JOURNAL OF MATERIALS SCIENCE **26** (1991) 4067–4075

Oxidation behaviour of titanium-containing brazing filler metals

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Brazements on alumina or partially stabilized zirconia (PSZ) of four silver- or copper-based brazing filler metals that contain titanium to promote wetting of and adherence to structural ceramics, were exposed in a thermogravimetric analyser at temperatures up to 700 °C to atmospheres of 100% O_2, Ar–20% O_2 and Ar–3 p.p.m. O_2. The alloys included Cu–41.1Ag–3.6Sn–7.2Ti, Ag–44.4Cu–8.4Sn–0.9Ti, Ag–41.6Cu–9.7Sn–5.0Ti and Ag–37.4Cu–10.8In–1.4Ti, at%. All formed external oxides that were more or less protective under all of the test conditions studied. The growth of the oxides followed a parabolic time law. The gains in weight due to oxidation observed were small, ranging (for 45 h exposure at 400 °C to Ar–20% O_2) from 0.20 mg cm^{-2} for the Ag–37.4Cu–10.8In–1.4Ti alloy to 0.46 mg cm^{-2} for Cu–41.1Ag–3.6Sn–7.2Ti. As expected, weight gain increased with increasing temperature or P_{O_2}. Unexpectedly, the titanium played a minor role in the scale formed on any of the filler metals with a titanium oxide, TiO_2, being found on only one alloy – Ag–41.6Cu–9.7Sn–5.0Ti. The brazements on PSZ gained weight at a higher rate than comparative brazements on alumina. We attribute this behaviour to oxygen transport through the zirconia resulting in the growth of an interfacial layer of titanium oxide.

1. Introduction

Many potential applications for structural ceramics require that these materials be joined to similar or different ceramics or to metallic alloys. Such applications include insulating or wear-resistant components for low heat rejection diesel engines, or turborotors and other components for advanced gas turbine engines. Although the in-service stress, temperature and atmospheric conditions vary greatly for these applications, joints are generally required to be strong, reliable and relatively inexpensive to manufacture. Brazing is potentially a viable process for joining structural ceramics for many applications. Unfortunately, most ceramics are not wetted by conventional brazing filler metals; and wetting is one of the principal requirements for brazing. This problem can be overcome by either precoating the ceramic surface with a suitable metal layer prior to brazing, or through the use of specially formulated filler metals that will wet and adhere directly to an untreated ceramic surface.

The wetting of a ceramic by a molten metal and the adhesion in such a system increases with growing affinity of the metal constituents for the elements that make up the solid phase [1]. Thus, chemically oxygen-active metals such as titanium, zirconium, aluminium, silicon, manganese or lithium should enhance both the wetting of and adherence to oxide ceramics by inherently nonwetting alloys. In the same way, the wetting of and adherence to SiC and Si_3N_4 are aided by filler metals containing elements that strongly interact with silicon, carbon or nitrogen. Whether the ceramic is an oxide, carbide or nitride, the active metal reacts with the ceramic surface, forming an interfacial layer that can be wetted by the bulk of the filler metal.

Titanium is the most extensively studied and widely used active element addition to filler metals formulated to braze directly high-melting oxide ceramics [2–6]. The critical interfacial reaction product in the case of oxide ceramics brazed with titanium-containing filler metals is either TiO or Ti_2O_3, with appreciably higher adhesion in systems that result in the formation of TiO [7]. Titanium additions to filler metals have also been shown to enhance wetting of and adherence to silicon carbide [8] and silicon nitride [9]. The wettable reaction products in the latter cases are titanium silicides, titanium carbides and titanium nitride.

Although a significant amount of research and development has shown the merit of titanium additions to filler metals for ceramic brazing, the oxidation resistance of oxygen-active brazing filler metals has not been extensively investigated. A notable exception to this statement is the work of Kapoor and Eagar [10] in which they studied the corrosion in air at 600 °C of a series of reactive-element-containing silver- and copper-based filler metals on Si_3N_4. This paper presents the initial results of oxidation studies for four titanium-containing filler metals roughly based on the Ag–Cu eutectic (Ag–40 at % Cu, 780 °C) [11]. Silver- and copper-based filler metals were selected because they are relatively inexpensive, are the

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most widely used of all the families of brazing filler metals, and have relatively low brazing temperatures. The latter feature is needed for some applications in which the properties of the base materials can be degraded by exposure to elevated temperatures.

When an alloy composed of a noble metal A and a less noble metal B is held at high temperature, oxidation occurs either externally or internally depending on the oxygen partial pressure, temperature and the concentrations, solubilities and diffusivities of the constituent metals and their oxides ([12], p. 114, [13]). At the time of initial exposure, the component B on the alloy surface produces nuclei of B O in a matrix of A. If the rate of diffusion of B to the surface is sufficiently rapid, external oxidation results in the formation of a potentially protective layer. If this condition is not met, diffusion of atomic oxygen into the alloy results in internal oxidation and the precipitation of B O particles. Consequently, the oxidation front progresses through the alloy as exposure continues. Thus, whether the oxidation process is external or internal depends on the balance between the outward flow of B and the inward flow of oxygen.

The conditions for the transition from internal to external oxidation have been described in detail by Wagner [14]. In general, there is a critical concentration of the less noble metal in the alloy required to ensure the formation of only an external oxide layer (B O) according to the following relationship [15]

$$N_B = \frac{V}{z_B M_O}(\pi \kappa_p / D)^{0.5} \qquad (1)$$

where N_B is the critical concentration of less noble B atoms, V is the molar volume of the alloy, z_B is the valency of the B atoms; M_O is the atomic weight of oxygen; D is the diffusion coefficient of B in the alloy; and κ_p is the parabolic rate constant for oxidation.

It has been found empirically that external oxidation occurs (in 1 atm oxygen) when the concentration of the less noble metal is higher than about 10 at % [15]. The brazing filler metals included in this study were quaternary alloys containing silver, copper, titanium and either tin or indium; and their oxidation behaviour would be expected to be much more complex than that of a simple binary. Each component of the filler metal has a different affinity for oxygen and does not diffuse at the same rate in the oxide or the alloy. At temperatures of interest, silver is the noblest metal; therefore, the other elements are subject to oxidation. Although the various binary systems would be expected to give general guidance to oxidation behaviour in a ternary or quaternary system, the interrelationships are so complex that actual testing under simulated service conditions is required.

