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Precursor film of tin-based active solder wetting on ceramics

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The phenomenon of the precursor film in a metal–ceramics wetting system was investigated using tin-based active solder (active element: Ti, Zr, Nb, V, Hf or Ta, the third element Ni, Cu, Ag, In or Al) wetting on the ceramics (sialon, mullite, barium titanate alumina and ZTA-SiC). The results show that the formation of a precursor film in the wetting system is dependent on the following factors. (1) The active metal: the presence of titanium, zirconium or hafnium in the solders induced the formation of a precursor film, but niobium, vanadium and tantalum did not. (2) Temperature: a precursor film will not form unless the critical wetting temperature is reached, while a weak film will form during a second wetting at higher temperature. (3) Ceramics: under the same wetting conditions for Sn–4Ti solder, a precursor film forms on the surface of sialon, ZTA–SiC, and red alumina, but not on white alumina, mullite or barium titanate. (4) The third element; small amounts of nickel (1–3 at %), copper (5 at %), or silver (5 at %) in Sn–5 at % Ti solder will enhance the precursor film. On the other hand, small amounts of Al (5 at %) will completely inhibit the occurrence of precursor film. SEM observation reveals the precursor film to be mainly composed of a continuous film with segregated active metal and some small tin islands on the film. Its thickness is several micrometres, similar to that of the interfacial reaction layer between the solder and the ceramic. Two early theories for the formation of a precursor film, surface diffusion and evaporation–condensation, cannot explain the above phenomenon very well. A new model of rapid absorption then film overflow is proposed here for the first time and some problems with the model are also discussed.

1. Introduction

A recent important development in welding engineering is the process of metal/ceramic joining because of the promising uses of the joints. Much effort has been focused on direct joining of ceramic and metal by a reactive brazing filler metal [1–10], which stimulated research into the problem of poor wettability of metal wetting on ceramics, both in science and technology. One view which is held is that interfacial chemical reactions between the ceramic and metal might even be necessary to produce any good wettability of an alloy on ceramic [11, 12]. Hence, it is a basic procedure to add a small amount of an active metal such as titanium to a brazing filler metal in order to improve the wettability of a convenient brazing alloy. On the other hand, knowledge of the processes by which a metal droplet spreads on the ceramic surface is still lacking.

A precursor film (halo) which shows up ahead of the nominal contact line is a common phenomenon in liquid spreading on a solid [13]. In some early studies of wetting systems such as liquid mercury wetting on copper, gold or silver [14], liquid tin on iron, copper or nickel [15, 16], liquid lead on iron or silver [15, 16], a precursor film has frequently been observed which has a fresh and bright colour ahead of the spreading drop itself. Moreover, in other wetting systems, such as water–glass or other organic and inorganic solution–solid system, the precursor film phenomenon has been recognized for many years [17–19]. Because the precursor film plays an important part in the liquid spreading on the solid, much attention has been focused on this phenomenon as a result.

Based on early observations and descriptions, the following four basic characteristics of the precursor film were recognized. (1) The precursor film is not a general phenomenon in liquid wetting; it only occurs under special conditions and special wetting systems. (2) For metal–metal wetting systems, a precursor film only exists in those binary alloy systems which have to form solid solutions or compounds. On the other hand, no precursor film exists in an immiscible binary system. (3) There is a critical temperature below which the precursor film does not form at all. (4) If a precursor film appears ahead of the spreading droplet, a better wettability of the liquid on the solid will be expected.

However, in metal–ceramic wetting systems, although we found a precursor film in the wetting system of Cu–Ti brazing alloy/sialon ceramic [10], relatively few details of the phenomenon have

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so far been reported. Because the precursor film phenomenon is related to better wettability, it is technologically advantageous to induce precursor film formation ahead of the spreading droplet to improve the liquid wettability. In particular, because the metal–ceramic wetting system has a relatively poor wettability, if one can induce a precursor film ahead of the spreading solder on the ceramic, it should produce an interesting and significant improvement in the wettability of the solder on the ceramic. The basic idea in present work was to try to achieve this.

2. Experimental procedure

A new series of tin-based active solders, developed by Kapoor and Eagar [7], was designed for observation of the precursor film phenomenon. The tin-based solders have a low melting point, so that the residual stress in a metal/ceramic joint will be very low. Therefore, tin-based active solder should have many potential uses in some particular cases. Because pure tin does not wet any ceramic at all, based on an early thermodynamic calculation for the metal–silicon nitride system [20], a possibly active metal such as titanium, zirconium, niobium, vanadium, hafnium or tantalum was chosen as additive to promote wetting and spreading of the tin-based solder on the ceramic. Because some active metals with high melting points such as hafnium, tantalum and vanadium, etc., can hardly be dissolved into liquid tin, some intermetallic compounds of nickel with a eutectic composition were used as additives. The amount of active metal added was always 4 at % in order that their effects could be compared with each other. In order to study the effect of a third element on the precursor film, five passive metals, silver, copper, nickel, indium and aluminium, were chosen as the additive to Sn–5Ti active solder. The additive amount varied from 5–40 at % for copper, silver and indium from 1–20 at % for nickel, and from 5–20 at % for aluminium. Some intermetallic alloys of X–Ti (where X is copper, silver, nickel, indium or aluminium) were first prepared as the additive of the third element in the solder.

The tin-based active solders were prepared by arc melting in a protective argon atmosphere. Multi-remelting was used to ensure the uniformity of the solders. The weight loss of the solders during arc melting was less than 1%. Details of the preparation of the tin-based solders was reported earlier [20]. Table I gives the chemical composition analysis by EDAX of some of the solders, which was reported earlier [21].

TABLE I EDAX analysis of the tin-based active solders (at %)

Solder	Sn	A[a]	Ni
Sn–4Ti	94.37	5.01	0.62
Sn–4Zr	96.47	2.77	0.76
Sn–4Nb	94.61	3.95	1.44
Sn–4V	93.17	4.52	2.31
Sn–4Hf	94.98	4.66	0.36
Sn–4Ta	95.15	3.37	1.48

[a] A is the active metal.

Six ceramics were prepared in order to observe their influence on the formation of a precursor film. The ceramics used in this experiment are shown in Table II. Of the ceramics, sialon was the most frequently used in this research (obtained from Shanghai Institute of Ceramics, Academia Sinica): Details of the ceramic were given previously [22]. The other ceramics, such as alumina and barium titanate, were commercial ceramics, and few details were supplied.

The ceramic surface was polished using diamond paste, to a finish approaching optical flatness, then the ceramic disc and the solder nugget weighing about 50 mg were carefully cleaned in acetone before the wetting test. The wetting tests were carried out in a water-cooled vacuum furnace with a rotary pump coupled to a diffusion pump. The dynamic pressure in the furnace chamber was kept to about 8 mPa during tests. The furnace chamber was rapidly heated to the test temperature and held there for 20 min. After the specimen was cooled from the test temperature to room temperature, the width of the precursor film and the contact angle of the solders on the ceramic were measured using a tool maker's microscope, then its microstructure was observed by SEM.

