Refinement of directed melt oxidized structures

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Abstract. Composite microstructures obtained via directed melt oxidation can be refined using external reinforcements and alloying additions. The mechanisms responsible for refinement of composite (alumina) microstructure are discussed.

Keywords. Oxidation; alloying; composites; microstructure; refinement.

1. Introduction

Composites containing interpenetrated network of metal and ceramic phases are produced by directed melt oxidation of liquid aluminium alloys. Commercially, this *in situ* reaction synthesis is known as DIMOXTM process, which was originally developed by Lanxide Corporation, USA (Newkirk *et al* 1986, 1987; Salas *et al* 1991). When a liquid aluminium alloy containing volatile species like Mg, Zn etc is oxidized, the reaction product, Al/Al₂O₃ composite, builds up on the surface by continuous wicking of liquid metal on to the oxidized surface. Thus, uninterrupted growth of composite occurs until the liquid alloy is entirely exhausted. After the process is complete, the final microstructure consists of uniformly dispersed aluminium and alumina interspersed with macro- and micro-porosities (typically 2–6%) (figure 1). These composites exhibit good strength and toughness (due to clamping by metal ligaments) compared to alumina, however, residual porosities restrict the maximum possible properties to some extent. By refining the composite structure (mainly alumina), mechanical properties can be improved by uniform and finer distribution of the metallic phase coupled with reduction in pore (defect) size in the structure. Refinement of alumina is feasible either by providing external nucleating sites in the path of oxidation growth front or by modifying the liquid chemistry, which makes nucleation of Al₂O₃ easier. Both proposed methodologies are examined considering Al–3Zn–3Mg as a base alloy. Salient points are discussed in the light of some experimental observations.

2. Experimental

Approximately 24 mm diameter cylinder bars of Al–3Zn–3Mg (wt%) alloys with addition of Ti and Zr (0.12 ± 0.05 wt%) were prepared using conventional melting techniques. For comparison Al–3Zn–3Mg was used without adding any alloying elements. All directed melt oxidation experiments were carried out in leakproof alumina crucibles at 1100°C for 16 h. When SiC monofilaments (AVCO SCS-6) were used for infiltration, chopped fibres were placed vertically on top of alloy billet. SiC monofilaments contain a carbon rich surface layer of ~ 6 µm. After infiltration, ground powders from the grown composites were used for X-ray diffraction studies. Both

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Figure 1. Al/Al₂O₃ structure produced by directed melt oxidation. Dark regions are Al₂O₃ and bright regions are Al.

optical and scanning electron microscopes (JEOL 840A) were used for carrying out microstructural studies.

3. Results and discussion

As mentioned earlier, heterogeneous nucleating sites can be provided by placing filler materials (oxide or non-oxide reinforcements of any form) in the path of oxidation growth front. Additionally, modified/deposited surface oxide layers of reinforcements can further ease the nucleation process. For instance, silica formed on SiC particulate reinforcements gets reduced by aluminium in the liquid melt ($\text{SiO}_2 + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Si}$) and secondary nucleation of alumina occurs in addition to the primary Al₂O₃ crystals that are growing in the liquid (Dhandapani *et al* 1994) (figure 2a). Further, the volatile solute atoms (Mg, Zn) in the liquid alloy vaporize and get deposited as respective oxides (figure 2b). These oxides further undergo displacive reduction reactions like silica, to nucleate Al₂O₃ (Murthy and Deepak 1996). When monofilaments are used, in addition to alumina, formation of Al₄C₃ is likely via a reaction between unoxidized carbon rich layer and the liquid aluminium alloy. Owing to secondary nucleation, the long columnar type of Al₂O₃ crystals in pure alloy oxidation get modified as equiaxed grains (figures 2c and d). Results here are in confirmation with the findings that were published by Manor *et al* (1993) and Hanabe *et al* (1996). However, for uninterrupted liquid metal wicking and oxidation to take place, optimum size and volume fraction of reinforcements need to be defined.

