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Flux-assisted infiltration of liquid Al-6063 into TiC beds in air

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This study details trials to produce aluminium metal matrix composites reinforced with TiC particles by means of a flux-assisted infiltration technique. Whilst no infiltration of TiC beds occurred, by using a K-Al-F flux infiltration was successful at temperatures as low as 680°C. Some reaction of TiC with the Al matrix, forming $TiAl_{2.3}Si_{0.1}$ and Al_4C_3, was observed in the microstructure along with flux trapped within the Al-6063 matrix. DSC showed exothermic oxidation of TiC to occur, until the flux melts at 545°C arresting and preventing further oxidation by spreading over, coating and cleaning the particle surfaces. As soon as the flux melts, it also starts dissolving the oxide layer on the Al alloy and prevents any re-oxidation by isolating the surface from the surrounding atmosphere. Sessile drop experiments suggest that when the alloy melts and the oxide layer has been dissolved by the flux, intimate contact occurs between the liquid and the particles. The low tensions for the solid/flux and liquid metal/flux interfaces facilitates spreading and wetting of liquid Al on the TiC particles, followed by infiltration of the bed and the displacement of the flux to the outer surfaces of the sample. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Melt infiltration is a well-established route for manufacturing Al-based composites [1–4]. Difficulties are, however, encountered when infiltrating molten Al into ceramic beds, due to poor wetting, exacerbated by the oxide film which covers Al melts. Achieving infiltration demands the use of high processing temperatures along with protective atmospheres, otherwise, an external pressure is needed to force the liquid metal into the ceramic body. This necessitates the use of specialised, custom-built equipment and careful process control. In order to overcome difficulties imposed by the oxide layer and the poor wettability exhibited in Al/ceramic systems, procedures such as alloying the melt, surface treating the ceramic and the use of fluxes have been attempted. The use of fluxes, in particular, has proved very effective [5–7], because the fluxes dissolve aluminium oxide on the melt surface enabling the wetting characteristics between the two phases to be realised [7].

TiC combines high stiffness with low density and it is known to be wetted by Al and Al-alloys at temperatures at which the aluminum oxide layer becomes unstable under inert or vacuum conditions [2, 3, 8–12]. Under these conditions, molten Al spontaneously infiltrates TiC preforms above 900°C [1–4]. The result is sound composites with high specific strength [1, 4]. To decrease the cost of processing, however, lower infiltration temperatures, similar to those used in Al casting (650–750°C), are required. This study explores the feasibility of manufacturing TiC-reinforced Al-based composites, in a non-protective atmosphere, at low temperatures using a flux-assisted infiltration technique.

2. Experimental procedure

Angular TiC powder, with a D_{50} value of 15 μm, a K-Al-F based flux and a commercial Al-6063 alloy tube (approximate composition 0.7 wt% Mg and 0.4 wt%Si), with an outside diameter of 16 mm and a 1.5 mm wall thickness, were used to conduct infiltration trials. Pieces of tube (35 mm long) were cleaned with an aqueous solution of NaOH to remove thick oxide films. The tube was crimped closed at one end, filled with powders, tapped to increase the packing density, to between 60–65%, and then the other end was also crimped closed. Processing was performed by positioning the packed beds on graphite supports, in a stainless steel boat, placed at the centre of a horizontal tube furnace and heating from room temperature, at a rate of 20°C/min, to either 680, 820 or 1100°C in air, holding for 60 min, followed by furnace cooling. Infiltration trials were carried out with a TiC/flux mixture in mass ratios 2:1 and 1:1 and without flux. Infiltrated specimens were microstructurally characterised using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). Differential scanning calorimetric (DSC) experiments were carried out

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TABLE I Results of the infiltration trails

Temperature (°C)	TiC	TiC/Flux (2:1)	TiC/Flux (1:1)
680	×	×	√
820	×	√	√
1100	×	√	√

×Non-infiltrated; √Infiltrated.

in order to follow the sequence of thermal events during the process. Samples were placed in BN crucibles and heated, at 20°C/min, to 800°C in atmospheric air. In order to reveal the wetting behaviour, sessile drop experiments were conducted upon 88% dense sintered TiC substrates at 900°C under Ar and air, with and without flux. The progress of the sessile drop experiments with flux was video recorded, at 15 frames per second, with a digital camera. The interfaces produced were observed using SEM.