3. Results

3.1. Macrograph of the precursor film

Fig. 1 shows a set of typical macrographs of the precursor films in the wetting systems of Sn–Ti–X solder on sialon ceramic, where X is the third element in the solder. The colour of the precursor film is fresher and brighter than that of the spreading droplet itself, therefore the precursor film is easily distinguished from the droplet body as the brighter wetting band around the metal droplet. When the precursor film appears, the wettability of the solder on the ceramic is always improved. Table III gives some of the wetting results; details of the wetting experiment will be published elsewhere [20, 23]. The true contact

TABLE II The ceramic materials

Ceramic	Main composition	Additive	Colour
Sialon	Si_3N_4	$AlN + Y_2O_3$	Grey
White alumina	Al_2O_3	5% $SiO_2 + CaO$	White
Red alumina	Al_2O_3	3% Cr_2O_3	Red
ZTA-SiC	$Al_2O_3 + ZrO_2$ + SiC whisker	2.5%Y_2O_3	Grey
Mullite	$3Al_2O_32SiO_2$		White
Barium titanate	$Ba_2Ti_9O_{20}$	2% SnO_2 + 0.5% Al_2O_3	White

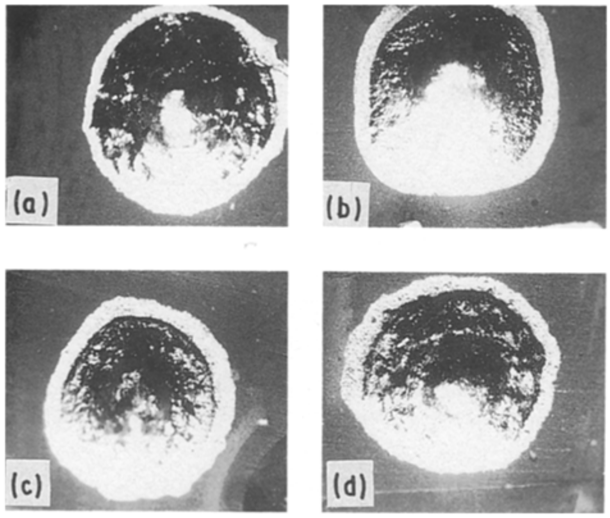


Figure 1 Typical macrographs of the precursor film for tin-based solders wetting on sialon ceramic at 1200 K for 20 min (a) Sn–5Ti–5Ag, (b) Sn–5Ti–3Ni, (c) Sn–5Ti–5Cu and (d) Sn–5Ti–5In.

TABLE III The contact angle and precursor film of the tin-based active solder spreading on sialon ceramic (in vacuum for 20 min)

Alloy	Contact angle (deg)	Width of precursor film (mm)	Test temperature (K)
Sn–4Ti	20	0.30	1300
Sn–4Zr	40	0.10	1300
Sn–4Hf	30	0.04	1300
Sn–4V	90	0	1300
Sn–4Nb	105	0	1300
Sn–4Ta	120	0	1300
Sn–5Ti–5Cu	25	0.22	1100
Sn–5Ti–5Ag	25	0.20	1100
Sn–5Ti–5In	20	0.20	1100
Sn–5Ti–5Ni	25	0.20	1100
Sn–5Ti–5Al	75	0	1100

angle of the precursor film on the ceramic is zero; in fact, the contact angle reported in this research is an apparent contact angle between the droplet and the precursor film when the film is present. The width of the precursor film is not always uniform; sometimes, the droplet is observed to flow fast at a wider precursor film, and relatively slowly at a narrower film, so that the spreading line appears in the form of an S configuration, as reported earlier [21].

A similar wetting band existing on the soldering seam can also be observed when soldering a ceramic/metal joint [20]. When this appears, the wettability of the solder on the ceramic and the ability of the solder to fill the soldering seam and to form fillet will be enhanced.

3.2. Influence of active metals

Fig. 2 shows the relationship between the width of the precursor film and the active metal in the solder under the same wetting conditions. It is clear that titanium is the most effective in inducing precursor film growth, zirconium is the second, and hafnium is the last which is the same order as these metals appear in the periodic table.

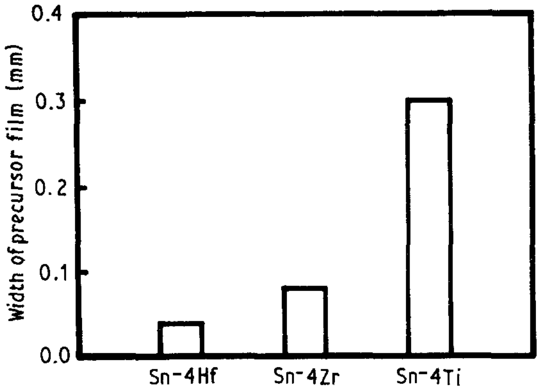


Figure 2 The relationship between the width of the precursor film and the active element in the tin-based solder on sialon at 1300 K for 20 min.

In the six active solders tested, listed in Table III, the precursor film appears only for Sn–Ti, Sn–Zr and Sn–Hf solder. For Sn–V, Sn–Nb and Sn–Ta solder, no precursor film appeared. In comparison, the former metals wet the ceramic better and the contact angles of the solder on the sialon ceramic were lower than 40° at 1300 K for 20 min. However, the latter metals wet the ceramic poorly and the contact angle of the solders under the same conditions exceed 90°. Details of the wettability of the solder on the ceramic have been published previously [20, 21].

3.3. Influence of ceramic materials

The influence of ceramic material on the precursor film and the contact angle is shown in Table IV. In the six ceramics tested, a precursor film of the Sn–4Ti solder occurs only on sialon, red alumina and ZTA–SiC (an $Al_2O_3 + ZrO_2$ composite ceramic strengthened with SiC whiskers); no precursor film was observed on mullite, white alumina and barium titanate. However, there does not seem to be a definite relationship between the width of the precursor film and the contact angle of the solder on the ceramics. It is noteworthy that, for Sn–4Ti solder spreading on an alumina-type ceramic, the precursor film forms on red alumina, but not on white alumina; this reflects the dependence of the formation of a precursor film on the main composition of the ceramic, and also on small sintered additives in the ceramics.

It is a very interesting question, based on above results, why ceramics that a precursor film form on were those containing transitional metals (i.e. had d

TABLE IV The contact angle and the precursor film width of Sn–4Ti solder wetting on various ceramics at 1200 K for 20 min in vacuum

Ceramics	Contact angle (deg)	Width of the precursor film (mm)
Mullite	19.5	0
White alumina	28.5	0
Barium titanate	22.0	0
Red alumina	11.0	0.21
ZTA-SiC	15.5	0.14–0.22
Sialon	20.0	0.15

electrons available: sialon has yttrium as an additive, red alumina has chromium as an additive, etc.), while those ceramics that a precursor film does not form on, were not doped with any transitional metal. It is suggested that a basic reason to explain the phenomenon warrants further study.

3.4. Influence of the third element

3.4.1. *Nickel*

Fig. 3 shows the effect of the third element nickel in the Sn–Ti solder on the precursor film: it very effectively promotes precursor film formation when added in small amounts. The width of the precursor film increases from 0.08 mm to 0.36 mm when the nickel addition in the solder varies from 0–1 at %. However, with additions of more than 5 at % Ni, the precursor film effect decreases markedly. In the range of test temperatures used, the precursor film is not present at all when the nickel content in the solder exceeds 10 at %. After the solder had been wetted on the sialon ceramic at 1100 K and cooled to room temperature, the specimen was reheated to 1200 K for 20 min in a vacuum. It was found that the width of the precursor film did not increase, but decreased, and this phenomenon was also found in other wetting experiments performed in this study. In order to distinguish it from the first wetting, this was termed the second wetting.

The strong influence of a small nickel (passive metal) content in the solder on precursor film formation reflects, in fact, an impurity effect. Because nickel in the solder is easy to segregate from liquid tin, and has an affinity with titanium and is prone to form Ni–Ti clusters; the segregation of the active element on the surface and the interface would be enhanced when small amounts of nickel are present, as has been observed from X-ray mapping (Section 3.6).

3.4.2. *Copper*

Fig. 4 shows the influence of copper as the third element in the Sn–Ti solder on the precursor film at different temperatures. The behaviour of copper in the solder is similar to that of nickel, and a small amount of copper in the Sn–Ti solder can promote growth of the precursor film. However, the width of the precursor film does not increase when the copper content in the solder is more than 5 at %. In fact, the width of the precursor film becomes very small, when too much copper is added to the solder, such as Sn–5Ti–30Cu and Sn–5Ti–40Cu.