To examine the second option, Al–Zn–Mg alloys with 0.12 wt% Ti and Zr additions were oxidized at 1100°C for 16 h and microstructures were examined using X-ray and

SEM. The resultant structures were compared with the unalloyed base alloy which was oxidized under similar conditions. X-ray diffraction patterns obtained from various composites are presented in figure 3. By comparing Al and Al_2O_3 peaks in all the alloys, it is evident that the formation of Al_2O_3 is dominant in alloyed compositions. The dispersed metal particles are much finer in Zr alloyed composites compared to

Figure 2. a, b.

Figure 2. (a) Secondary nucleation of Al_2O_3 on the surface of a SiC particulate, (b) ZnO deposition on the surface of SiC fibre which was placed ahead of the reaction front, (c) growth of Al_2O_3 crystals during directed melt oxidation of a base alloy (without reinforcements) and (d) equiaxed Al_2O_3 crystals in a SiC fibre reinforced composite.

unalloyed composites. This is expected due to greater oxygen transport in the presence of Ti and Zr which can also modify the oxide layer morphology to some extent (Shida and Anada 1993). The microstructures of these composites (figure 4) also indicate the

Figure 3. X-ray diffraction patterns obtained from directed melt oxidized composites obtained from oxidation of (a) Al–Zn–Mg alloys, (b) and (c) Al–Zn–Mg alloys doped with zirconium and titanium (0.12 wt%) respectively.

refinement of composite structure in Ti and Zr containing composites. In addition to the microstructural refinement, there is also a variation in the metal to ceramic ratio in the alloyed samples. Alloying additions seem to modify both the ceramic matrix and the composition of the alloy retained in the matrix (Brevel *et al* 1993). Further, these additions form alloy constituents and/or intermetallics; depending on the nature of the phase, oxygen solubility changes. Normally reduced aluminium activity results in a high oxygen solubility (Johnson and Negelberg 1995). Earlier, Brevel *et al* (1993) also demonstrated that nickel additions to an Al–Si–Sr alloy change the composite microstructure.

Microstructural refinement in alloyed systems could be explained by examining the nucleation of Al_2O_3 in these composites. In directed melt oxidized alloys, solute atom concentration significantly affects the formation of Al_2O_3 . For example, when Mg level

Figure 4. Backscattered SEM micrographs of (a) Al–Zn–Mg, (b) Al–Zn–Mg with a 0.12 wt% Zr and (c) Al–Zn–Mg with 0.12 wt% Ti-oxidized in air at 1100 °C for 16 h. All micrographs are taken at same magnification.

drops to $\text{Al}_2\text{O}_3 + \text{MgAl}_2\text{O}_4$ phase field in Al–Mg–O phase diagram, the surface of the wicked nodules are covered with spinel, whereas inside the nodule Al_2O_3 begins to nucleate (Murthy and Rao 1995). Although the exact mechanism of Al_2O_3 nucleation is not clear, one probable route could be by dissociation of spinels, where Al_2O_3 precipitation occurs readily to grow as large crystals (Lewis 1969; Kingery *et al* 1991). As the Mg level still drops further (below 0.3 wt%), Al_2O_3 nucleated earlier can continue to grow. Otherwise fresh Al_2O_3 crystals nucleate, since composition lies in the phase field of Al_2O_3 . Fresh nucleation can occur on pores of MgO, since the energy required for nucleation is minimum. Alloying additions of Ti and Zr must be influencing the nucleation of Al_2O_3 by one or more of the following mechanisms: (a) Ti and Zr may be getting adsorbed at the nucleation site and minimize the energy required for and/or (b) formation of TiO_2 , ZrO_2 or their reaction products with other oxides present in the system can act as nucleation sites in the presence of Mg, Zn etc. However, more detailed work is needed to establish the precise mechanism of nucleation. When Zr containing alloy is infiltrated into SiC fibre preform, combined effects viz. refinement through secondary nucleation and alloying, with fine dispersion of metal particles are seen (figure 5).

4. Summary

Modification of directed melt oxidized structures is possible either by external reinforcements or by alloy additions. In the present investigation, both methodologies have been tried using SiC monofilaments and alloying additions such as Ti and Zr. The role of alloying addition is briefly discussed.

Figure 5. Composites structure after adopting both refinement methods viz. reinforcement with SiC fibre and alloying with Zr.

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