2. Experimental procedure

2.1. Materials

The composition of the brazing filler metals included in this study are listed in Table I. One of the filler metals (Incusil ABA™, Ag–37.4Cu–10.8In–1.4Ti (at %) Wesgo Division, GTE Products Corporation, Belmont, California) is commercially available as rolled foil. The others, which are experimental alloys being studied at Oak Ridge National Laboratory (ORNL), were made by gas tungsten-arc melting high-purity stock into 125 g buttons on a water-cooled copper hearth. After the sixth melting cycle, the buttons were drop cast into a 4.9 mm × 25 mm cross-section copper mould. The low titanium content of these filler metals results in relatively low brazing temperatures (~760 °C for Incusil ABA and ~800 °C for the experimental filler metals). The AJM-100a alloy is ductile and was cold rolled into foil for preplacement in the braze joint. The AJM-95a and AJM-96a filler metals were fabricated into foil by melt spinning. As will be shown below, the Cu–41.1Ag–3.6Sn–7.2Ti filler metal was studied more extensively than the others in order to simplify the experimental work.

TABLE I Compositions of the brazing filler metals

Filler metal	Composition (at %)					Brazing temperature (°C)
	Ag	Cu	In	Sn	Ti	
AJM-100a	41.1	48.1	–	3.6	7.2	800
AJM-95a	46.3	44.4	–	8.4	0.9	800
AJM-96a	43.7	41.6	–	9.7	5.0	800
IN-ABA	52.0	37.4	10.8	–	1.4	760

The low brazing temperatures of these filler metals may seem inconsistent with some potential high-temperature applications. However, although the maximum surface temperature of the insulating ceramic piston cap is expected to be about 1000 °C in low heat rejection diesel engines, the joint between the cap and metallic piston will reach only 345 °C [16]. Also, the turbine rotor in some advanced automotive gas turbine engines will operate at about 1100 °C; but the joint between the ceramic rotor and metal shaft operates at about 400 °C [17]. Thus, "low" brazing temperature filler metals are worthy of consideration for these and other applications on the basis of service conditions. In addition, the low brazing temperatures minimize possible thermal damage to the components and result in lower residual stresses in ceramic–metal joints.

The ceramics were AD-998 alumina (99.8% Al_2O_3, Coors Ceramics Company, Golden, Colorado); and two MgO-partially stabilized zirconias (PSZ) – Nilcra TS grade manufactured by Nilcra Ceramics Pty Ltd, Victoria, Australia, and TTZ grade made by Coors Ceramics Co. The transformation toughened zirconias were selected to determine if the greater oxygen mobility in zirconia compared to alumina was detrimental to brazement oxidation. In other words, in such materials the braze joint might be oxidized both from the atmosphere and from oxygen transport through the ceramic itself. The ceramics were cleaned by rinsing in acetone and firing for 15 min in air at 800 °C. The filler metal foil pieces were degreased in acetone immediately prior to placement on the ceramic for brazing.

2.2. Experimental procedure

The test specimens consisted of a filler metal coating on one face of a ceramic coupon, not a brazed joint in the traditional sense. An ~ 0.1 mm thick layer of filler metal foil was placed on one 22 mm × 25 mm surface of ceramic coupons that had dimensions ≈ 3 mm × 22 mm × 25 mm. Brazing was done in a vacuum of about 7 MPa (5×10^{-5} mm Hg) in a resistance-heated alumina tube furnace. A typical cycle consisted of heating to the brazing temperature (760 °C for samples brazed with Incusil ABA, or 800 °C for those brazed with AJM-95, 96 or 100) in about 15 min, holding for 5 min and cooling to room temperature in about 45 min.

The brazed samples were suspended on a platinum wire and exposed to flowing gases in a specially designed thermogravimetric analyser (TGA) system. This system controls the oxygen level from 3 p.p.m. up to 100%, dew point from − 60 to + 20 °C. The TGA has a sensitivity of ± 2 μg, and is capable of temperatures up to 1500 °C. The parameters used in the present study were: temperature 400, 500, 600 and 700 °C; atmospheres 100% O_2, Ar–20% O_2 and Ar–3 p.p.m. O_2; and times up to 100 h. The gas flow rate was held constant at 1.2 cm sec^{-1} during each run. The samples were held at constant temperature throughout the test, i.e. there was no thermal cycling. The surface area of exposed brazing filler metal in the TGA specimens ranged from about 500 to 600 mm^2. Selected samples were fractured after testing so that the extent and morphology of the corrosion product could be examined in a Hitachi S-800 field emission scanning electron microscope equipped with a Tracor Northern energy dispersive X-ray spectrometer (EDS) system.

3. Results and discussion

3.1. Oxidation of Cu–41.1Ag–3.6Sn–7.2Ti at %

Weight gain was observed under all test conditions for all the samples of alumina brazed with the Cu–41.1Ag–3.6Sn–7.2Ti filler metal. As expected, the oxidation rates increased with increasing temperature or with oxygen content in the atmosphere at a given temperature. Fig. 1 shows the weight gain–time curves for these samples exposed to an Ar–20% O_2 atmosphere at different temperatures. These data indicate that this filler metal oxidized at a very slow rate at a temperature of 400 °C or less.

The relationship between oxidation and time (weight change–time in this work) can generally be described by a simple logarithmic, inverse logarithmic, cubic, parabolic, linear or asymptotic equation ([12], p. 70). The type of relationship depends on scale thickness, so that a change from one time law to another may be observed even under isothermal conditions. As an initial film of oxide thickens, a parabolic relationship is the time law most commonly observed. Several mechanisms have been proposed to explain each of the growth relationships. The most widely accepted mechanism to explain parabolic growth, attributed to Kubaschewski and Hopkins [12], is one of film thickening controlled by diffusion due to a concentration gradient. Thus, if parabolic growth occurs, the oxidation rate is controlled by the diffusion of reactant or product species through the oxide scale, and the square of the weight gain (W) is proportional to the time (t) as follows:

$$W^2 = Kt \tag{2}$$

where $K = K_0 \exp(-\Delta E/RT)$ is the parabolic rate constant and ΔE is the activation energy for the oxidation reaction. Fig. 2 shows the same weight gain data for the Cu–41.1Ag–3.6Sn–7.2Ti/alumina samples replotted according to Equation 2. The straight lines in this plot indicate that the oxidation of this brazing filler metal on alumina follows classical parabolic oxidation behaviour. Such behaviour is indicative of the formation of a nonporous, coherent oxide film acting as a physical barrier to restrict further oxidation. In such a case, growth of the oxide layer is dependent on the relatively slow ionic diffusion of one or more species through the scale. An Arrhenius plot