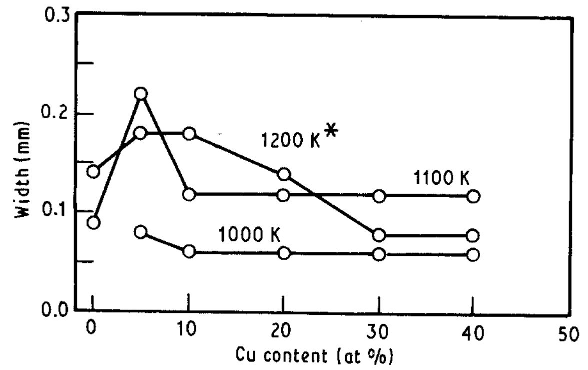


Figure 4 The influence of copper as the third element in Sn–5Ti solder on the precursor film, wetting on sialon. (*) Second wetting.

3.4.3. *Silver*

Fig. 5 shows the influence of silver in the Sn–Ti solder on the precursor film. Similar to that of nickel and copper, a small silver in the solder is effective in enhancing the precursor film of the solder. However, if the silver content is more than 10 at %, the width of the precursor film will decrease considerably. In the second wetting, the precursor film of the Sn–Ti–Ag solder becomes very small; for example, for Sn–5Ti–10Ag solder, the width of the precursor film in the second wetting is only one-third that in the first wetting.

3.4.4. *Indium*

Fig. 6 summarizes the influence of indium in the Sn–Ti solder on the precursor film. Unlike nickel, copper and silver, a small amount of indium (5 at %) in the solder does not obviously affect the precursor film until it reaches 20–30 at %. When the content of indium in the solder is more than 30 at %, it was found that the Sn–Ti–In solder had a very poor flowability [23]. In fact, it was observed that there were two flow steps ahead of the spreading droplet. The outer step was related to the width of the precursor film in this case, which was thicker than that of other precursor films under the tool microscope observation.

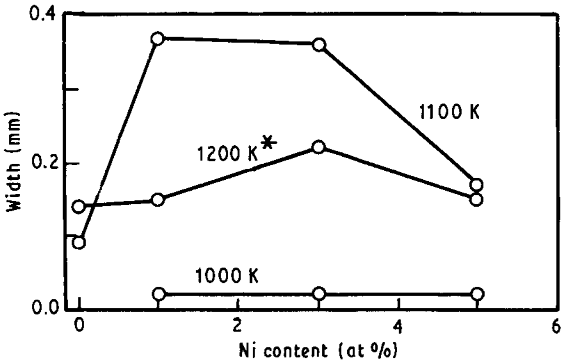


Figure 3 The influence of nickel as the third element in Sn–5Ti solder on the precursor film, wetting on sialon. (*) Second wetting.

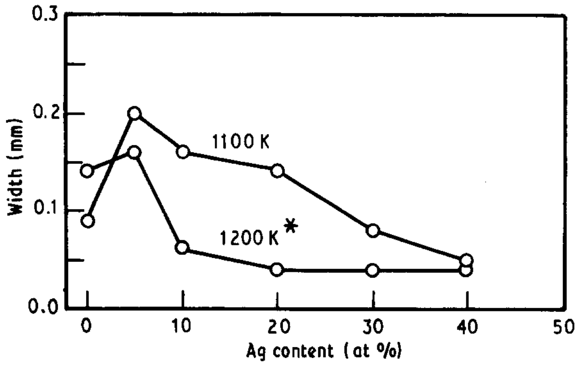


Figure 5 The influence of silver as the third element in Sn–5Ti solder on the precursor film, wetting on sialon. (*) Second wetting.

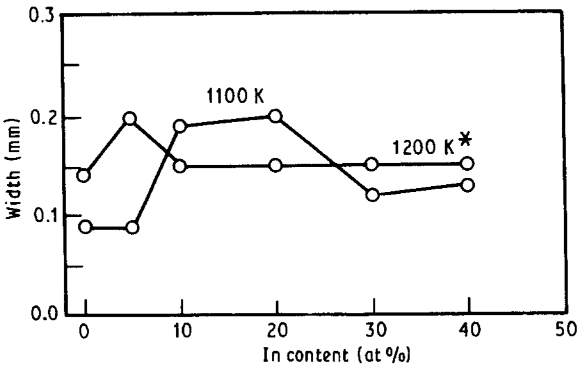


Figure 6 The influence of indium as the third element in Sn–5Ti solder on the precursor film, wetting on sialon. (∗) Second wetting.

3.4.5. Aluminium

Aluminium is a harmful element to the formation of precursor film; it can effectively prevent its formation. For Sn–5Ti–Al solder, it was found that the precursor film did not occur in any case when aluminium in the solder varied from 5–20 at % with wetting temperatures between 800 and 1200 K. Moreover, the Sn–5 at % Ti–Al solder has a poor wettability on the ceramic, and a layer of oxidation film on the droplet surface is obviously present after cooling the specimen in vacuum. In comparison, the contact angle of Sn–5 at % Ti solder on sialon ceramic at 1100 K is 20°, but it increases to about 75° for Sn–5 at % Ti–5 at % Al solder under the same conditions, as shown in Table III.

3.5. Influence of temperature

Fig. 7 shows the influence of temperature on the precursor film. When the temperature is lower, although the tin-based solders have melted completely, no precursor film appears at all below 1000 K. Moreover, the contact angle of the solders on sialon ceramic is high below 1000 K, and the droplet has a spherical shape; a similar phenomenon was also observed by Kapoor and Eagar [7]. The question of why the critical temperature phenomenon was only observed in the tin-based active solder wetting on the ceramic will be discussed in the next section. When the wetting temperature is higher than 1000 K, the contact angle of the Sn–Ti solder on sialon ceramic decreases rapidly, and a very narrow precursor film appears ahead of the spreading droplet. On increasing the temperature to 1100 K, the width of the precursor film will increase quickly. However, it changes little with further increase in temperature for most cases. For the second wetting at higher temperatures, mentioned above, the width of the precursor film of some solders does not increase but decreases rapidly, indicating that the formation of a precursor film depends not only on the wetting temperature but also on the heating history of the wetting system.

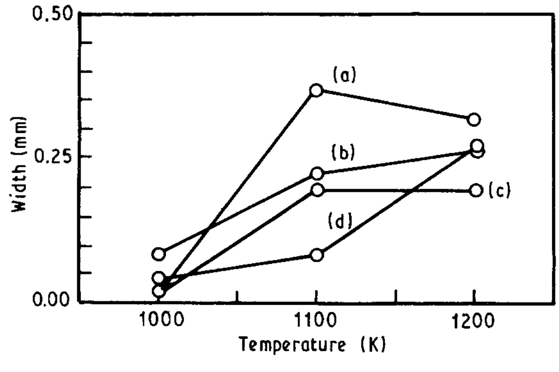


Figure 7 The influence of temperature on precursor film (on sialon): (a) Sn–5Ti–3Ni, (b) Sn–5Ti–5Cu, (c) Sn–5Ti–5Ag, (d) Sn–5Ti–5In.

3.6. Microstructure of the precursor film

Fig. 8 shows scanning electron micrographs of the precursor film for Sn–5Ti–3Ni solder wetting on sialon ceramic at 1200 K for 20 min. The X-ray maps of the precursor film, which reveal the distribution of each chemical composition in the precursor film, are shown in Fig. 9. It is clear that the precursor film is composed of two parts: a layer of continuous thin film adhering to the ceramic, and many small islands lying on the film. The continuous thin film is mainly composed of the active metal titanium in the Sn–Ti–X solder, and a small amount of tin covering part of the film. The small islands mainly composed of tin are distributed very non-uniformly, and they are isolated from each other. It was also found that the third element, nickel, in the solder also segregates on the precursor film, coexisting with titanium and forming some very small particles, which is important in understanding why a small amount of nickel in the solder can effectively strengthen the precursor film.