3. Results and discussion

3.1. Infiltration trials and microstructure

Table I shows the results of the infiltration trials. It was found that TiC beds without flux could not be infiltrated across the interval of temperatures studied (680–1100°C). Conversely, when the flux was present, successful infiltration occurred at temperatures as low as 680°C. The presence of an oxide skin on Al melts represents a mechanical obstacle that has to be overcome before the actual wetting characteristics are exhibited in Al-alloy/TiC systems. Since it was impossible to infiltrate TiC beds without flux even at 1100°C, it is evident that the presence of flux in the TiC beds plays a decisive role assisting the infiltration process by, primarily, removing the oxide skin that envelops the melted tube. Thus the K-Al-F flux, which is similar to cryolite and has high solubility for Al_2O_3, is thought to dissolve the oxide skin and prevent further oxidation of the melt.

Typical microstructures of the infiltrated samples are shown in Fig. 1 in backscattered mode. The light phase corresponds to the TiC particles embedded in the Al-6063 matrix. TiC-free regions are observed throughout the microstructure and these are similar in scale to the average flux particle size. It is thought that when the flux melts it spreads through the TiC network. When the Al melts it flows by displacing the flux and filling the interstices left behind. At 680°C, besides the irregular TiC particles, small angular blocks are present, such as the one indicated by the arrow. At higher magnifications a black blocky phase was observed. At 820°C the microstructure was dominated by the presence of isolated but large blocks and relatively short needles, along with a black phase, but at 1100°C no blocks were seen, only large needles. EDX analysis revealed the blocks and needles to be ternary compounds with the average composition $TiAl_{2.3}Si_{0.1}$ and the black phase to be an Al-C compound, most closely corresponding to Al_4C_3. SEM also showed the presence of discontinuities such as porosity and round defects, both small and large, within the Al matrix. The later were found to be, according to EDX analysis, flux trapped in the matrix.

Fig. 2 shows an elemental X-ray map of the phases present in a sample infiltrated at 820°C. TiC particles, the Al matrix, small Al_4C_3 blocks commonly associated with the Al/TiC interface, $TiAl_{2.3}Si_{0.1}$ intermetallics and trapped flux are clearly identifiable. Complementary XRD analysis exhibited, in addition to TiC and Al, reflections corresponding to the flux and the main reflection for the intermetallic in all the XRD patterns, but

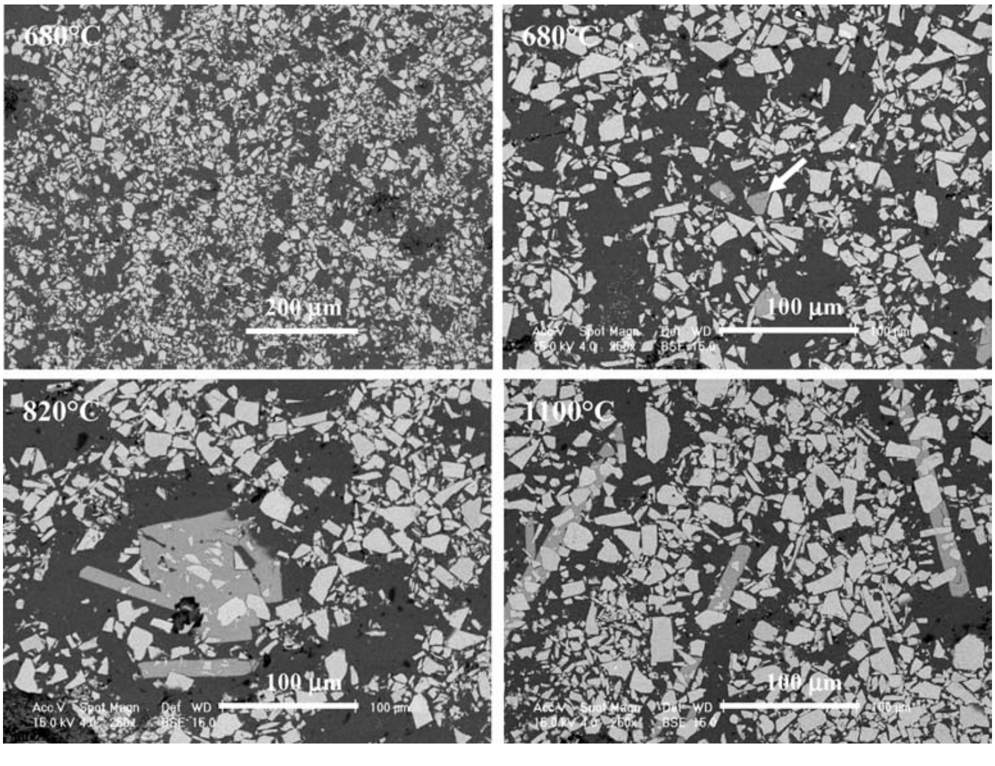

Figure 1 Typical microstructures of the samples infiltrated at different temperatures.

