Ce, Ga) Filler

S.Y. Chang, L.C. Tsao, M.J. Chiang, C.N. Tung, G.H. Pan, and T.H. Chuang

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Indium tin oxide (ITO) ceramics are bonded with ITO and Cu at 250 °C in air using an active solder Sn3.5Ag4Ti(Ce, Ga). The mechanism for such low temperature soldering of ITO ceramics in air has been investigated. Electron probe microanalyzer (EPMA) analyses reveal that the element oxygen distributes uniformly within the solder matrix after soldering, while Ti segregates effectively at the ITO/solder and Cu/solder interfaces at such a low temperature, giving satisfactory joining results of Cu/Cu, ITO/ITO, and ITO/Cu in air.

Keywords active filler, active soldering, air, copper, interface, ITO, Sn3.5Ag4Ti(Ce, Ga)

1. Introduction

Direct brazing with active filler metals such as Ag26.5Cu3Ti, Ag4Ti, and Ag1In1Ti alloys has been widely used in joining ceramic/ceramic or ceramic/metal.[1] However, the high melting temperatures of these filler metals cause severe thermal stress along the joint interfaces, which may even result in the fracture of the brazements. To solve this problem, low-melting-point filler metals such as Sn10Ag4Ti and Pb4In4Ti alloys were developed.[2] Although the act of brazing using these filler metals must also be conducted at temperatures above 850 °C (similar to the case using traditional Ag-Cu-Ti active filler metals), the thermal stress could be alleviated by their lower solidification temperatures (200-300 °C).[3]

For engineering applications, certain ceramic materials are sensitive to the temperatures applied due to their inducement to hot cracking or functional degradation. As a result, these materials can be joined only at low temperatures, for which the indium tin oxide (ITO) sputtering targets are an example. The huge touch-panel market incurs a great demand for transparent conductive ITO films, whereas the sputtering ITO films call for the use of ITO targets.[4] In recycling, the used ITO targets are debonded from their Cu backing plates, and the soldering process is generally executed in turn to rebond a new ITO target to the recycled Cu backing plate.[5] To avoid the dissociation of oxygen from the ITO material, the soldering temperature must be lower than 300 °C. Premetallization with nickel films has been the traditional method, followed by soldering with pure

S.Y. Chang, L.C. Tsao, M.J. Chiang, and **T.H. Chuang,** Department of Materials Science and Engineering, National Taiwan University, 106 Taipei, Taiwan; and **C.N. Tung** and **G.H. Pan,** Metal Industries R&D Centre, 811 Kaohsiung, Taiwan. Contact e-mail: tunghan@ccms.ntu.edu.tw.

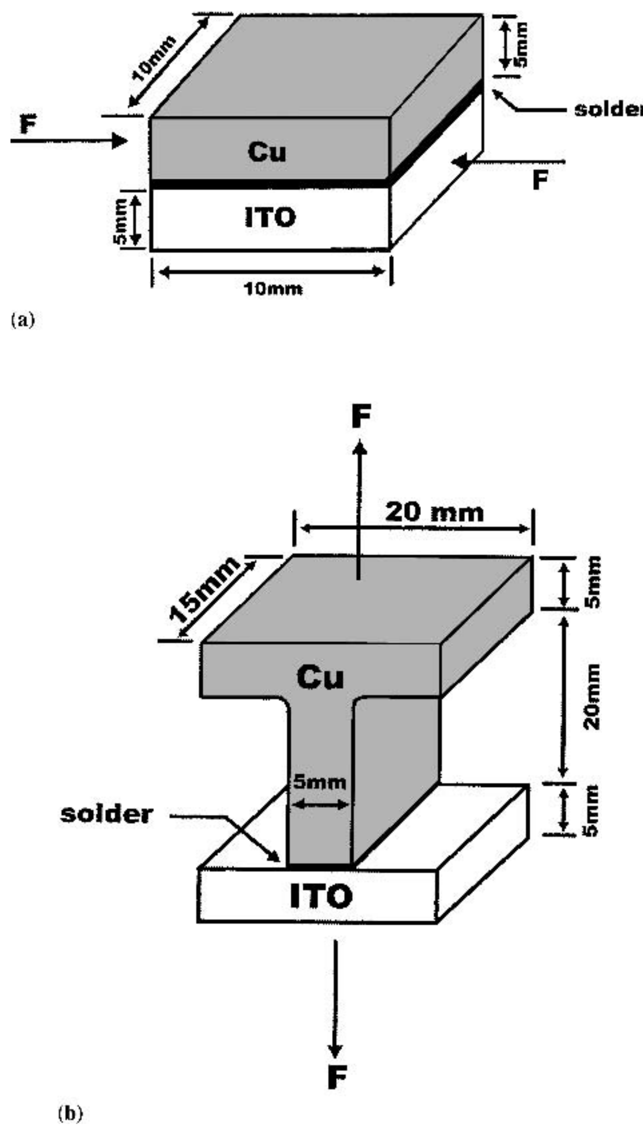


Fig. 1 Schematic representation of the soldered specimens in this study: **(a)** shear testing; **(b)** tensile testing

indium. In this case, premetallization is usually performed in a high vacuum chamber, leading to an escalation of the bonding costs.