Chemical composition analysis on the precursor film and the surface of the solder droplet was made by SEM–EDAX; the results are shown in Table V. It is easy to see that the chemical composition of the precursor film varies greatly; the data are so scattered in different positions that data cannot even be obtained from the point analysis by EDAX. However, a general trend is obvious, namely, the active element titanium in the solder segregates on both the precursor film and the surface of the solder droplet, and the enriched amounts in both of them are also similar. The result implies that the precursor film could directly originate from a thin layer of liquid of the spreading droplet; a possible model of the active atom movement will be discussed in the next section.

The small tin islands lying on the precursor film appear to be in a contractive state. It is interesting to postulate from where the small tin islands emanate. In the next section, it is suggested from a preliminary discussion that the small tin islands just signify overflow of the liquid film during the formation of the precursor film.

Micrographs of the precursor film for Sn–5Ti–5Cu solder wetting at 1200 K for 20 min, which is very similar to the results of Sn–5Ti–3Ni solder, are shown in Fig. 10. Fig. 11 shows X-ray maps of tin, titanium and copper for a transverse section of the precursor film. It is clear that the precursor film is mainly composed of titanium with a covering layer of tin. The thickness of the precursor film is several micrometres, similar to that of the interfacial reaction layer. In

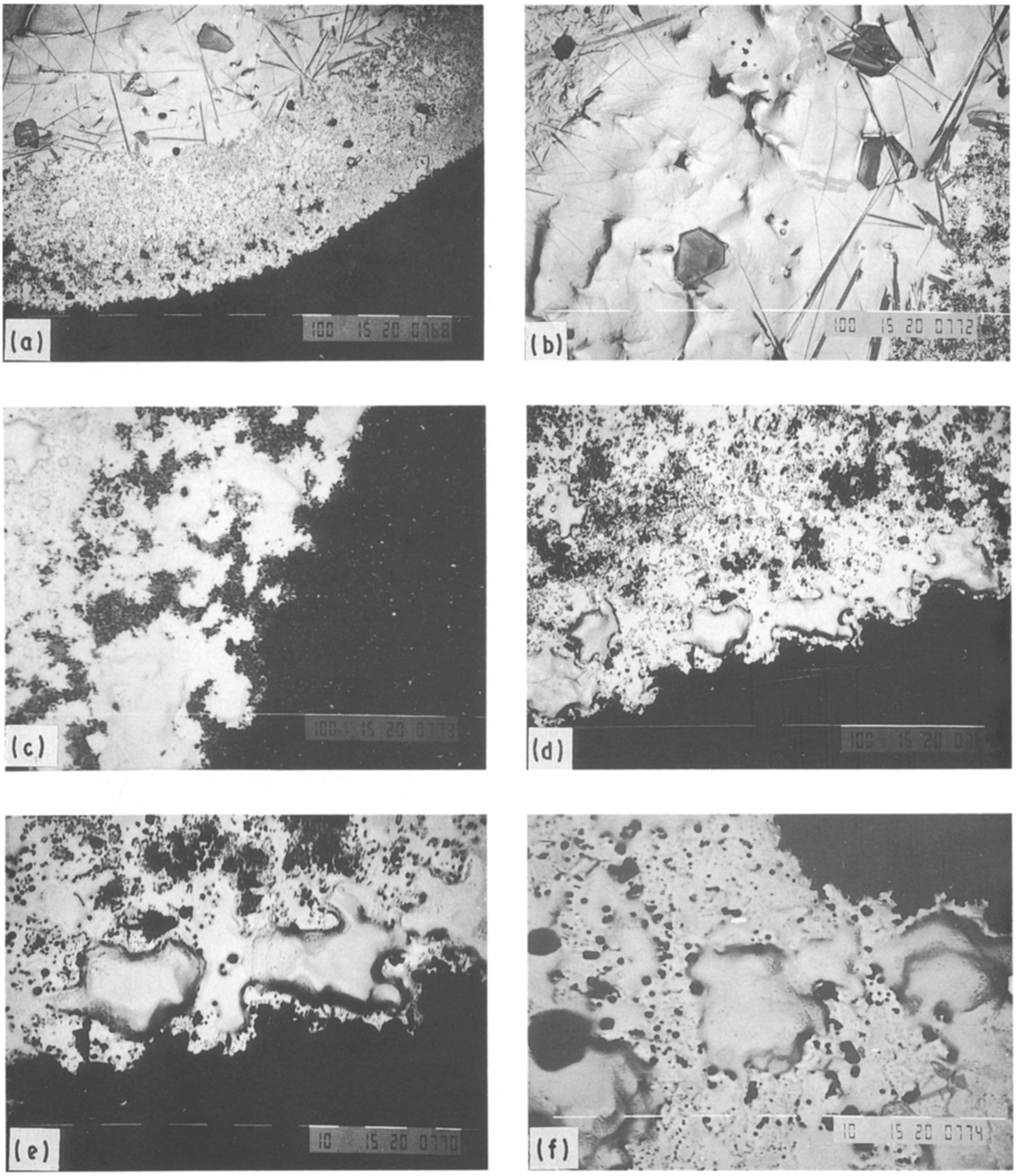


Figure 8 Micrographs of the precursor film for Sn–5Ti–3Ni solder wetting on sialon ceramic at 1200 K for 20 min. (a) macrograph (× 50), (b) liquid surface (× 100), (c, d), tin islands (× 250), (e, f) tin islands (× 500).

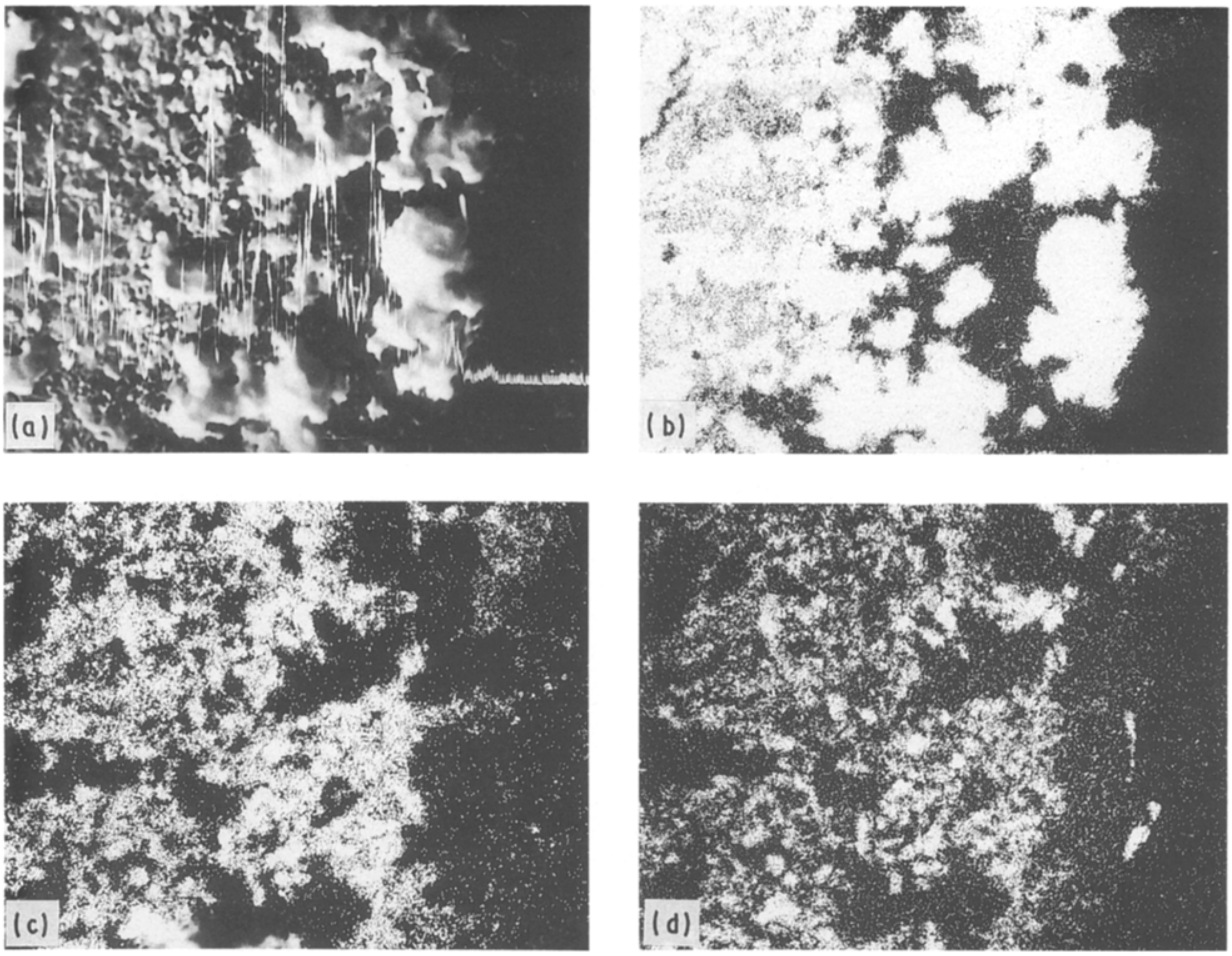
appearance, the precursor film seems to be an epitaxy of the interfacial reaction layer.

