Preparation of net-shape $\text{Al}_2\text{O}_3$/Al$_3$Ni in situ composites by reactive melt penetration

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By reacting silica preforms with a molten Al-Ni alloy net-shape, in situ $\text{Al}_2\text{O}_3$/Al$_3$Ni composites were prepared. Presence of Ni in the melt was found to slow down the reaction between silica and aluminium. The density of the composites was found to be 3.98 ± 0.12 g/cc, and they were found to be much harder than $\text{Al}_2\text{O}_3$/Al composites.

Reactive melt penetration is a new process developed for producing net-shape $\text{Al}_2\text{O}_3$/Al composites by reacting an oxide preform with molten Al at high temperatures. The composite consists of dense alumina having a network aluminum channels and having the same size and shape as the preform. Though the process is very attractive on account of its simplicity, the usefulness of the composites for high temperature applications is limited by the low melting point of the aluminum phase. Fahrenholtz et al. suggested that by reacting NiO or TiO$_2$ with molten Al the respective aluminides could be produced as the dispersed phase in alumina. However, to retain the advantage of the net-shape forming of the process the oxide preform may be reacted with a molten Al alloy which on solidification will form an intermetallic compound of high melting point. In Al-TM (TM - transition metal) systems several intermetallic compounds having melting points in the range about 1100 K to more than 1500 K form and may be examined for their usefulness in the composites. The present report deals with the preparation of $\text{Al}_2\text{O}_3$/Al$_3$Ni net-shape, in situ composites using silica and molten Al-Ni alloy as the reactants. The Al-Ni alloy system was chosen because Al/Al$_3$Ni in situ composites made by directional solidification have been widely investigated.

Experimental Procedure

Vitreous silica rods (Vitrosil, England) of 7.0 mm diameter and Al-43 wt% Ni alloy, prepared from commercial purity Al and 99.9% purity Ni shots were used as the reactants. For comparison, a few experiments using commercial Al and silica were also performed. The reaction was carried out in alumina crucibles in a Kanthal wound furnace maintained at 1273 or 1373±5 K in ambient atmosphere. Standard experimental methods were employed for microscopic examination, Vicker's hardness testing and density determination. Phases present in the composites were determined by XRD using filtered Co radiation. Progress of the reaction was determined by microscopic examination of polished sections.

Results and Discussion

Samples of the $\text{Al}_2\text{O}_3$/Al$_3$Ni composites were dark grey in colour and similar in appearance and microstructure to those of the $\text{Al}_2\text{O}_3$/Al composites, as shown in Fig. 1. When solid silica preform is introduced into molten aluminium or aluminium alloys the Al atoms react with SiO$_2$ to form $\text{Al}_2\text{O}_3$ on the surface. Since the molar volume of alumina is less than that of silica, the alumina layer formed will be porous. This facilitates the progress of the reaction until the entire silica preform is converted into alumina. The silicon formed by the reaction dissolves in the melt and is rapidly transported away from the reaction front by diffusion. At the end of the reaction the original preform is converted into the alumina composite of identical shape and size and containing a network of the aluminium phase. A small volumetric contraction, about 2 to 3%, is observed between the preform and the composite. The composition of the aluminium phase will depend on the amount of aluminium taken in the reaction vessel. Generally, a large quantity of Al is taken in the reaction vessel so that at the end of the reaction the melt will contain ≤ 1 wt% Si. In the present investigation the silica preforms were introduced into a molten Al-43% Ni alloy maintained at 1273 or 1373 K. At these
temperatures the alloy will be in the form of two phases, liquid Al(Ni) alloy and solid Al$_3$Ni$_2$. The formation of the composites at the experimental temperatures, $T$, is based on the following reactions.

\[ \text{SiO}_2(s) + \text{Al(Ni)}(s) \rightarrow \text{Al}_2\text{O}_3(s) + \text{Al}_3\text{Ni}_2(s) \]  

(1) (Two Phase Melt) (Composite) (Excess Melt)

When the silica preform is introduced into the melt Al$_2$O$_3$ will form by reaction (1) and Si produced in the reaction will dissolve in the melt. The reaction easily goes to completion because the free energy change of reaction (1) is negative. The alumina formed will be porous in nature on account of the difference in the molar volumes of the two oxides (SiO$_2$ and Al$_2$O$_3$). At the end of the reaction dense alumina of the same shape and size as the silica preform having a network of interconnected channels filled with the two phase melt is formed. When the sample is cooled to room temperature the two-phase melt undergoes peritectic transformation, reaction (2), and Al$_3$Ni is formed. The rate of reaction of silica with the aluminium of the two phase melt was found to be somewhat slower than with the pure Al melt as shown in Fig. 2. This is in agreement with earlier report$^1$ that the rate of reaction increases with the purity of Al used.

The major constituents of the composites were found to be $\alpha$-Al$_2$O$_3$ and Al$_3$Ni, as shown in Fig. 3. In the XRD pattern a few reflections corresponding to Al$_3$Ni$_2$ and Ni$_3$Si$_2$ were also detected. Since Al$_3$Ni is a line compound it will be very difficult to adjust the melt composition exactly and in order to prevent the formation of any low melting Al phase the alloy composition was chosen to be slightly on the hyper peritectic side. Hence, a few reflections of Al$_3$Ni$_2$
were observed. The silicon formed in reaction (1) will dissolve in the melt at the experimental temperatures. Al₃Ni can dissolve about 0.4 to 0.5% Si and any excess Si in the melt will form silicides as per by the Al-Ni-Si phase diagram. The formation of silicides can be easily avoided by simply increasing the quantity of the melt in the reaction vessel.

The presence of about 30 vol% Al₃Ni instead of Al has been found to increase the hardness and density of the composites, as shown in Table 1. Since densities of Al₃Ni and Al₂O₃ are almost the same (3.95 g/cc), the density of the composite is independent of the vol% of the former. Al₃Ni has a Vicker’s hardness of about 7 GPa which remains constant up to about 600 K and then decreases linearly to 2 GPa at 850 K. However, Al₂O₃ is reported to slightly expand on solidification and the fine radial cracks seen in the samples of Fig. 1 may be attributed to that.

The present investigation has shown that net-shape composites containing some aluminium based intermetallic compounds can be produced by the reactive melt penetration process. Since the intermetallic compounds have a much higher melting points than Al, the useful working temperature of the composites can be easily increased. However, their usefulness will depend on the properties of the intermetallics, which are, in general, very hard and brittle. There are other intermetallic compounds in the binary alloys of Al-Ni, Al-Cr and Al-Mo, which occur over a wider composition range and may be examined for their usefulness in Al₂O₃ composites.

Conclusions

The following conclusion may be drawn from the present investigation:

1. Net-shape Al₂O₃ composites containing a network of dispersed intermetallic phase can be produced by the reactive melt penetration process.

2. Reaction between silica and a molten Al-43 wt% Ni alloy can be carried out in the two-phase region.

References