Recently, a new active filler metal Sn3.5Ag4Ti(Ce, Ga) has been developed, which can successfully join the non-wetting materials at low temperatures in air.[6] The addition of trace

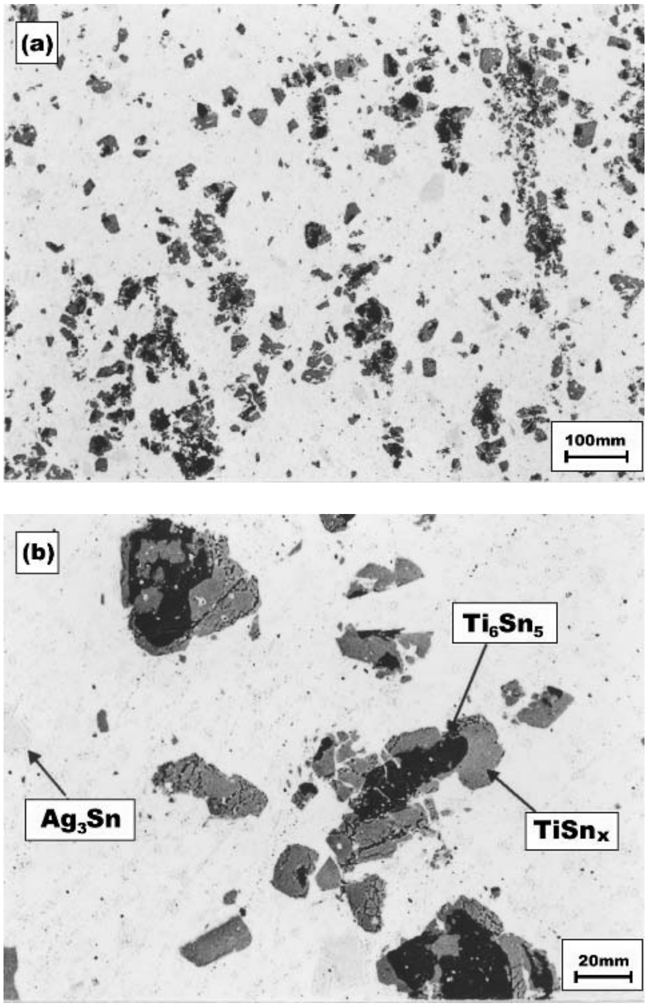


Fig. 2 Microstructure of the as-received Sn3.5Ag4Ti(Ce, Ga) active solder

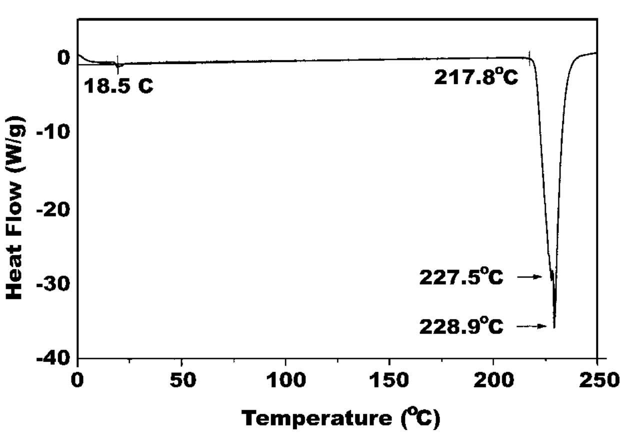


Fig. 3 DSC analysis of Sn3.5Ag4Ti(Ce, Ga) active solder

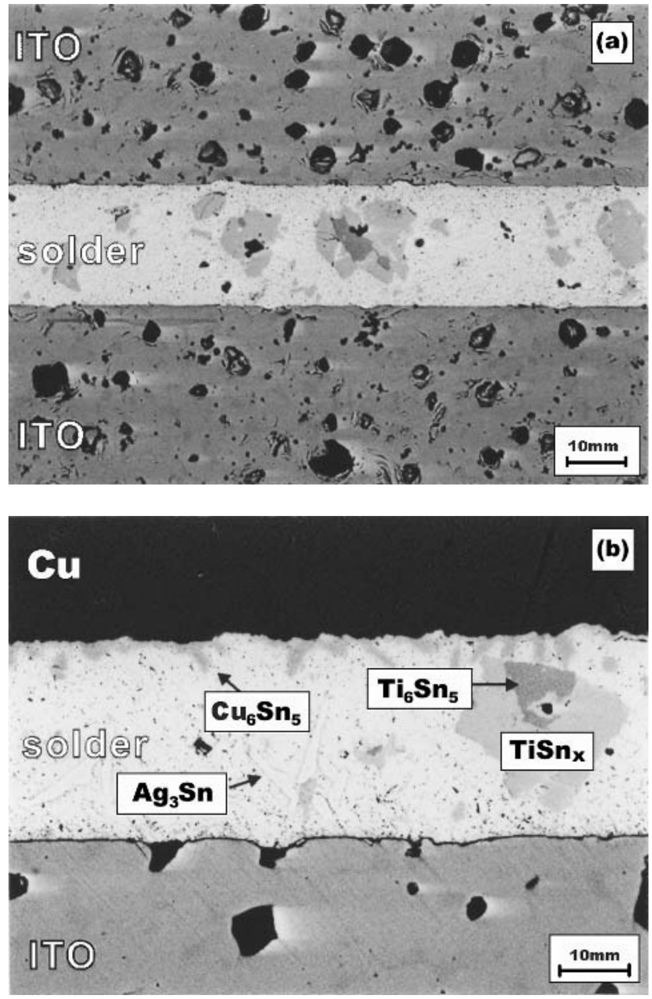


Fig. 4 SEM micrographs of ITO/ITO and ITO/Cu interfacial microstructures bonded with Sn3.5Ag4Ti(Ce, Ga) active solder

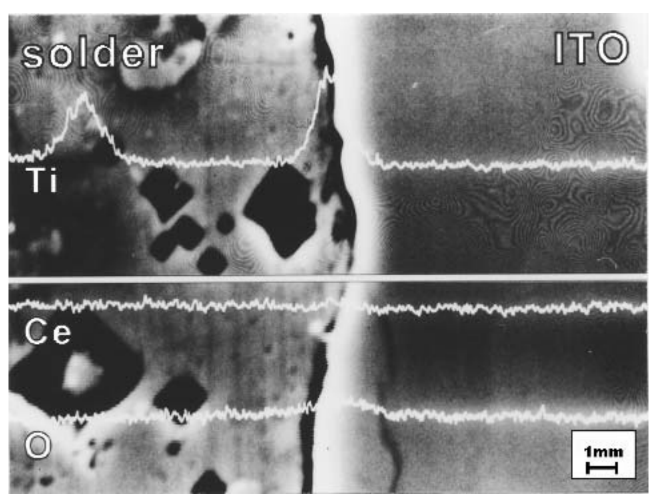


Fig. 5 EPMA line scanning of elements across the ITO/solder interface

amounts of rare-earth elements (Ce or La) to this active solder can remove oxides at the reaction interfaces of the workpieces during joining, thus eliminating the necessity of a protective atmosphere otherwise required for the soldering process.[6,7] This study focuses on the evaluation of its applicability in joining the ITO sputtering targets to their recycled Cu backing plates.

2. Experimental

The active solder Sn3.5Ag4Ti(Ce,Ga), shaped in 0.3 mm thick foil, with a chemical composition (wt.%) of Sn3.55Ag4.07Ti0.12Ce0.14Ga as analyzed, was supplied by Euromat Co. (Heinsberg, Germany). The ITO target material used for joining is a mixture of 90% In_2O_3 and 10% SnO_2. The ITO and Cu bond specimens were cut from a sputtering target and its backing plate, respectively. Figure 1 demonstrates the geometry and dimensions of two types of the soldered specimens subjected to tensile and shear testing. The bond surfaces of the specimens were ground and polished with a suspension containing 1 μm Al_2O_3. Prior to soldering, which was to be conducted in air, the ITO specimens were preheated on a heating plate at 250 °C for 5 min. The active solder was then placed on the bond surfaces. The molten solder was agitated for 30 s; then the Cu specimen was placed on the molten solder to join with an ITO specimen by rubbing each other for 30 s. The joints were held firmly in place and cooled down, leading to the solidification of the molten solder. After bonding, the specimens were cut into cross sections. The microstructures and distributions of the elements were analyzed by an electron probe microanalyzer (EPMA) to ascertain the bonding mechanism and related interfacial reactions. The bonding strengths were measured via shear and tensile testing.