4. Discussion

4.1. Early assumptions

From the experimental results mentioned above, obviously, the behaviour of the precursor film found in metal–ceramic systems in four main areas is very similar to that reported in other solid–liquid wetting systems. This implies that there are some general characteristics in the phenomenon, so it is valuable to compare them with each other.

An early explanation of the formation of a precursor film was the evaporation–condensation mechanism [13, 14, 17], because the earliest studied wetting system was one in which the spreading liquid had a high evaporation pressure, such as mercury, water, and some organic or inorganic solvents. The mechanism assumed that there was a local narrow liquid evaporating band at the spreading front of the droplet, and the liquid molecules could be condensed here by gas-phase transportation to form a precursor film.



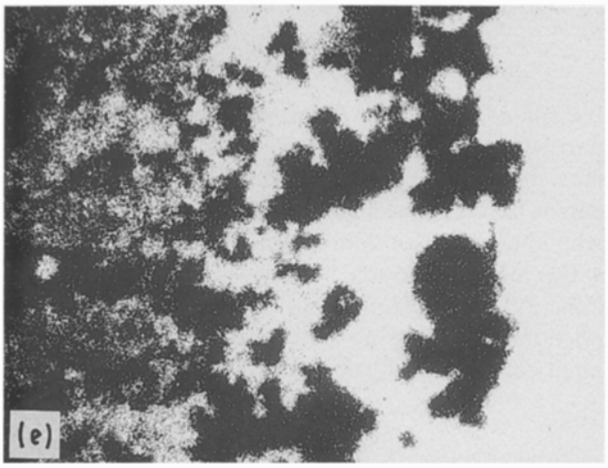


Figure 9 X-ray maps of the precursor film, (×400) (Sn–5Ti–3Ni wetting on sialon at 120 K for 20 min). (a) Micrograph, (b) Sn X-ray map, (c) Ti X-ray map, (d) Ni X-ray map, (e) Si X-ray map.

TABLE V EDAX analysis of the precursor film and the liquid surface for the Sn–5Ti–3Ni solder wetting on sialon ceramic at 1200 K for 20 min; the data are from different positions (at %)

Position	Sn	Ni	Ti	Si
Liquid surface	78.02	0.47	21.51	0
	79.30	0.38	20.32	0
Precursor film	69.02	0.84	22.77	7.37
	56.43	0.60	28.71	14.27
	14.64	0	12.28	73.08
	50.81	0	27.38	21.82
	27.18	11.02	29.65	32.16
	9.81	0.86	5.45	83.88

This model can easily explain why a small amount of aluminium in the solders can strongly prevent the precursor film from forming, because aluminium has a very low evaporating pressure.

Based on this explanation, however, some difficulties exist in understanding the following phenomena reported in this paper. (1) The precursor film is mainly composed of reactive metals such as titanium, which have a very low evaporating pressure. In fact, they are non-volatile elements at the testing temperature and under vacuum. (2) Liquid evaporation should be rapidly enhanced at high temperature. Therefore, the precursor film effect at high temperature should be obviously strengthened; however, the experimental results of the second wetting at higher temperatures are not in agreement with this presumption. (3) A small amount of a third element with a low evaporating pressure can effectively strengthen the precursor film, which directly contradicts the evaporation–condensation mechanism. (4) Using this model it is also difficult to explain why the ceramic materials can influence the formation of a precursor film, because the liquid evaporation and condensation mainly depend on the liquid itself instead of solid material.

Another early explanation of the formation of a precursor film was the surface diffusion mechanism [16, 24]. It assumes that some active atoms in