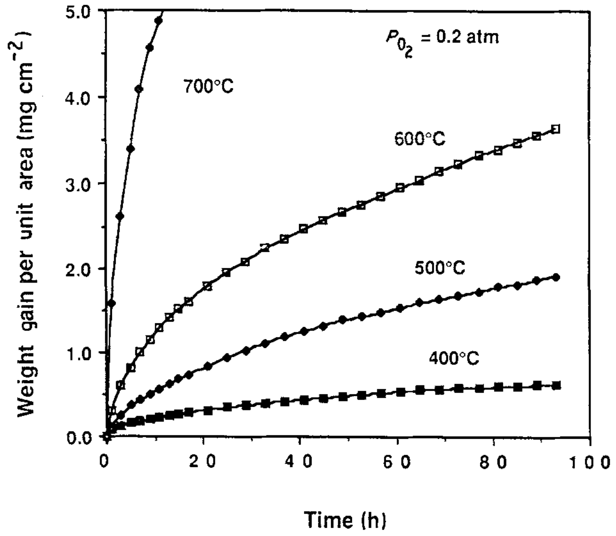

Figure 1 Specific weight change (ΔW) of Cu–41.1Ag–3.6Sn–7.2Ti/alumina brazements exposed to flowing Ar–20% O_2 at various temperatures.

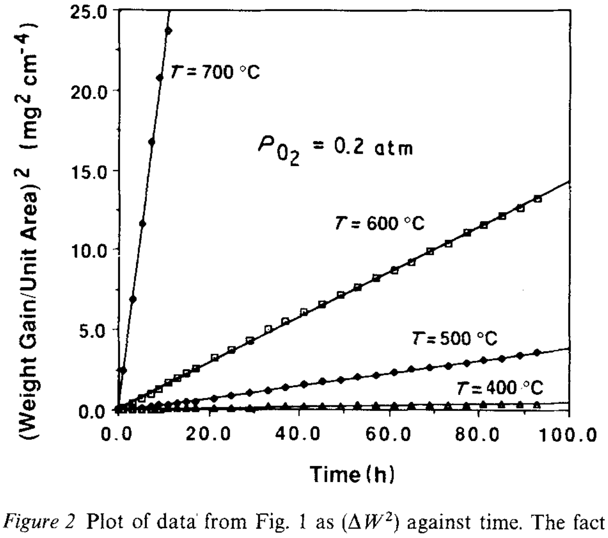

Figure 2 Plot of data from Fig. 1 as (ΔW^2) against time. The fact that these curves are straight lines that intersect the zero point of the coordinate axes indicates that the oxidation of this filler metal follows a simple parabolic law.

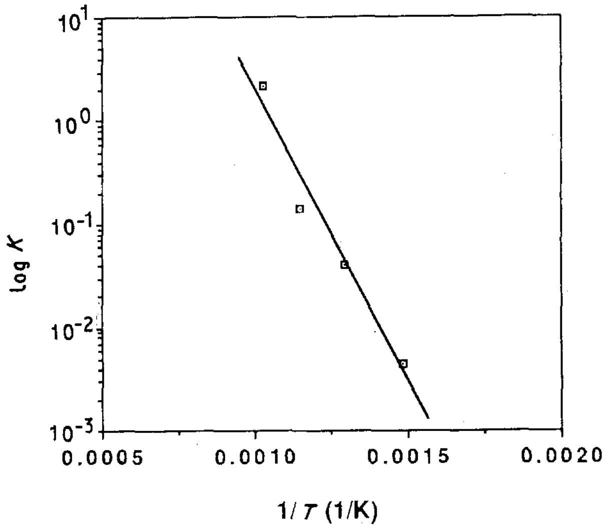

Figure 3 Arrhenius plot of parabolic rate constant K against temperature for the data in Fig. 2. From the slope of this plot, the activation energy (ΔE) for the oxidation of the Cu–41.1Ag–3.6Sn–7.2Ti filler metal was found to be 25.7 kcal mol^{-1}.

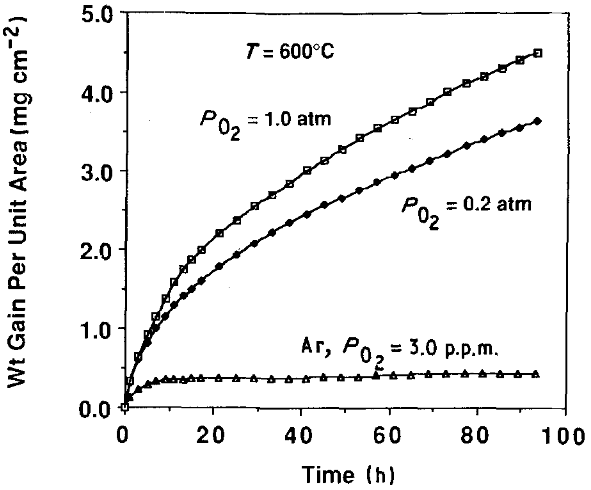

Figure 4 Effect of P_{O_2} on the specific weight change (ΔW) of the Cu–41.1Ag–3.6Sn–7.2Ti filler metal oxidized at 600 °C.

of the parabolic constant K against reciprocal temperature is shown in Fig. 3. From this graph, the activation energy for the reaction is calculated to be 25.7 kcal mol^{-1}, which is somewhat lower than the published values of 31.5 to 33.5 kcal mol^{-1} for the oxidation of pure copper [18, 19]. Nevertheless, analysis of the reaction product (discussed below) indicates that the corrosion of this filler metal is mainly caused by oxidation of the copper in the alloy and that the effect of both tin and titanium is negligible. The effect of oxygen partial pressure on the oxidation behaviour at 600 °C of the Cu–41.1Ag–3.6Sn–7.2Ti filler metal is plotted in Fig. 4. This figure shows that the oxidation is strongly influenced by the oxygen partial pressure. The effect of increasing the oxygen pressure is to increase the flux of oxygen entering the brazement (depending on both the solubility and diffusion of oxygen in the alloy), without affecting the flux of metal atoms to the surface.