3. Results and Discussion

Figure 2 shows the microstructure of the as-received Sn3.5Ag4Ti(Ce, Ga) active solder, where a large number of coarse clusters are seen embedded in the Sn3.5Ag eutectic phase. As analyzed by EPMA, the Sn3.5Ag eutectic phase

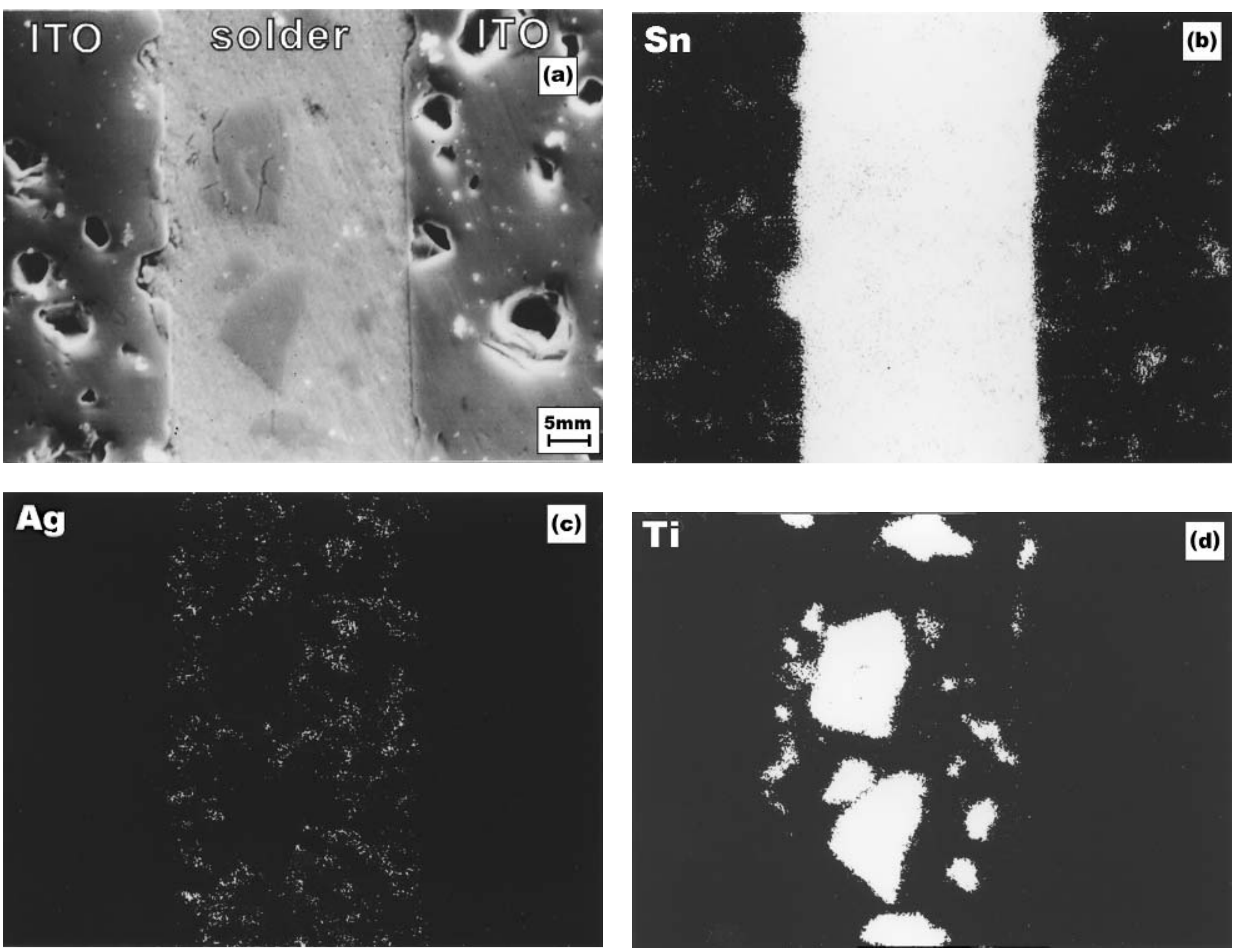


Fig. 6 Micrograph and EPMA analyses of ITO bonded with ITO using Sn3.5Ag4Ti(Ce, Ga) active solder: **(a)** the interfacial microstructure; **(b)-(d)** elemental mapping of Sn, Ag, Ti, respectively (continued on next page)

consists of a pure Sn matrix with a fine dispersion of Ag_3Sn particles (seen in white). The α-Ti_6Sn_5 phase (black) and the surrounding $TiSn_x$ ($x = 1.55$~1.67) phase (gray) are formed in the coarse clusters. Such a $TiSn_x$ phase has not appeared in any published phase diagram as yet. However, Kuper et al. first reported on the existence of such a formerly unknown phase in various types of Ti-Sn samples (powder samples, alloy samples, and bulk and thin film diffusion couples).[8] Differential scanning calorimetry (DSC) analysis in Fig. 3 shows that this active solder has a melting range of 218-229 °C, nearly the eutectic point of Sn3.5Ag alloy. An exothermic peak (18.5 °C) appeared in the DSC curve, which might be attributed to the existence of a low-melting-point Ga-rich eutectic phase in the active solder.

