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Interface studies on crystallized alumina–silica fibre-reinforced Al-Si alloy composites

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On applying heat treatments to the amorphous alumina–silica fibre (55% Al_2O_3, 45% SiO_2), the mullite crystal is separated out, and the crystallinity depends on the heat treatment parameters. The crystallized alumina–silica fibre shows higher hardness than amorphous alumina–silica fibre and a remarkable stability to chemical reaction with molten metal. The primary interfacial reaction zone product was found to be $2MgO \cdot SiO_2$.

1. Introduction

At present, ceramic fibre-reinforced aluminium alloys (FRM) are in use as the top ring groove and crown of high-performance diesel engine pistons. Alumina fibres as reinforcements are very expensive and the cost of the resulting composite material is high. In fact, the problem of cost is one of the biggest current drawbacks to the above-mentioned alumina fibres (so-called alumina–silica fibres) whose principal components are the relatively inexpensive alumina and silica. They are normally used as heat insulation fibres in the amorphous crystalline form. However, alumina–silica fibres, particularly in the amorphous crystalline phase, are structurally unstable; this problem tends to arise during manufacture of the composite material, when either the wettability of the reinforcing fibres with the molten matrix metal is poor, or if well wetted by the molten matrix metal, the reaction between them causes a deterioration of the reinforcing fibres.

This paper reports research on the crystallization of amorphous alumina–silica, the surface of the crystallized fibres and the interfacial reaction between the crystallized fibres and the matrix metal.

2. Principles of crystallization

The chemical structure of amorphous alumina–silica (55% Al_2O_3 and 45% SiO_2) is $Al[AlSiO_4]O$, and when heated above 1253 K (980 °C), mullite crystals appear, which are embedded in a matrix of alumina–silica which can be amorphous. During this process, Si^{4+} is replaced by Al^{3+} in each alumina–silica unit cell; the change can be written

$$Al_{32}Si_{16}O_{80} - 4Si^{4+} + 4Al^{3+} - 2O^{2-}$$
(four units of alumina–silica)

$$= Al_{36}Si_{12}O_{78} \quad (1)$$
(six molecules of mullite)

The crystallinity was investigated by X-ray diffraction, and the surface composition of fibres before and after heating is investigated by X-ray photoelectron spectroscopy (XPS).

2.1. X-ray diffraction of the fibres

The process of fibre crystallization is explained below. The amorphous alumina–silica fibre was heat treated for 2 h at different temperatures ranging from 1473–1533 K; fibres containing different quantities of mullite crystals were obtained through this heat treatment. The degree of mullite crystallization was measured by pulverizing the fibres, determining the peak area of X-ray diffraction and comparing it with the peak area of a standard specimen (100% mullite crystal).

According to the equation for the diffraction intensity of the polycrystalline material, and applying the law in which the mass quantity of coherent scattering is unchanged with the state of structure for the same weight polycrystalline material, a method of determining the crystallinity of amorphous alumina–silica fibres was established on the basis of the X-ray diffraction principles in this paper. It should be pointed out that the crystallinity was in the unstable equilibrium state during the crystallization process of amorphous alumina–silica fibres under conditions of varied temperature and a given time of heating. A study of the crystallinities could provide the basis for controlling the crystalline transformation.

The crystallinity equations are as follows

$$X_c = \frac{W_c}{W_A + W_c} = \frac{I_c}{I_c + KI_A} \quad (2)$$

$$X_A = \frac{W_A}{W_A + W_c} = \frac{KI_A}{I_c + KI_A} \quad (3)$$

$$X_c + X_A = 1 \quad (4)$$

where I_c is the intensity of the crystalline phase, I_A the intensity of the amorphous phase, X_c the weight fraction of the crystalline phase, X_A the weight fraction of the amorphous phase, and K is a constant related to the experimental conditions.

0022-2461

Thus, the crystallinities at 1473, 1493, 1513 and 1533 K are 25.2%, 32.5%, 40.3% and 55.0%, respectively. Fig. 1 shows the microstructure of fibres before and after heat treatment by X-ray diffraction.

2.2. XPS

With XPS, the ejected electrons are separated according to their kinetic energies, and the subsequent spectrum can be viewed as a plan of the orbital energy levels of the atom studied. Thus by applying XPS technology, excellent quantitative elemental information is available. The area under a given XPS peak can be relatively easily related to the concentration of surface species, and therefore absolute quantitative surface information can also be accrued. The XPS results showed that the crystallized alumina–silica short fibres had an SiO_2-rich region on the outermost surface (< 150 nm), but that amorphous alumina–silica short fibres showed no segregation. Fig. 2 shows the Si^+ XPS peak of short fibres surface before and after heat treatment.

3. Interface studies

The composite fabrication process was a liquid–metal infiltration technique. The reinforcements were amorphous alumina–silica short fibres and crystallized alumina–silica short fibres (40% mullite crystal).