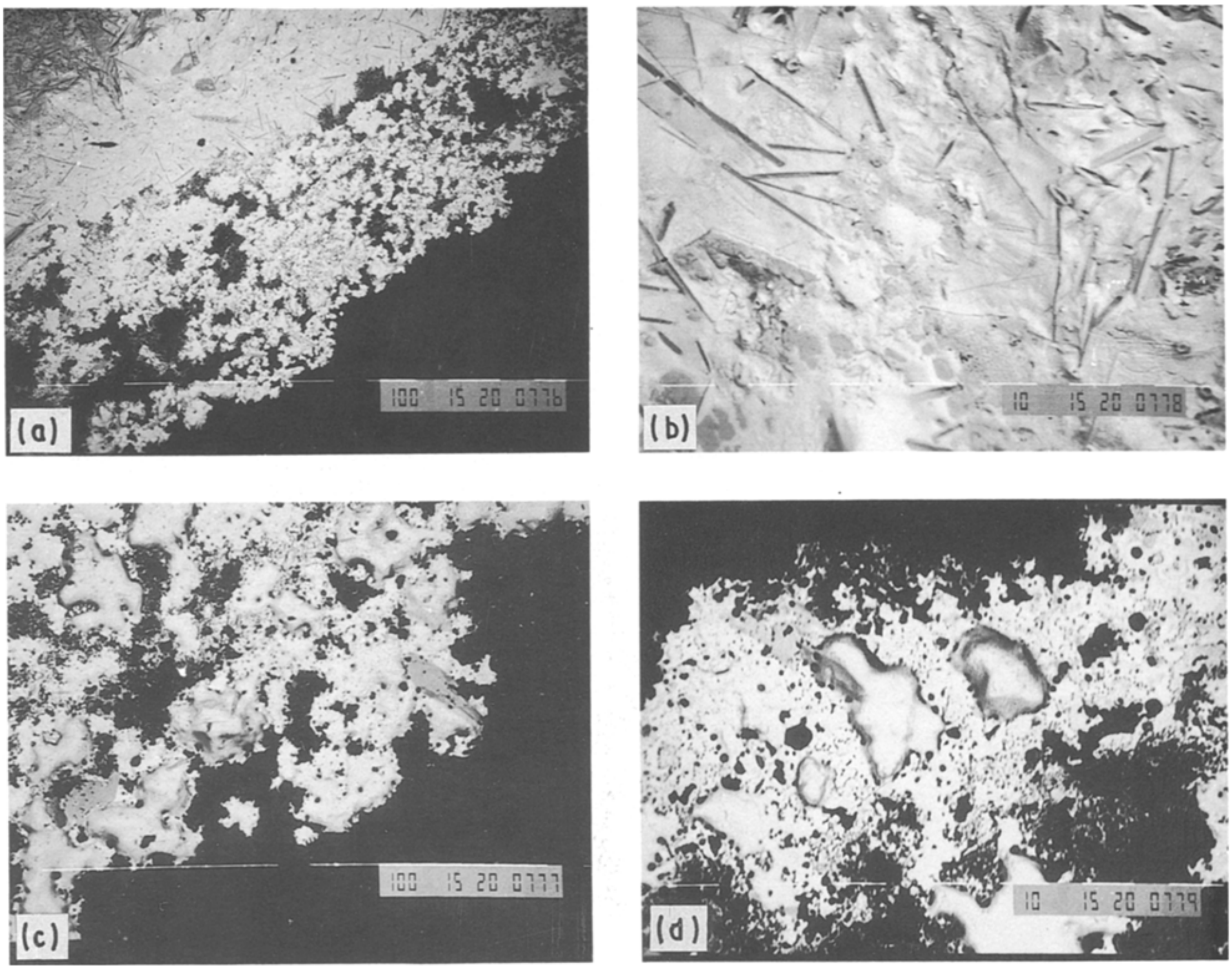


Figure 10 Micrographs of the precursor film for Sn–5Ti–5Cu solder wetting on sialon ceramic at 1200 K for 20 min. (a) Macrograph (× 50), (b) liquid surface (× 500), (c) tin islands (× 250), (d) tin islands (× 500).

the spreading droplet diffuse along the solid surface, particularly, along some surface defects, such as surface channels or grain boundaries, to form the precursor film. The mechanism is successful in explaining why the precursor film is mainly composed of the active metal in the solder; however, it also meets with difficulty in explaining the following experimental phenomena. (1) As no active atom does not have the ability of surface diffusion, why does the precursor film

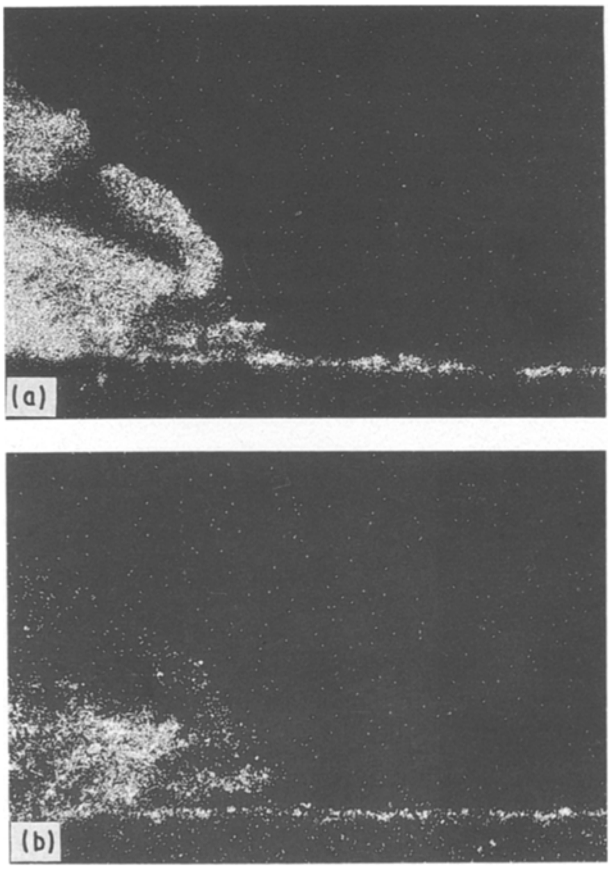
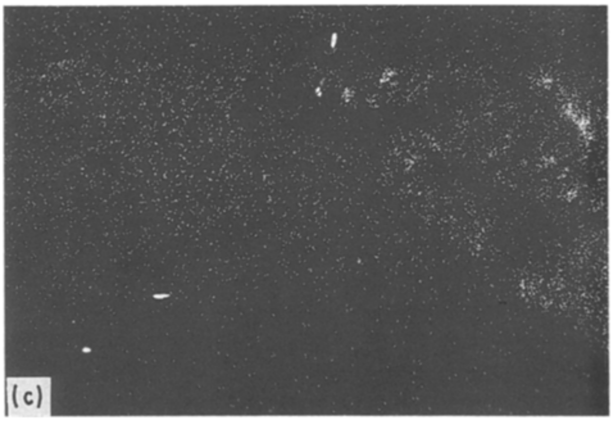


Figure 11 The X-ray map of the transverse section of the precursor film (Sn–5Ti–5Cu wetting on sialon at 1200 K for 20 min, × 400). (a) Sn X-ray map, (b) Ti X-ray map, (c) Cu X-ray map.



on the ceramic only occur in solders with titanium, zirconium or hafnium and not in solders with vanadium, niobium or tantalum? (2) A basic hypothesis of the surface diffusion mechanism is that the precursor film should be in a solid state during its formation and movement, otherwise it would become an overflowing liquid instead of atom diffusion. However, with this assumption it is difficult to explain why many small tin islands exist on the precursor film and where they come from. (3) It is also difficult to explain with this mechanism why a small amount of a third element in the solders can strongly influence the precursor film, because this model assumes that film formation is only caused by the surface diffusion of the active element in the solder, instead of the passive element. (4) Finally, there is also difficulty in explaining the influence of temperature on the precursor film, because the diffusion movement is a thermal agitation process and is very sensitive to temperature; however, the precursor film behaviour does not reflect this character.

Based on the above discussion, this early assumption of the formation of a precursor film can hardly explain the precursor film behaviour observed in a metal–ceramic wetting system, which implies that there are other mechanisms operating in the formation of a precursor film in these systems. Hence, it is valuable to study and establish a new mechanism to explain how a precursor film forms in a metal–ceramic wetting system.

4.2. A new model for the formation of a precursor film by rapid adsorption then film overflow

The fact that the active metal in the solders is strongly segregated on the precursor film indicates that the formation of the precursor film is dependent on the movement of the active atoms in the liquid. In spite of its importance, a clear physical model to describe how an active atom in the spreading droplet moves into the solid–liquid interface is still lacking.

There are two possible ways by which an active atom in a spreading droplet may move into the liquid–solid interface. The first is to pass directly from the droplet to the interface by Brownian motion. The active atom, after innumerable collisions with other atoms, may ultimately reach the solid–liquid interface. If the attractive force of the solid surface to the active atom is stronger than that of the liquid body, the active atom would remain on the interface. The second way is indirect. The active atom first reaches and stays at the surface of the spreading droplet (i.e. the liquid–gas interface) by Brownian motion, then continues to move to the interface from the liquid surface. In both ways the most important factors are the segregating ability of the active atoms in the liquid and the strength of the attraction of the solid surface to the active atom.

The segregating ability is mainly determined by the heat of solution of the active element in the liquid: the higher is the heat of solution of the active metal in the liquid, the lower is the solubility of the element in the liquid [25], and the stronger will be the segregating ability of the active atom [26]. On the other hand, the higher the Gibbs' free energy of the chemical reaction between the active metal and the ceramic, the stronger will be the attraction force of the solid surface to the active atom [20]. In fact, after the active atoms, which tend to segregate in the liquid, make an original movement and tend towards metastable equilibrium, the active atoms will occupy two positions: liquid surface or inside the liquid. The latter, with an agglomeration state, is in fact, a non-soluble part of the active element in the solder. Therefore, only these atoms located on the liquid surface are able to move to the solid–liquid interface.