A satisfactory joint can be obtained using the Sn3.5Ag4Ti(Ce, Ga) active solder to bond ITO with ITO (Fig. 4a). The original Ti-rich clusters remain unaffected in the solder matrix. However, elemental line scanning across the ITO/solder interface indicates that Ti segregates actively at the interface (Fig. 5), which should be responsible for the solderability of Sn3.5Ag4Ti(Ce, Ga) on the ITO surface.

EPMA elemental mapping of the ITO/ITO joint, bonded with Sn3.5Ag4Ti(Ce, Ga) active solder, reconfirms the segregation of Ti at the ITO/solder interface (Fig. 6d). The trace amounts of Ce and Ga distribute uniformly in the solder matrix (Fig. 6c,f). The oxygen in ITO seems to diffuse into the solder due to the attraction of the active element Ce (Fig. 6g). From Fig. 6(b-h), it can also be seen that some tin-oxide particles dissolve locally at the ITO/solder interface. Elemental mapping of the ITO/Cu joint shows that Cu dissolves irregularly at the Cu/solder interface to form a scallop-shaped Cu_6Sn_5 intermetallic compound (Fig. 7), while Ti segregates at both the ITO/solder and Cu/solder interfaces. The reaction of Ce with O, which causes the stronger distribution of oxygen in Sn3.5Ag4Ti(Ce, Ga) solder, can be observed more distinctly in Fig. 7(g). Evidently, the affinity of Ce to oxygen promotes the reaction of the active element Ti with ITO at such a low soldering temperature.

The bonding strengths of Cu/Cu, ITO/ITO, and ITO/Cu joints using the Sn3.5Ag4Ti(Ce, Ga) solder after shear testing are given in Fig. 8. The ITO/Cu joint possesses a shear strength of 3.4 MPa, which is considerably lower than those for the cases of Cu/Cu and ITO/ITO joints of similar materials.