Scanning electron micrographs of a polished cross-section of a Cu–41.1Ag–3.6Sn–7.2Ti/alumina brazement after oxidation for 100 h at 400 °C in an Ar–20% O_2 atmosphere are shown in Fig. 5. Fig. 5a indicates that the oxide is a single layer about 3 to 4 μm in thickness. The scale did not spall off on cooling, but does not appear to be tightly adherent to the filler metal. A region containing sizeable voids exists beneath the oxide layer, and this region is somewhat depleted in the darker, copper-rich phase. These voids apparently are the result of mass transport of copper ions through the oxide layer at a greater rate than the inward movement of oxygen. According to Rapp [20], cuprous oxide forms on pure copper by the diffusion of Cu^+ through the scale from the metal/oxide interface to the oxide/gas interface. We assume that a similar process occurred here during oxidation resulting in a copper-depleted zone and voids in the filler metal below the oxide. At a higher magnification, Fig. 5b, the oxide scale appears to be porous and detached. Such a scale might be susceptible to spallation although such behaviour is a function of specimen geometry, thermal shock and mechanical and thermal stresses. The scale produced under these conditions was identified by X-ray diffraction as cupric oxide, CuO. Cuprous oxide, Cu_2O, was not detected. According to Kubaschewski and Hopkins ([12],

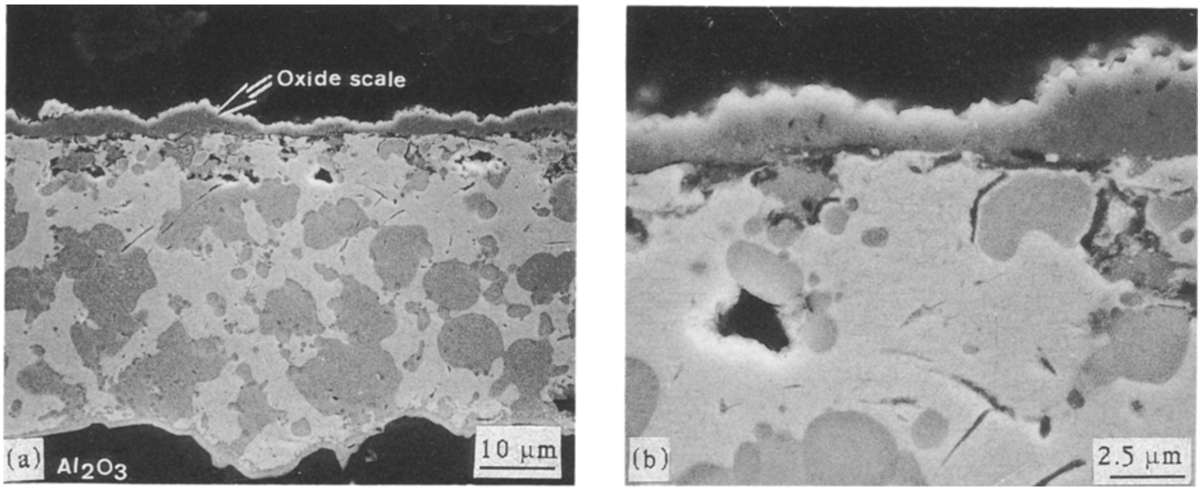

Figure 5 Scanning electron micrographs of polished section through Cu–41.1Ag–3.6Sn–7.2Ti/alumina brazement after oxidation for 100 h at 400 °C in an Ar–20% O_2 atmosphere.

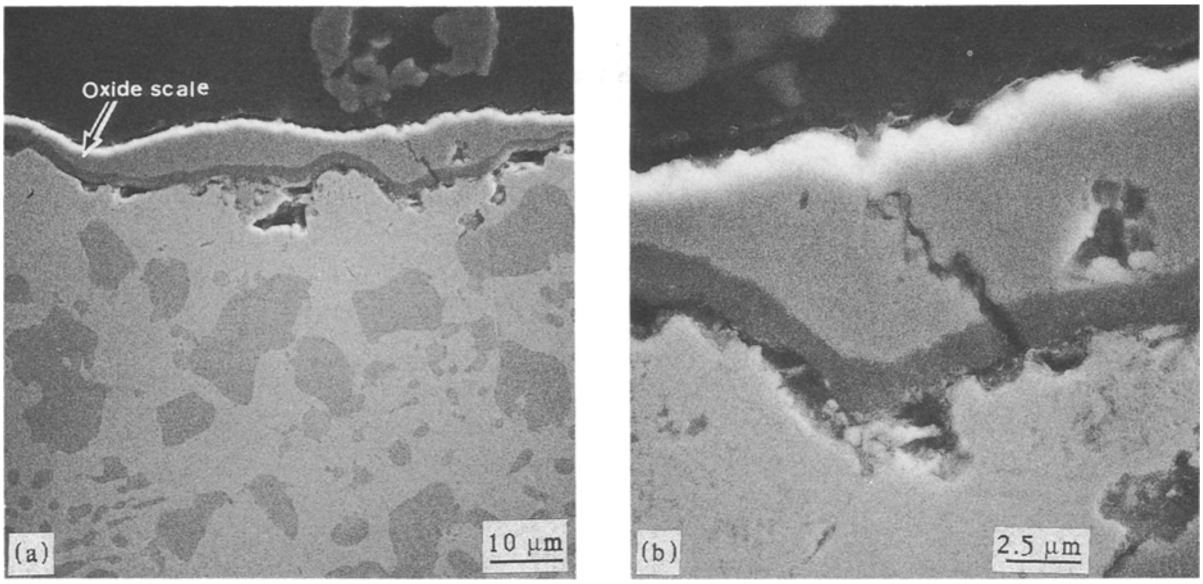

Figure 6 Scanning electron micrographs of polished section through Cu–41.1Ag–3.6Sn–7.2Ti/alumina brazement after oxidation for 100 h at 500 °C in an Ar–20% O_2 atmosphere.

p. 2), a metal with several oxidation states forms a number of compounds with oxygen; and these compounds are arranged in layers in the scale with the one richest in oxygen at the oxide–gas interface, and the one richest in metal at the metal–oxide interface. The sample in Fig. 5, therefore, must have an underlying layer of cuprous oxide at the interface with the filler metal; but apparently the Cu_2O was too thin to be discernable. The presence of an $\sim$ 0.7 µm thick reaction layer at the interface between the alumina and filler metal is also evident in Fig. 5. Moorhead *et al.* [21], using wavelength dispersive X-ray analysis in an electron microprobe, identified this layer at the as-brazed interface between alumina and a similar filler metal, Cu–44Ag–4Sn–4Ti as mixed oxides of titanium, copper and tin. However, using analytical transmission electron microscopy, Santella *et al.* [22] were able to identify in similar samples a very thin (100 nm thick) layer of cubic TiO at the filler metal/alumina substrate interface beneath a much thicker layer of TiCu intermetallic compounds.