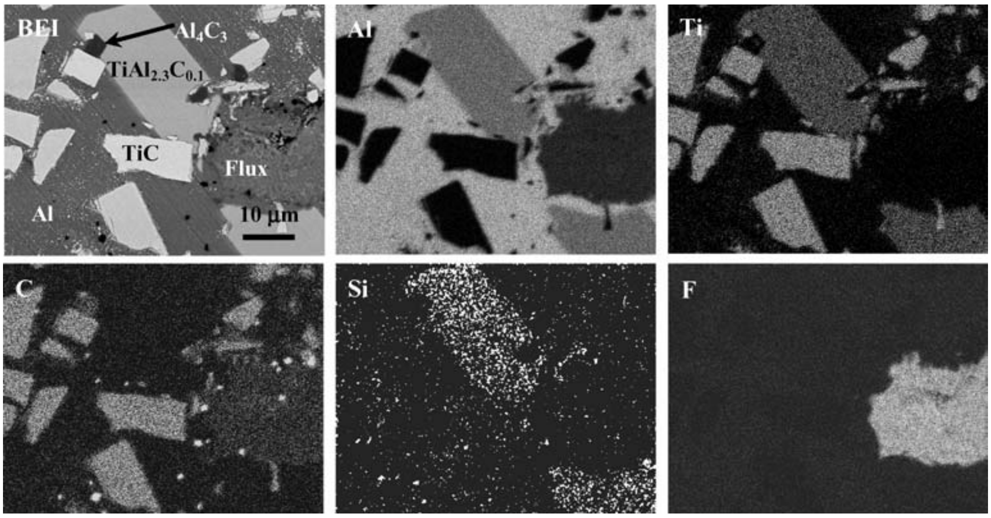

Figure 2 Elemental X-ray dot map of a sample infiltrated at 820°C.

no matching peaks were observed for Al_4C_3, indicating that this phase is present, as observed in the SEM, but below the detection limit of the XRD technique.

The majority of the flux was displaced to the outer surfaces of the samples but there was a random distribution of flux trapped within the Al matrix. The flux entrapment mechanism is not fully understood, liquid flux and Al are not miscible one in another, although, effects such as a minimal difference in density, an increase in the viscosity of the flux due to dissolution of the oxide and the multi-directional nature of the infiltration process are likely to contribute to flux entrapment. A similar problem is encountered in the production of Al-Ti-B grain refining master alloys, in which Al reduces fluoride salts under a KF-AlF_3 flux layer. Lee and Grieveson [13] stated that interfacial tensions determine the ease of metal-flux separation and argued that because the liquid phases in contact exhibit a very low interfacial tension an emulsification process takes place, leading to entrapment of flux within the Al during solidification.

SEM observations showed different levels of TiC reaction with the matrix according to the infiltrating temperature, the reaction products being Al_4C_3 and $TiAl_{2.3}Si_{0.1}$ with the maximum reactivity at 820°C. Reaction products in the pure Al-TiC system are Al_4C_3 and $TiAl_3$ and the reaction kinetics are slow with long holding periods being required to produce appreciable dissolution of TiC [14]. Si has, however, been found to accelerate the dissolution of TiC in liquid Al to produce Al_4C_3 and $TiAl_{2.14}Si_{0.38}$ with maximum dissolution at 800°C [15]. The present study shows that even low Si additions (0.4 wt%) dramatically affect the thermodynamic stability of TiC particles in molten Al.

3.2. Thermal analysis

Fig. 3 shows DSC traces for the single components (TiC, flux and 6063 alloy) and for binary combinations of these phases. Exothermic oxidation of TiC occurs in a number of stages, starting at approximately 430°C. Melting of the flux and of the 6063 alloy occur at approximately 545 and 630°C respectively. Thermal events for the Al-6063/flux couple shows, in addition to melting of both phases, an exothermic event after melting of the flux. The TiC/flux couple exhibit two consecutive exothermic events followed by endothermic melting of the flux after which the trace returns to the baseline. The thermal events for the ternary TiC/flux/Al-6063 combination are broadly consistent with the events observed for the single and binary combinations.