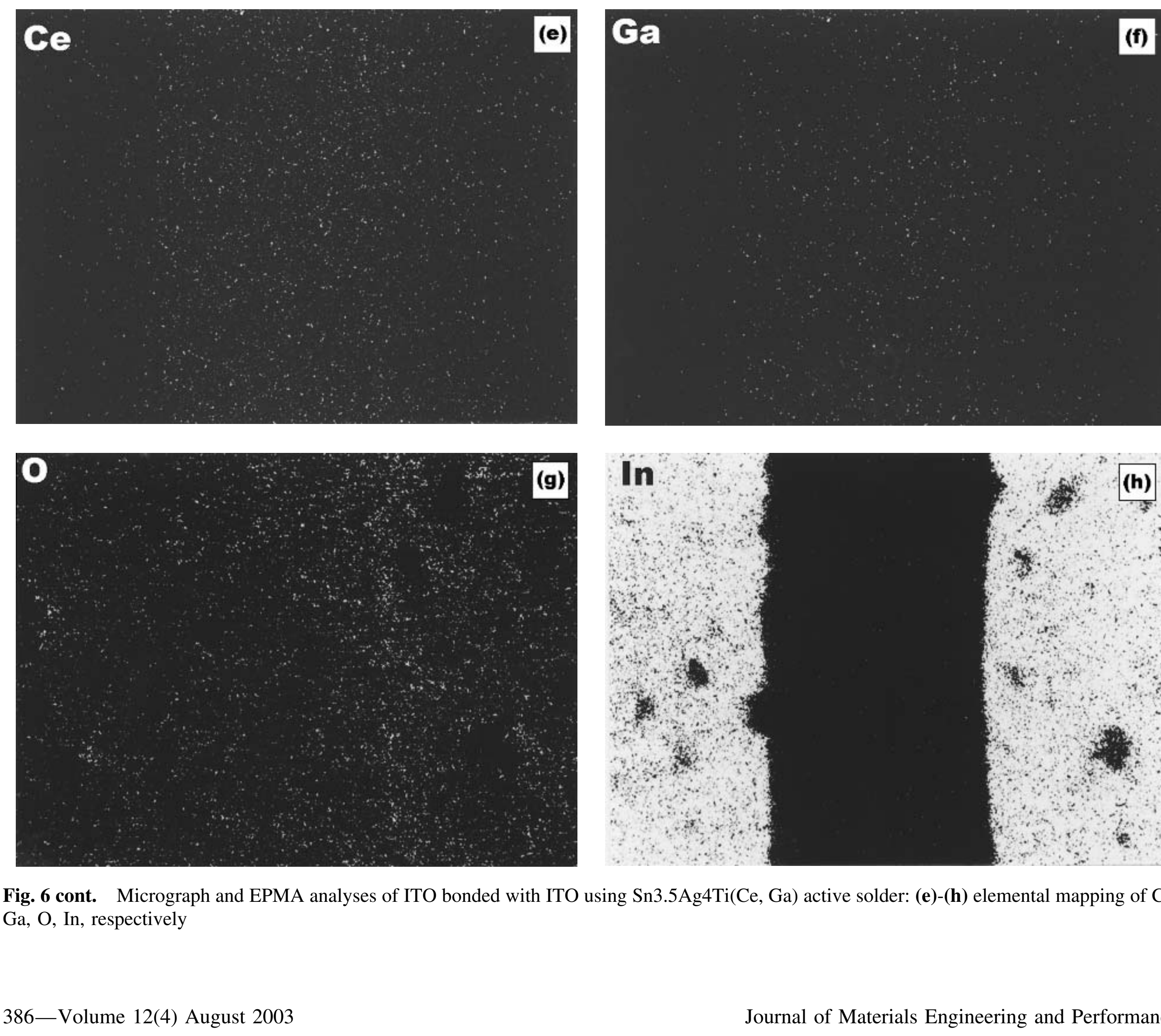


Fig. 6 cont. Micrograph and EPMA analyses of ITO bonded with ITO using Sn3.5Ag4Ti(Ce, Ga) active solder: **(e)**-**(h)** elemental mapping of Ce, Ga, O, In, respectively

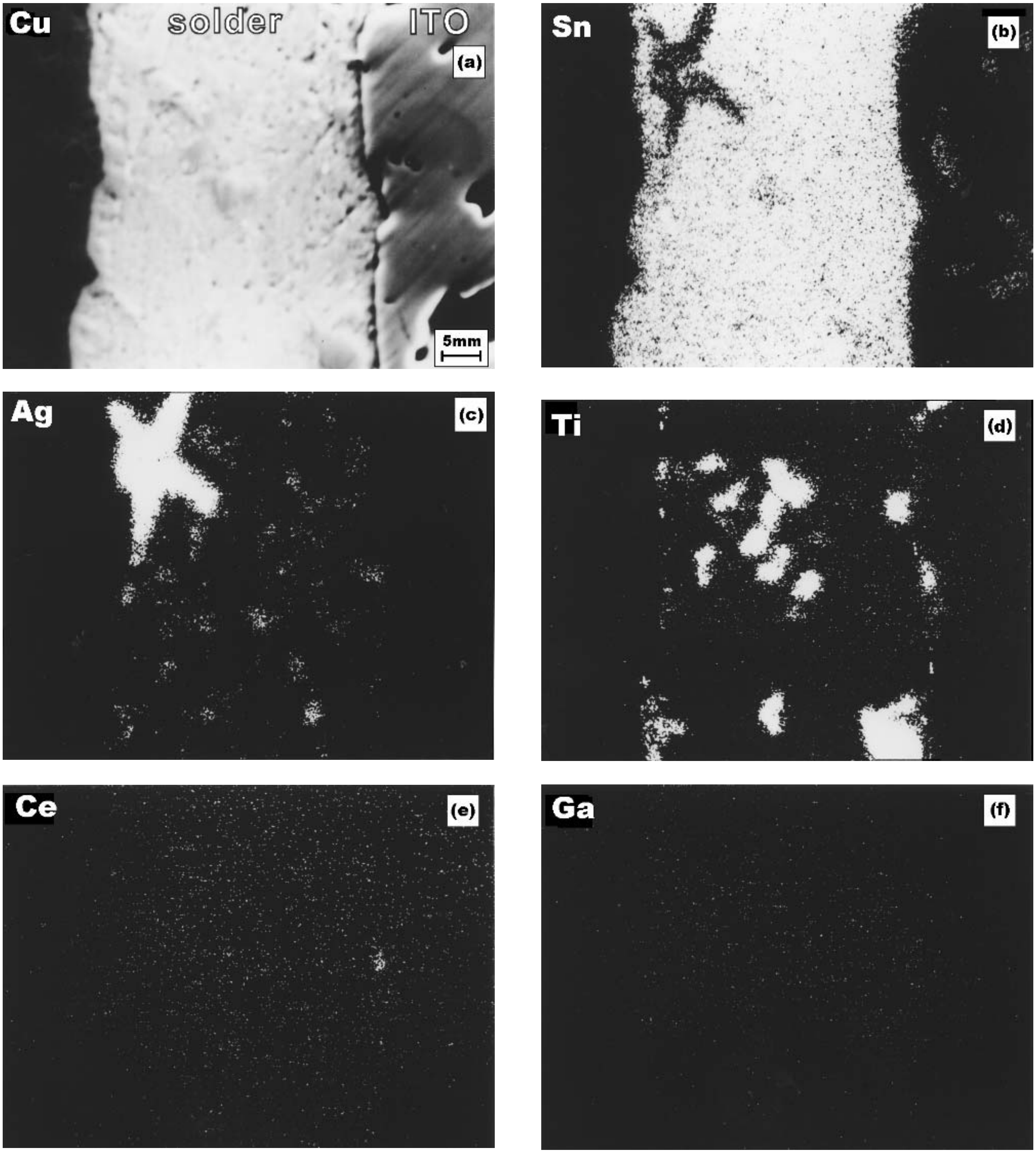
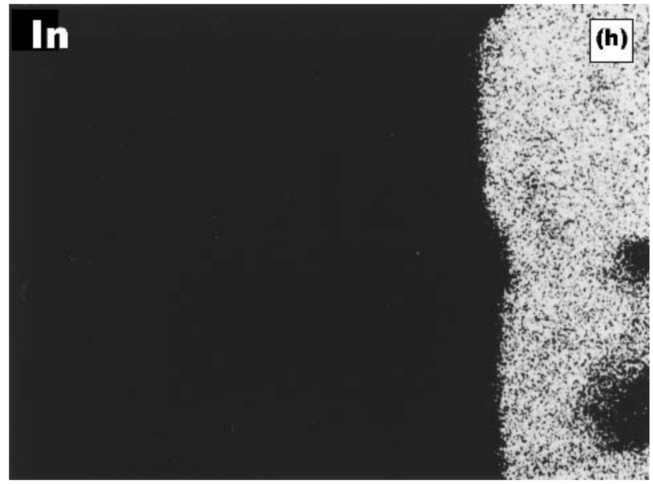