Scanning electron micrographs of a cross-section of a Cu–41.1Ag–3.6Sn–7.2Ti/alumina brazement after oxidation for 100 h at 500 °C in an Ar–20% O_2 atmosphere are shown in Fig. 6. These micrographs show a loosely adherent double-layer oxide scale with a total thickness of about 7 µm, about twice the thickness after 400 °C exposure as would be expected from the weight gain data of Fig. 1. The outer layer was identified by X-ray diffraction as CuO. We assume the inner layer is Cu_2O, but the X-rays were not able to penetrate to that depth. The thickness of the intermetallic interfacial layer in contact with the alumina was about 1.5 µm, also about twice that of the sample exposed at 400 °C.

The scanning electron micrograph of the surface of the as-brazed filler metal on alumina (Fig. 7) shows that the solidified alloy has a eutectic structure. Using EDS, we characterized this structure as a copper-rich (dark) phase dispersed in a silver-rich matrix. The surface morphology of this filler metal has also been changed considerably by exposure for 100 h to flowing Ar–20% O_2 at 400 °C, as shown in Fig. 8. This micrograph shows that blocky crystals (identified by the EDS spectra as silver) are formed in a fine crystalline matrix that is identified by EDS and X-ray diffraction as CuO.

We suggest the following mechanism to explain the observed morphology of the oxidation product. As the oxidation of the filler metal proceeds, phase separation occurs between the silver and CuO; and, at the same time, stresses are developed in the alloy due to volume expansion. During oxidation of most metals,

Figure 7 Scanning electron micrograph of the as-brazed surface of the Cu–41.1Ag–3.6Sn–7.2Ti filler metal. Dark phase is copper-rich; light phase silver-rich.

Figure 8 Scanning electron micrograph of surface of Cu–41.1Ag–3.6Sn–7.2Ti after 100 h exposure to Ar–20% O_2 at 400 °C. Blocky crystals of silver are dispersed in fine matrix of CuO.

this stress is relieved by plastic deformation of the oxide scale or spalling of the scale from the metal [23]. In this case, however, the stress developed during oxidation is apparently at least partially relieved by the removal of the silver from the oxide scale. Large silver crystals are formed on the surface as the result of growth of smaller crystals that are extruded from the scale by the expansion stresses.

The weight gain measured for the samples of Cu–41.1Ag–3.6Sn–7.2Ti brazed to partially stabilized zirconia (PSZ) were found to be higher than for comparative brazements on alumina (Fig. 9). We attribute this difference to the added effect of oxidation of the alloy at the ceramic/filler metal interface by oxygen from the atmosphere being transported through the PSZ. The micrographs of polished cross-sections of a Cu–41.1Ag–3.6Sn–7.2Ti/PSZ brazed joint before and after 100 h oxidation at 500 °C in flowing Ar–20% O_2 (Fig. 10), support our hypothesis. The external oxide scale in this case is about 7 μm thick, the same as for the sample of this filler metal on alumina (Fig. 6). The scale was identified as CuO by X-ray diffraction; but, in contrast to the alumina brazement oxidized under the same conditions, consists of a single layer (Fig. 10b). The TiCu layer at the filler metal/PSZ interface is about 2 μm thick, compared to 1.5 μm at the interface with alumina. Also in the PSZ sample, the dark TiO interfacial layer (not discernable in the alumina brazement) has grown from a barely visible line (Fig. 10a) to a layer about 0.5 μm thick (Fig. 10b).

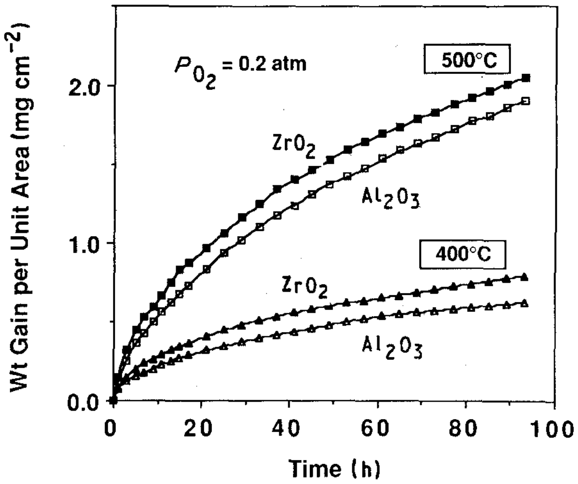

Figure 9 Comparison of specific weight change of Cu–41.1Ag–3.6Sn–7.2Ti on alumina and grade TS MgO–PSZ. The increased weight change in the zirconia brazement is attributed to oxidation at the filler metal/ceramic interface.

3.2. Oxidation of other titanium-containing filler metals

For purposes of comparison, brazed samples of three other filler metals (Ag–44.4Cu–8.4Sn–0.9Ti, Ag–41.6Cu–9.7Sn–5.0Ti and Ag–37.4Cu–10.8In–1.4Ti) on alumina were exposed in the TGA to flowing