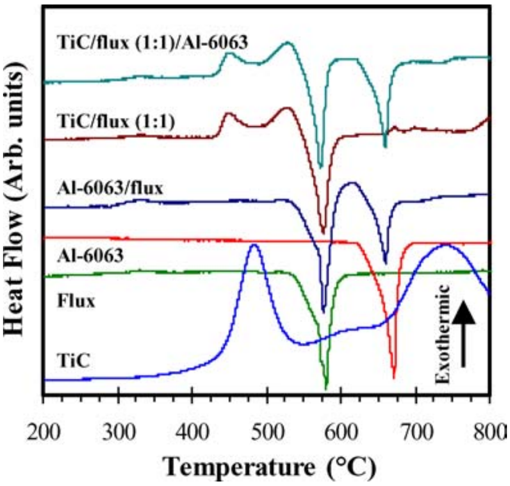

Figure 3 DSC traces for the single components and combinations of the phases involved in the process.

The sequence of events occurring during the infiltration process can be described as firstly exothermic oxidation of TiC, until the flux melts at 545°C, followed by endothermic melting of Al-6063 at 630°C. An exothermic event was observed between Al-6063 and the flux in both the binary and ternary mixtures and is thought to be an interaction between the melted flux, the oxide associated with the Al and oxygen in the environmental air. The type of interactions between aluminium oxide and the flux species are reported by Danek *et al.* [16]. The order of these events means that after the flux melts, and before it dissolves the Al_2O_3 layer, it spreads over the entire surface of the TiC particles forming a liquid shield which protects the particles from further oxidation and perhaps cleans the particles of the light oxidation that had occurred up to that point.

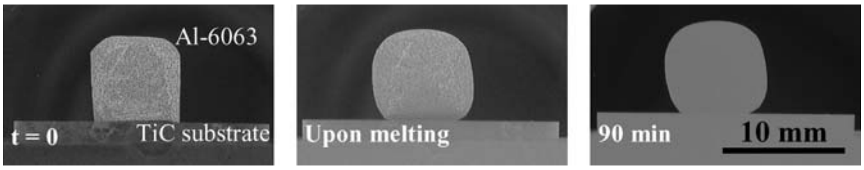

Figure 4 Wetting behaviour of the Al-6063/TiC couple in Ar at 900°C.

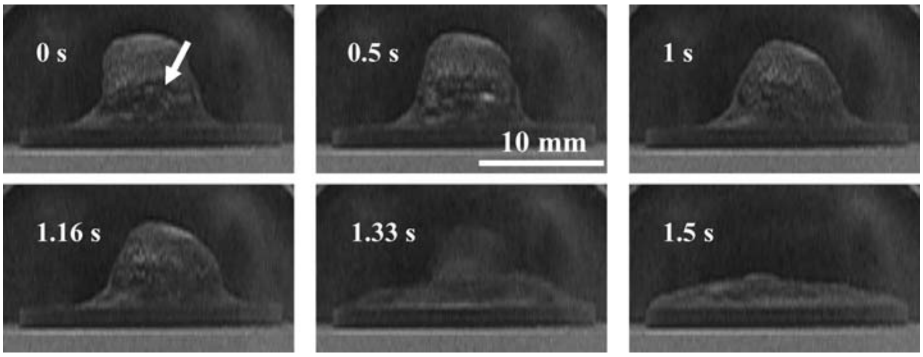

Figure 5 Spreading of the assembly Al-6063/flux/TiC in air at 900°C.