Fig. 7 Micrograph and EPMA analyses of ITO bonded with Cu using Sn3.5Ag4Ti(Ce, Ga) active solder: **(a)** the interfacial microstructure; **(b)-(f)** elemental mapping of Sn, Ag, Ti, Ce, and Ga, respectively (continued on next page)

Through tensile testing, a higher bonding strength of 5.5 MPa is found in the ITO/Cu joint region. As the ITO material exhibits low strength, this study consequently also discerns low bonding strengths in the ITO/ITO and ITO/Cu joints. Such a fact can be confirmed via fractography of the soldered specimens after tensile testing (Fig. 9). Figure 9(a) indicates that the fractured surface of the Cu specimen is covered with an ITO layer, while Fig. 9(b) provides a contrasting example of the



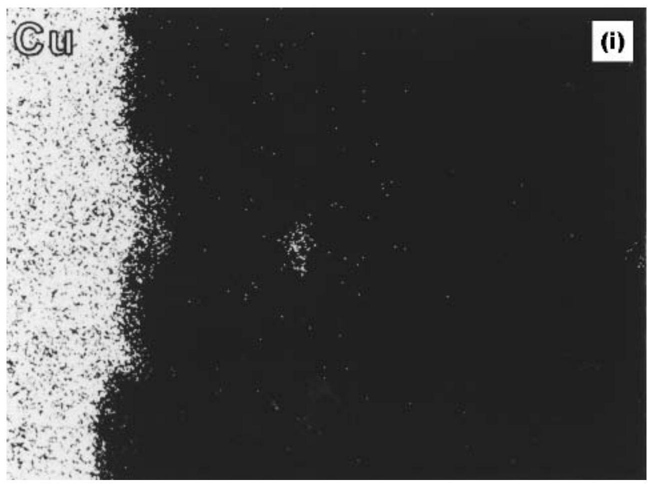


Fig. 7 cont. Micrograph and EPMA analyses of ITO bonded with Cu using Sn3.5Ag4Ti(Ce, Ga) active solder: **(g)-(i)** elemental mapping of O, In, and Cu, respectively