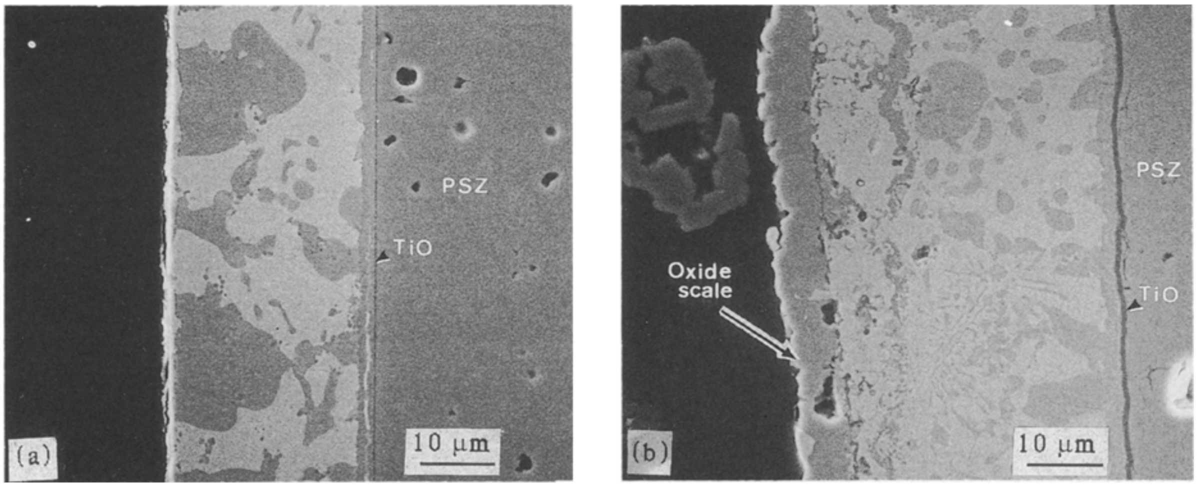

Figure 10 Scanning electron micrographs of sections of a Cu–44Ag–4Sn–4Ti/PSZ brazed joint (a) before and (b) after 100 h oxidation at 500 °C in flowing Ar–20% O_2.

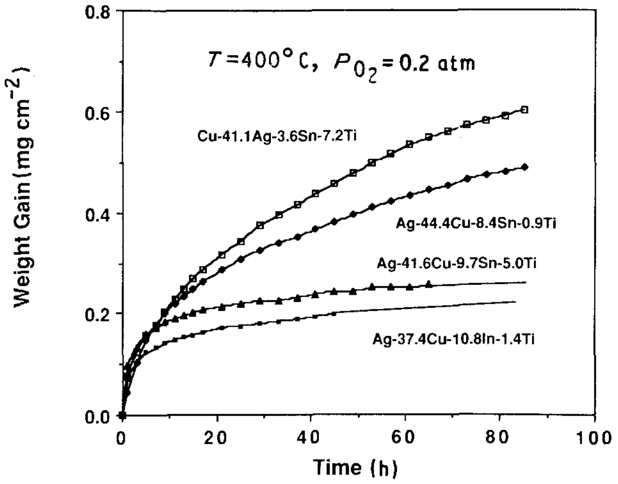

Figure 11 Comparison of specific weight changes of brazements of four filler metals (Cu–41.1Ag–3.6Sn–7.2Ti, Ag–44.4Cu–8.4Sn–0.9Ti, Ag–41.6Cu–9.7Sn–5.0Ti and Ag–37.4Cu–10.8In–1.4Ti) on alumina during exposure to flowing Ar–20% O_2 at 400 °C.

Ar–20% O_2 at 400 °C for times up to 90 h. The weight gain data for these alloys are plotted, along with data for the previously discussed Cu–41.1Ag–3.6Sn–7.2Ti filler metal, in Fig. 11. These results show that the indium-containing filler metal is the most oxidation resistant of the four alloys included in this study.

Typical scanning electron micrographs of the surface of the Ag–37.4Cu–10.8In–1.4Ti brazement on alumina before and after exposure to Ar–20% O_2 at 400 °C are shown in Fig. 12. These micrographs are also representative of the other two filler metals. The morphology of the surface of these brazements (both as-brazed and after oxidation) is very different from that of the Cu–41.1Ag–3.6Sn–7.2Ti filler metal brazement in Figs 7 and 8. Note, in Fig. 12a, the lack of the eutectic structure seen in Fig. 7. Fig. 12b shows more noticeable porosity in the surface of the Ag–37.4Cu–10.8In–1.4Ti brazement. Also, these brazements did not display the relatively large crystals of silver after oxidation that were so prominent on the surface of the Cu–41.1Ag–3.6Sn–7.2Ti brazement. Analysis of the oxidized surfaces by EDS and X-ray diffraction identified the corrosion products as CuO on the Ag–44.4Cu–8.4Sn–0.9Ti filler metal, both SnO_2 and TiO_2 on the Ag–41.6Cu–9.7Sn–5.0Ti and only In_2O_3 on the surface of the sample brazed with Ag–37.4Cu–10.8In–1.4Ti.

Scanning electron micrographs of polished cross-sections of the brazements of Ag–44.4Cu–8.4Sn–0.9Ti, Ag–41.6Cu–9.7Sn–5.0Ti and Ag–37.4Cu–10.8In–1.4Ti on alumina following exposure to flowing Ar–20% O_2 at 400 °C are shown in Fig. 13. Note that, as would be expected from the weight change data, the scale is thickest on the Ag–44.4Cu–8.4Sn–0.9Ti brazement and thinnest on the Ag–37.4Cu–10.8In–1.4Ti sample. An estimate of oxide thicknesses, based on the locations shown in these micrographs, is 2.5 μm on the Ag–44.4Cu–8.4Sn–0.9Ti, 0.75 μm on the Ag–41.6Cu–9.7Sn–5.0Ti, and 0.38 μm on the Ag–37.4Cu–10.8In–1.4Ti. However, the difference in thicknesses is not as significant as it appears, because the Ag–44.4Cu–8.4Sn–0.9Ti sample was exposed for 90 h, the Ag–41.6Cu–9.7Sn–5.0Ti sample for 65 h and the Ag–37.4Cu–10.8In–1.4Ti for only 45 h.

The results of this investigation can be summarized in the schematic representation (Fig. 14) of cross-sections of the samples after elevated temperature exposure to Ar–20% O_2 showing the observed reaction products. In all cases the filler metals formed external scales during oxidation, apparently satisfying the criteria of Equation 1. The AJM-96a (Ag–41.6Cu–9.7Sn–5.0Ti) and Incusil-ABA (Ag–37.4Cu–10.8In–1.4Ti) alloys oxidized more slowly than the other two