Dussan and Davis [27] observed the motion of the liquid near the nominal contact line by marking the upper surface of the liquid with small spots of dye. As a result, they suggested a useful model of spreading dynamics, in which the movement of a liquid spreading on a solid is by a rolling motion like a caterpillar vehicle, so that the movement and arrival of the atoms located on the surface of the liquid to the solid–liquid interface will be easier than that of the atoms in the inside of the liquid. If the movement model is suitable for metal–ceramic wetting systems, the active atoms segregated on liquid surface could easily move to the solid–liquid interface in this short-circuit way. A schematic drawing of the model is shown in Fig. 12.

In the wetting system of an active solder–ceramic, the driving force of the Dussan–Davis movement which transfers surface atoms to the solid–liquid interface should come from the adsorption of the active atoms on the solid–liquid interface [28] and chemical reaction [20]. If there was an imbalance in atom numbers between the adsorption and reaction at the interface, the spreading of the droplet on the solid would vary considerably.

Assuming that the numbers of the active atoms arriving at the interface, which depends on both the adsorption potential and the adsorption velocity by the interface, are more than that of the active atoms being consumed at the interface, which depends on the velocity of the interfacial reaction, a temporary stack of active atoms at the interface may occur. There are two possible ways of eliminating this dynamic stack of the active atoms. First, the surplus active atoms at solid–liquid interface may diffuse into the liquid again. Secondly, it would be quite possible, under the attractive field of the solid surface ahead of the spreading droplet, for a thin layer of liquid enriched with the active metal to pass beyond the liquid–gas–solid three-phase line, in front of the spreading droplet,

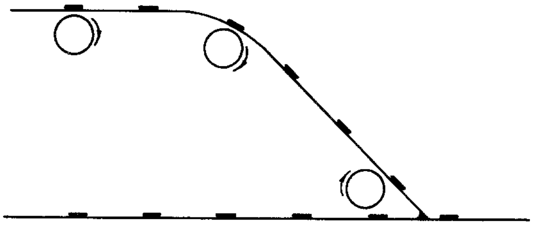


Figure 12 A schematic diagram of how the active atoms in the spreading droplet move to the liquid–solid interface from the liquid surface by a rolling manner.

and overflow on to the ceramic surface to form the precursor film. In this case, because there is segregation of the active metal on the precursor film, the surface tension of the precursor film will be higher than that of the liquid body. From De Gennes' discussion [13], the chemical composition gradient in this area would induce a gradient of surface tension along the precursor film to the droplet, which would cause the droplet to flow along this direction. The new liquid–solid reaction may mainly occur at the precursor film, while a new course may begin again. In other words, the formation of a precursor film should be composed of two processes: the active elements quickly move to the solid–liquid interface under the attractive field of the interface, then the thin layer of liquid which had enriched the active metal overflows on to the surface of the ceramic. On the other hand, if the velocity of arrival of the active atoms at the interface is lower than that of the interfacial reaction, no precursor film could form. Even if a little liquid film occasionally passes beyond the liquid–solid–gas three-phase line, a fast reaction should occur; this results in the formation of solid reaction products instead of a precursor film. In this case, the liquid droplet will spread homogeneously along the surface, or attack the solid *in situ* [24].

Based on the above discussion, there are three basic conditions required to form a precursor film: (1) a fresh liquid surface, (2) fast movement of the active atoms to the liquid–solid interface because of the selective adsorption of active atoms by the interface, and (3) a suitable interfacial reaction velocity.

This mechanism of rapid adsorption followed by film overflow, which forms a new model to explain the formation of a precursor film, is consistent with the four basic characteristics mentioned earlier. First, the precursor film could not be a general phenomenon of wetting, because its formation depends on some special conditions in the wetting system such as rapid adsorption. Second, without a strong attractive force field of the interface (such as an immiscible system), the active atoms could not quickly adsorb to the solid–liquid interface, so that it is impossible, in this case, for the active atoms to make the film overflow to form the precursor film. Third, the selective chemical adsorption and reaction by the interface is sensitive to temperature; as a result, a critical temperature for precursor film formation should exist. Finally, once a precursor film forms ahead of the spreading droplet, it indicates that the active atoms in the liquid can quickly move to the solid–liquid interface. In this case, the wetting driving force would be strong [28], and thus the wettability of the liquid on the solid would be improved.

Based on above discussion, the surface of a liquid should play an important role in the formation of a precursor film. In the wetting test in Section 3.4.5, aluminium, a harmful element to the precursor film formation, reflects this importance, while analysis of the chemical composition of the liquid surface and the precursor film Table V show the model should be reasonable. Because aluminium in the solder can strongly promote the liquid surface to be oxidized, the oxidized liquid surface may block the route of active atoms moving into the liquid–solid interface. As a result, it is easy to understand why it is critical in the oxidation of the liquid surface in both precursor film formation and wettability of a metal on ceramic.

It is also interesting to discuss from where the small tin islands on the precursor film first observed in this experiment emanate. There are two possible times of formation of the tin islands, i.e. during liquid spreading or during cooling.

The first possibility involves a process of automatic decomposition of a liquid film, which has been studied in other wetting systems. In thermodynamics, a super-thin liquid is unstable because of surface tension, particularly when it involves a chemical reaction. Aksay *et al.* suggested [29] that, in non-equilibrium wetting, if a droplet spreads on a solid which is too thin at the onset of wetting, which will not be able to contract to one droplet during the following second spreading because of chemical reaction, the super-thin liquid film will automatically decompose into many small droplets. The precursor film can be referred to as a super-thin film; if the above explanation is also suitable for the precursor film of metal–ceramic wetting system, the formation of the tin islands on the film can be understood very well.

It is also quite possible that the tin islands could arise because the tin solubility is exceeded in the liquid film during cooling. The liquid film with a high active metal content such as titanium, has a correspondingly high melting point. As a result, part of the liquid with high titanium content will first solidify at the beginning of cooling. Because the liquid with a very low titanium content, corresponding to a low melting point gradually separates out from the precursor film on cooling, the small tin droplets will have a relatively poor wettability, which results in a high contact angle of the droplet separated out on the film, and corresponding to the contraction shape of the tin islands observed above.

Although details of the formation of the small tin islands are not quite clear, it can now be deduced that the precursor film should be in a liquid state instead of a solid state during its formation and movement, which is consistent with the model of formation of a precursor film, suggested in this paper, i.e. rapid adsorption then film overflow. In other words, because the assumption of a solid state is the basis of the surface diffusion mechanism [16, 24], the small tin islands provide good evidence for the formation mechanism of the precursor film.

4.3. Critical wetting temperature

As a physical chemical phenomenon, the critical wetting temperature has been reported in the wetting system of metal–metal [11, 30]. For example, the critical wetting temperature of tin on molybdenum is 1023 K, of tin on nickel is 673 K, of bismuth on nickel is 923 K, and of tin, lead or bismuth on iron is 873 K, etc. Generally, the critical wetting temperature of a refractory metal such as tungsten, molybdenum or tantalum is roughly estimated to be about one-third of the melting point of the metal [11].

A basic cause of the existence of critical wetting temperature is often analysed first by thermodynamics. Consider the solid chemical reaction between titanium and silicon nitride ceramic

$$4Ti + Si_3N_4 = 4TiN + 3Si \qquad (1)$$

A thermodynamic calculation [31] shows that an equation relating the Gibbs' free energy of the reaction to temperatures between 298 and 1155 K is (in kJ mol^{-1})

$$\begin{aligned} \Delta G = & -651 + 0.743T + 6.15\times 10^{-5}T^2 \\ & - 0.103T\ln T - 4.52\times 10^{-9}T^3 + 2683/T \quad (2) \end{aligned}$$

where ΔG is the Gibbs' free energy and T the absolute temperature. Based on this equation, the Gibbs' free energy of the reaction is -579 kJ mol^{-1} at 498 K, and -556 kJ mol^{-1} at 1098 K. This result revealed that the Gibbs' free energy of the reaction varies very little with reaction temperature, namely, there is no critical point in the thermodynamics to explain the existence of a critical wetting temperature of the Sn–Ti active solder on the ceramic.