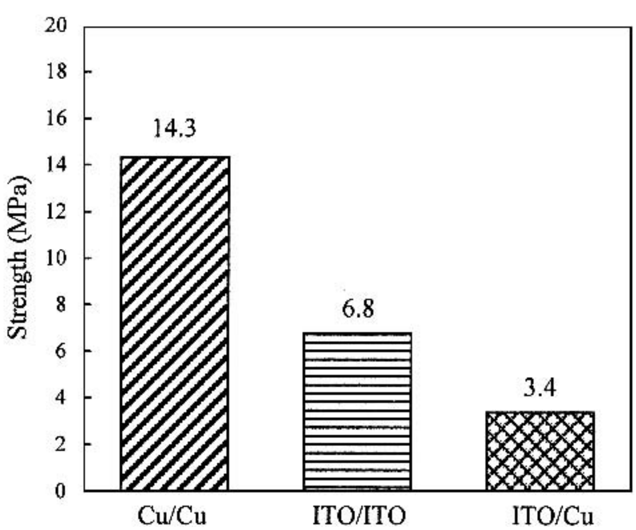
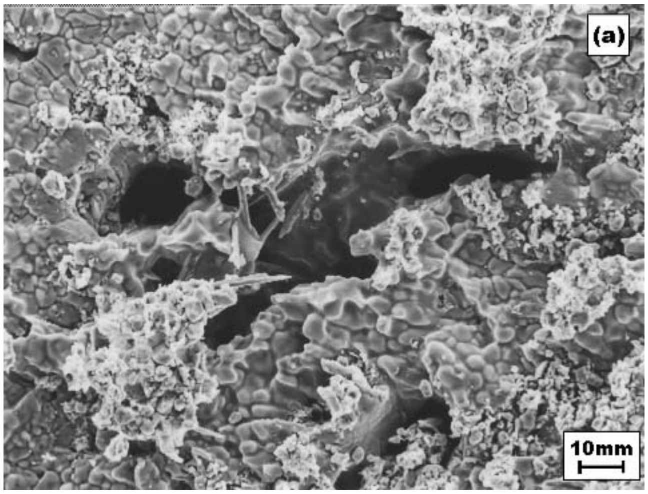


Fig. 8 Shear strengths of Cu/Cu, ITO/ITO, and ITO/Cu joints bonded with Sn3.5Ag4Ti(Ce, Ga) active solder

fractured ITO specimen. It is obvious that the ITO/Cu joint has fractured in the ITO matrix.

4. Conclusions

Sn3.5Ag4Ti(Ce, Ga) solder contains a eutectic Sn3.5Ag matrix in which a large amount of Ti-rich clusters are embedded and composed of Ti_6Sn_5 cores surrounded by a newly reported $TiSn_x$ ($x = 1.55$~1.67) phase. The joining of indium tin oxide (ITO) with ITO and Cu can be achieved at 250 °C in air using this active solder. The affinity of Ce to oxygen gives rise to the reaction of Ti with ITO and Cu at such a low temperature. EPMA reveals a strong tendency of Ti to segregate at the ITO/solder and solder/Cu interfaces. After soldering, Cu dissolves into Sn3.5Ag4Ti(Ce, Ga) solder to form a scallop-shaped Cu_6Sn_5 intermetallic compound. Shear-tested bonding strengths for Cu/Cu, ITO/ITO, and ITO/Cu joints are 14.3, 6.8, and 3.4 MPa, respectively. For the ITO/solder/Cu joint, fracture occurs in the ITO matrix after tensile testing.



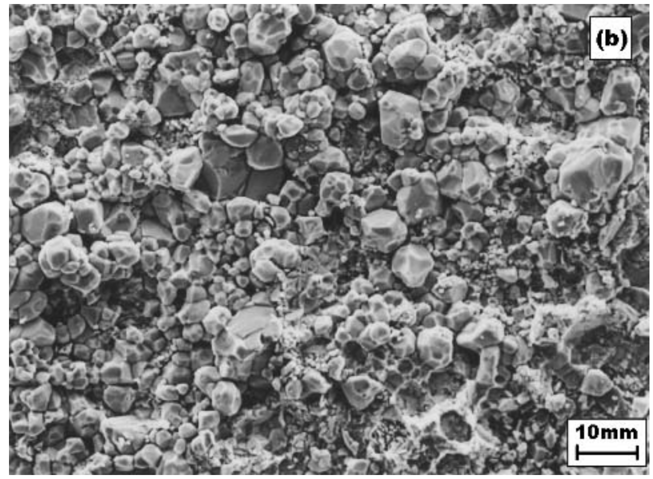


Fig. 9 Fractographs of ITO/Cu joint bonded with Sn3.5Ag4Ti(Ce, Ga) active solder after tensile testing: **(a)** the Cu specimen side; **(b)** the ITO specimen side

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