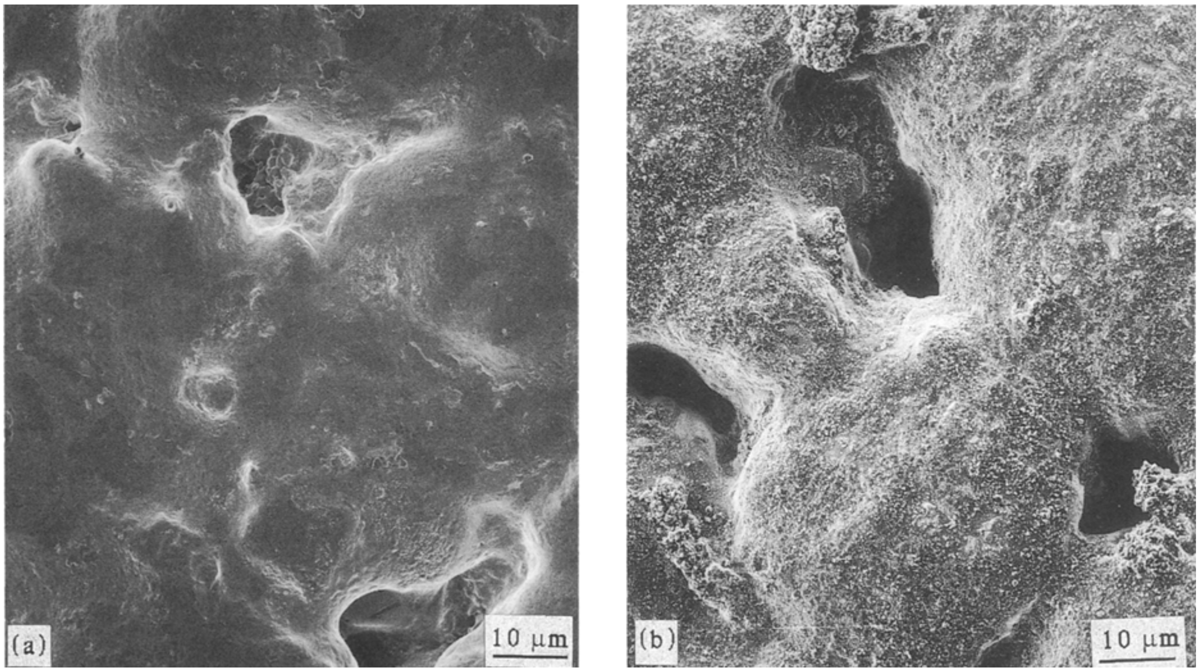

Figure 12 Scanning electron micrographs of surface of brazement of Ag–37.4Cu–10.8In–1.4Ti on alumina (a) as brazed, and (b) after 45 h exposure to flowing Ar–20% O_2 at 400 °C.

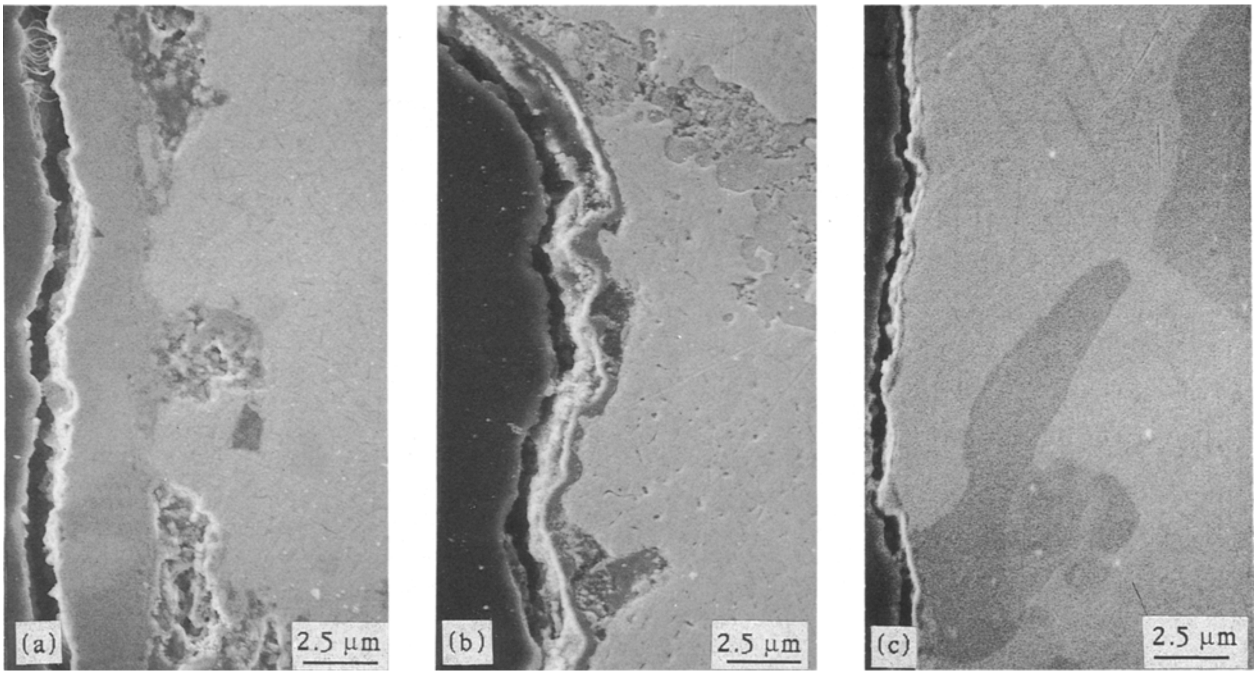

Figure 13 Scanning electron micrographs of sections of brazements of (a) Ag–44.4Cu–8.4Sn–0.9Ti, (b) Ag–41.6Cu–9.7Sn–5.0Ti and (c) Ag–37.4Cu–10.8In–1.4Ti on alumina following exposure for (a) 90 h, (b) 65 h and (c) 45 h to flowing Ar–20% O_2 at 400 °C.

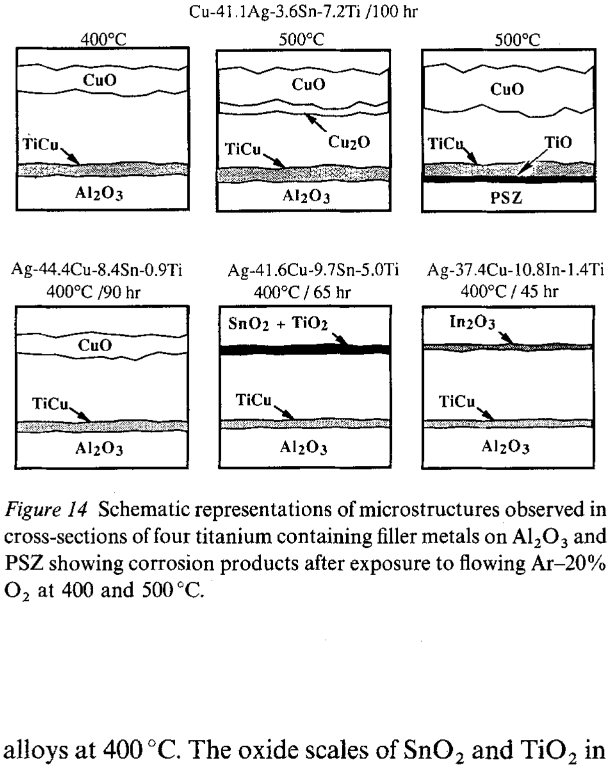

Figure 14 Schematic representations of microstructures observed in cross-sections of four titanium containing filler metals on Al_2O_3 and PSZ showing corrosion products after exposure to flowing Ar–20% O_2 at 400 and 500 °C.