3.3. Interfacial phenomena

Fig. 4 depicts the progress of the Al-6063/TiC sessile droplet couple, during heating, upon melting of the alloy and after holding for 90 min in Ar. A high contact angle was observed throughout the experiment with no significant change with time. The presence of flux, applied as a methanol-based paint coating on the surface of the TiC substrates, had a dramatic effect on spreading and wetting in both atmospheres, so that melting of both flux and Al-6063 and full spreading of the droplets to a perfect wetting condition took place in less than 2 min. Fig. 5 shows the flux-assisted spreading of molten Al-6063 on TiC. The flux, upon melting, forms a liquid coating on the substrate and spreads on the still solid Al-6063. The liquid flux wets the alloy and the substrate, thus forming a "bridge" between them along the basal periphery of the alloy. The sequence of stills, taken from the video recording, show that spreading occurs, in air, in less than 1.5 s, from the point at which the droplet was still standing. The same process took about 2.5 s in Ar. In both cases the flux was seen to strongly interact with the surface of the alloy, forming a darker layer along the basal periphery of the alloy, which eventually ascended its surface. When reaching approximately the mid-height of the alloy, as indicated by the arrow in Fig. 5, the spreading process began.

For Al and Al-alloys to spread on and wet TiC, the oxide skin has first to be removed and it occurs when the partial pressure of O_2 is low enough, at a given temperature above 800°C, so that deoxidation of the droplet takes place [3, 9–12]. It is evident that capillary infiltration of molten Al into TiC beds is impossible, in air, due to the presence of a thick and compact oxide layer which encapsulates the liquid metal, not withstanding that oxidation of TiC is also expected. The use of a flux makes the surrounding atmosphere a non-critical issue. When the flux melts, it spreads over the substrate and the Al, creating a local atmosphere that prevents oxygen contamination of the liquid metal/solid interface. Furthermore, it dissolves and weakens the oxide skin on Al, perhaps creating some local heating, through Al-flux interactions, as was observed in the Al-6063/flux DSC trace. The replacement of the solid/gas and liquid metal/gas interfacial tensions with solid/flux and liquid metal/flux interfaces with lower forces, enables spreading and wetting of liquid Al on TiC to take place spontaneously and instantaneously.

Time and temperature dependant spreading and wetting of molten Al and Al-alloys on TiC has been observed under vacuum and in Ar at temperatures between 750 and 1100°C. This was accompanied by the formation of an Al_4C_3 reaction layer at the interface, for stoichiometric TiC, or the precipitation of $TiAl_3$ within the Al for hypostoichiometric $TiC_{(1-x)}$ [2, 3, 9–12]. In the flux-assisted sessile drop experiments, liquid Al-6063 was in contact with TiC for less than 3 min and the Al-6063/TiC interfaces were found to be, under the limits of resolution of the SEM, free from any reaction products, as shown in Fig. 6. This fact indicates that interfacial reaction and/or low TiC stoichiometries [9] are not a pre-requisite for spreading and wetting in the Al-alloy/TiC systems and that a true and high affinity does exist in terms of wettability and adhesion between these phases.

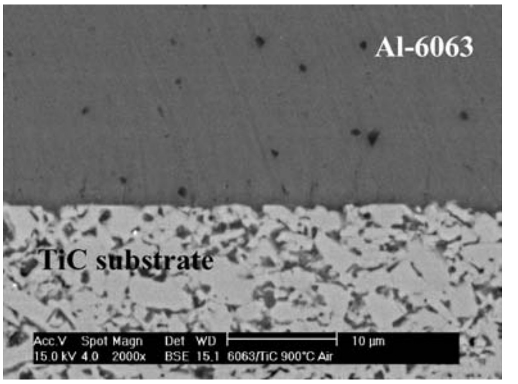

Figure 6 Interface produced at 900°C, in air, by flux coating the TiC substrate.

4. Conclusions

Melt infiltration of Al-6063 into TiC beds is possible at temperatures as low as 680°C in air by using a K-Al-F based flux which enables spontaneous and instantaneous wetting conditions. According to the findings of the present study, the proposed mechanism of the flux-assisted infiltration process is as follows. During heating, light oxidation of the TiC particles occurs until the flux melts at 545°C arresting and preventing further oxidation by spreading over, coating and cleaning the surfaces of the particles. As soon as the flux melts, it also ascends over the metal surface starting to dissolve the oxide layer on the still-solid Al-6063 alloy and preventing any re-oxidation by isolating the surface from the surrounding atmosphere. When the alloy melts and the oxide layer has been dissolved by the flux, intimate contact occurs between the liquid and the particles. The low tensions for the solid/flux and liquid metal/flux interfaces facilitates spreading and wetting of liquid Al on the TiC particles, followed by infiltration of the bed and the displacement of the flux to the outer surfaces of the sample. The wetting behaviour observed suggests that the infiltration process takes place in short periods of time and that it is not strongly temperature dependant.

Acknowledgements

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