However, it was indeed found that, not only in this experiment but also in Kapoor's report, such a critical temperature does exist; if the test temperature is lower than this temperature, the melting droplet is neither wetting nor adhesive on the ceramic.

Because the wetting of the active solders on the surface of the ceramic is in the nature of a chemical wetting, namely, a local chemical reaction. The existence of the phenomenon of critical wetting temperature implies that there could be a critical reaction temperature between the active metal and the ceramic. Although the reasons for the existence of a critical reaction temperature are not clear, an early experiment on this assumption was made [32], in which a layer of pure titanium was deposited on the silicon nitride, then the sample was heated to various temperatures. The test showed that no reaction occurred below 973 K, but that TiN and Ti_5Si_3 formed from 1073–1123 K. This result is very approximate to the critical wetting temperature 1000 K, which again reflects that the interfacial chemical reaction between the active metal in the solders and the ceramic is an essential condition in the wetting of a metal on a ceramic.

On the other hand, in some of the early wetting systems studied, because the melting points of all the copper- [5, 6, 10], nickel- [33, 34], silver- [3, 9, 35, 36] and gold-based [37] active brazing alloys are higher than that of the critical reaction temperature, once the brazing alloy melts, they will react with and then wet the ceramic immediately. As a result, no critical wetting temperature was found in the early studies on active brazing alloys. However, the tin-based solders have a melting point lower than the critical reaction temperature, and hence the critical wetting temperature of the metal on the ceramic is only found in tin-based active solders. This is indeed a new interesting phenomenon in ceramic–metal wetting systems and is worthy of careful research.

5. Conclusion

The precursor film phenomenon in metal–ceramic wetting systems was investigated and described. The precursor film is present as a bright wetting band ahead of the spreading droplet. If the precursor film occurs in the wetting system, the wettability of the solder will be improved. The precursor film is mainly composed of two parts, a thin layer of continuous film enriched by the active element and adhering to the ceramic, and many very small tin islands lying on the thin film. The chemical composition of the precursor film is like that of the liquid surface of the solder. The thickness of the precursor film is several micrometres, similar to that of the interfacial reaction layer. By careful observation, it was found that the formation of a precursor film depends on the following factors. (1) The active metal: titanium, zirconium and hafnium in the tin-based solder were found to induce the formation of a precursor film, but niobium, vanadium and tantalum did not. (2) Temperature: no precursor film will appear unless the critical wetting temperature is reached. The effect of temperature on the precursor film decreases in the second wetting when the specimen is reheated at a higher temperature. (3) Ceramics: under the same conditions as for Sn–4Ti solder, a precursor film will form on the surface of sialon, ZTA-SiC, and red alumina, but will not form on the surface of white alumina, mullite or barium titanate. (4) The third element: a small amount of Ni (1–3 at %), Cu (5 at %), or Ag (5 at %) in Sn–5 at % Ti solder will enhance the effect of the precursor film. On the other hand the addition of a small amount of aluminium (5 at %) will strongly prevent the occurrence of the precursor film.

Two early mechanisms postulated for the formation of a precursor film, namely surface diffusion and evaporation–condensation, cannot explain the above mentioned phenomena very well. A new mechanism, of rapid adsorption followed by film overflow, to explain how a precursor film forms is proposed in this paper for the first time and several problems with the new model are also discussed.

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References

1. A. J. MOORHEAD, *Weld J.* **62** (1983) 17.
2. A. J. MOORHEAD and H. KEATING, *ibid.* **65** (1986) 17.
3. H. MIZUHARA and K. MALLY, *ibid.* **64** (1985) 27.
4. H. MIZUHARA, US Pat. 4591 535 (1986).
5. M. G. NICHOLAS, T. M. VALENTINE and M. J. WAITE, *J. Mater. Sci.* **15** (1980) 2197.
6. M. G. NICHOLAS and T. M. VALENTINE. GB Pat. 2066 291A (1981).

7. R. R. KAPOOR and T. W. EAGAR, *Metall. Trans.* **20B** (1989) 919.
8. *Idem, J. Amer. Ceram. Soc.* **72** (1989) 448.
9. A. P. XIAN and Z. Y. SI, *J. Mater. Sci.* **25** (1990) 4483.
10. A. P. XIAN, X. M. XUE and Z. Y. SI, *J. Mater. Sci. Lett.* **10** (1991) 246.
11. J. V. NAIDICH, *Prog. Surf. Membr. Sci.* **14** (1981) 353.
12. F. DELANNAY, L. FROYEN and A. DERUYTTERE, *J. Mater. Sci.* **22** (1987) 1.
13. P. G. de GENNES, *Rev. Mod. Phys.* **57** (1985) 827.
14. G. TAMMANN and F. ARNSTZ, *Z. Anorg. Allgem. Chem.* **192** (1930) 45.
15. G. TAMMANN and A. RUHENBECK, *ibid.* **223** (1935) 192.
16. G. L. J. BAILEY and H. C. WATKINS, *J. Inst. Metals* **80** (1951/52) 57.
17. W. HARDY, *Philos. Mag.* **38** (1919) 49.
18. D. BANGHAM and S. SAWERIS, *Trans. Faraday Soc.* **34** (1938) 554.
19. H. GHIRADELLA, W. RADIGAN, H. L. FRISCH, *J. Coll. Interface.* **51** (1975) 522.
20. A. P. XIAN, PhD dissertation, Institute of Metal Research, Academia Sinica, Shenyang 110015, China (1991).
21. A. P. XIAN and Z. Y. Si, *J. Mater. Sci. Lett.* **10** (1991) 1315.
22. L. P. HUANG, Z. K. HUANG, X. L. XU and X. L. FU, *Acta Inorg. Mater. Sinica* **1** (1986) 123 (in Chinese).
23. A. P. XIAN, *J. Mater. Sci.* submitted.
24. Y. S. YI, X. M. QIU and H. Y. WANG, in "Proceedings of Sixth Conference of Welding in China", Vol. 1, edited by Z. Y. Si (Xian, China, 1990) pp. 12, 21 (in Chinese).
25. D. FONG, "Metal Physics", Vol. 1, edited by D. Fong (Science Press, Beijing, 1987) in Chinese.
26. E. HONDROS and M. P. SEAH, *Int. Met. Rev.* **22** (1977) 262.
27. V. E. DUSSAN and S. DAVIS, *J. Fluid. Mech.* **65** (1974) 71.
28. A. P. XIAN and Z. Y. SI, *Chin. J. Met. Sci. Technol.* **6** (1990) 182.
29. I. A. AKSAY, C. E. HOGE and J. A. PASK, *J. Phys. Chem.* **78** (1974) 1178.
30. A. BONDY, *Chem. Rev.* **52** (1953) 417.
31. A. P. XIAN and Z. Y. SI, *Comput. Appl. Chem.* **8** (1991) 232 (in Chinese).
32. *Idem, Acta Metall. Sinica* (*Engl. Ed.*) **B3** (3) (1990) 207.
33. M. NAKA, T. TANAKA, I. OKAMOTO and Y. ARATA, *Trans. JWRI* **12** (2) (1983) 337.
34. N. IWAMOTO, Y. MAKINO and H. MIYATA, *ibid.* **15** (1) (1986) 55.
35. A. P. XIAN and Z. Y. SI, *J. Mater. Sci. Lett.* **10** (1991) 1381.
36. *Idem, J. Mater. Sci.* **27** (1992) 1560.
37. M. HOWARD, EP Pat. 0104 623 A2 (1984).

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