alloys at 400 °C. The oxide scales of SnO_2 and TiO_2 in the former and In_2O_3 in the latter are apparently much more resistant to cation and/or oxygen transport than the CuO formed on the surface of the Cu–41.1Ag–3.6Sn–7.2Ti and Ag–44.4Cu–8.4Sn–0.9Ti filler metals.

4. Observations and conclusions

Brazements of alumina or PSZ of four silver- or copper-based brazing filler metals that contain titanium to promote wetting of and adherence to structural ceramics were exposed isothermally in a TGA at temperatures up to 700 °C to atmospheres of 100% O_2, Ar–20% O_2 and Ar–3 p.p.m. O_2. Our observations and conclusions can be summarized as follows.

1. The specific gains in weight due to oxidation ranged (for 45 h exposure at 400 °C to Ar–20% O_2) from 0.20 mg cm^{-2} for the Ag–37.4Cu–10.8In–1.4Ti alloy to 0.46 mg cm^{-2} for Cu–41.1Ag–3.6Sn–7.2Ti.

2. The titanium played a minor role in the scale formed on any of the filler metals. The oxidation product of only one alloy (Ag–41.6Cu–9.7Sn–5.0Ti) contained a titanium oxide, in this case TiO_2.

3. The Ag–41.6Cu–9.7Sn–5.0Ti and Ag–37.4Cu–10.8In–1.4Ti alloys, apparently protected from the atmosphere by films of SnO_2 and TiO_2 in the former and In_2O_3 in the latter, oxidized at significantly lower rates than the other two filler metals which formed scales of CuO.

4. The brazements on PSZ gained weight at a higher rate than comparative brazements on alumina. We attribute this behaviour to oxygen transport through the zirconia resulting in the growth of an interfacial layer of titanium oxide.

5. All four filler metals appear suitable for service in oxidizing atmospheres at temperatures to at least 400 °C. All formed external oxides that were more or less protective under all of the test conditions studied. The growth of the oxides followed a parabolic time law.

6. The observed corrosion rates could be significantly increased by spallation as observed by Kapoor and Eagar [10] in a study of similar filler metals on Si_3N_4. However, such behaviour would depend on a number of factors including adhesion of the filler metal to the particular ceramic, the difference in coefficients of thermal expansion of the ceramic and oxide scale, the thermal cycle including rate and frequency

and geometrical affects including the surface area of the brazement actually exposed to the atmosphere.

Acknowledgements

We thank G. C. Marsh for preparing the samples for microscopic examination and J. I. Federer and M. L. Santella for their helpful comments on reviewing the manuscript.

References

1. Yu. V. NAIDICH, "The Wettability of Solids by Liquid Metals", in "Progress in Surface and Membrane Science", Vol. 14 (Institute of Material Problems, Academy of Sciences, Ukranian SSR, 1981) pp. 333–484.
2. M. G. NICHOLAS, *Br. Ceram. Trans. J.* **85** (1986) 144.
3. M. G. NICHOLAS, T. M. VALENTINE and M. J. WAITE, *J. Mater. Sci.* **15** (1980) 2197.
4. H. MIZUHARA and K. MALLY, *Weld. J.* **64**(10) (1985) 27.
5. A. J. MOORHEAD, *Adv. Ceram. Mater.* **2** (1987) 159.
6. A. J. MOORHEAD and H. KEATING, *Weld. J.* **65**(10) (1986) 17.
7. Yu. V. NAIDICH and V. S. ZHURAVLEV, *Ogneupory* **1** (January) (1974) 50 (translated).
8. T. ISEKI, H. MATSUZAKI and J. F. BOADI, *Amer. Ceram. Soc. Bull.* **64**(2) (1985) 322.
9. R. E. LOEHMAN and A. P. TOMSIA, *Am. Ceram. Soc. Bull.* **67** (1985) 375.
10. R. KAPOOR and T. EAGAR, *J. Am. Ceram. Soc.* **72** (1989) 448–454.
11. T. MASSALSKI (ed.), "Binary Alloy Phase Diagrams", Vol. 1 (American Society for Metals, Metals Park, Ohio, 1986) p. 19.
12. O. KUBASCHEWSKI and B. E. HOPKINS, "Oxidation of Metals and Alloys", 2nd Edn (Butterworth, London, 1962).
13. C. WAGNER, *J. Electrochem. Soc.* **99** (1952) 369.
14. *Idem., ibid.* **103** (1956) 627.
15. G. C. WOOD, *Oxid. Metals* **2** (1970) 11.
16. M. E. WOODS, W. F. MANDLER Jr and T. L. SCHOFIELD, *Amer. Ceram. Soc. Bull.* **64** (1985) 287.
17. D. W. RICHERSON, *ibid.* **64** (1985) 282.
18. D. W. BRIDGES, J. P. BAUR and W. M. FASSELL Jr, *J. Electrochem. Soc.* **103** (1956) 475.
19. S. MROWEC and A. STOKLOSA, *Oxid. Metals* **3** (1971) 291.
20. R. A. RAPP, *Corrosion Nat. Assoc. Corros. Eng.* **21** (1965) 382.
21. A. J. MOORHEAD, H. M. HENSON and T. J. HENSON, in "Ceramic Microstructures '86", edited by J. A. Pask and A. G. Evans (Plenum, New York, 1988) pp. 949–958.
22. M. L. SANTELLA, A. T. FISHER and C. P. HALTOM, *J. Elect. Micros. Technol.* **8** (1988) 211.
23. D. L. DOUGLASS, *Oxid. Metals* **1** (1969) 127.

Received 6 July
and accepted 23 October 1989