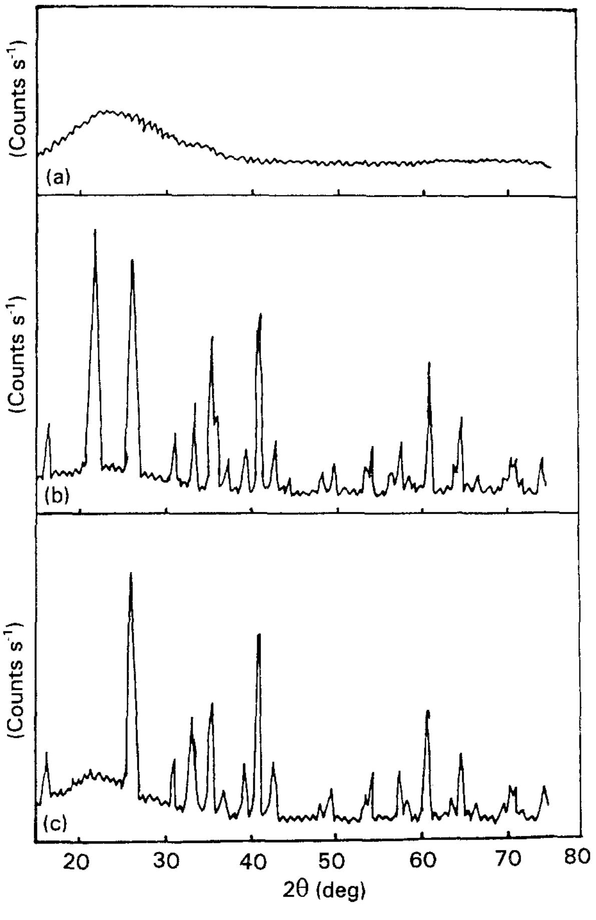

Figure 1 The microstructure of fibres (a) before and (c) after heat treatment at 1533 K for 2 h determined by X-ray diffraction. (b) Mullite fibre.

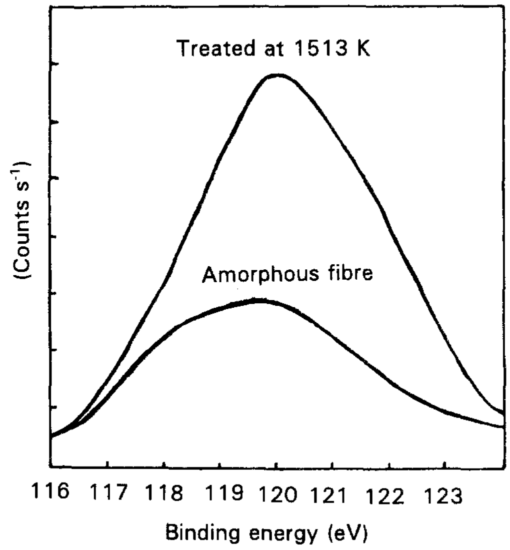

Figure 2 The Si^{4+} peak of one surface of short fibres determined by XPS.

The matrix metal was Al–Si alloy (Al–12% Si–2.5% Cu–0.6% Mg). Samples for scanning electron microscopy and electron probe microanalysis (EPMA) were polished with diamond compound on nap cloth after grinding with 600 grit SiC paper in the normal fashion. Element distribution maps, step and continuous scanning patterns through the fibres and their surroundings were obtained from EPMA.

The specimen for transmission electron microscopy was obtained by preforation under high vacuum using an ion beam operated at 5.0 keV. Each sample was then examined in a transmission electron microscope (CM12, Philips) with an accelerating voltage of 120 kV.

Fig. 3a shows that elemental magnesium existed in almost the whole section of amorphous alumina–silica fibre which apparently reacts with magnesium in the matrix alloy, while elemental magnesium only existed in the surface of the crystallized alumina–silica fibre, as illustrated in Fig. 3b. The reaction zone was examined by X-ray diffraction analysis, and revealed that there are different reaction products for different fibres. $Al_2O_3 \cdot MgO$ and $2MgO \cdot SiO_2$ were found in the reaction zone between the amorphous alumina–silica fibre and the matrix metal, and the reaction zone would be extended by the diffusion mechanism. However more reaction product and a larger reaction zone would degrade the fibre and the properties of the resulting composite material. As a result of X-ray diffraction, only $2MgO \cdot SiO_2$ was found in the reaction zone between the crystallized alumina–silica short fibres and the matrix metal. This is because the crystallized alumina–silica short fibre had an SiO_2-rich region on the surface (< 150 nm). It is assumed that in the case of the crystallized alumina–silica short fibre, only the surface reacted with magnesium in the matrix, because SiO_2 is more reactive with magnesium than Al_2O_3, and is bonded tightly to the matrix. The $2MgO \cdot SiO_2$ reaction zone would act as a blocking layer to protect the diffusion of magnesium to the centre of fibre. Thermodynamic

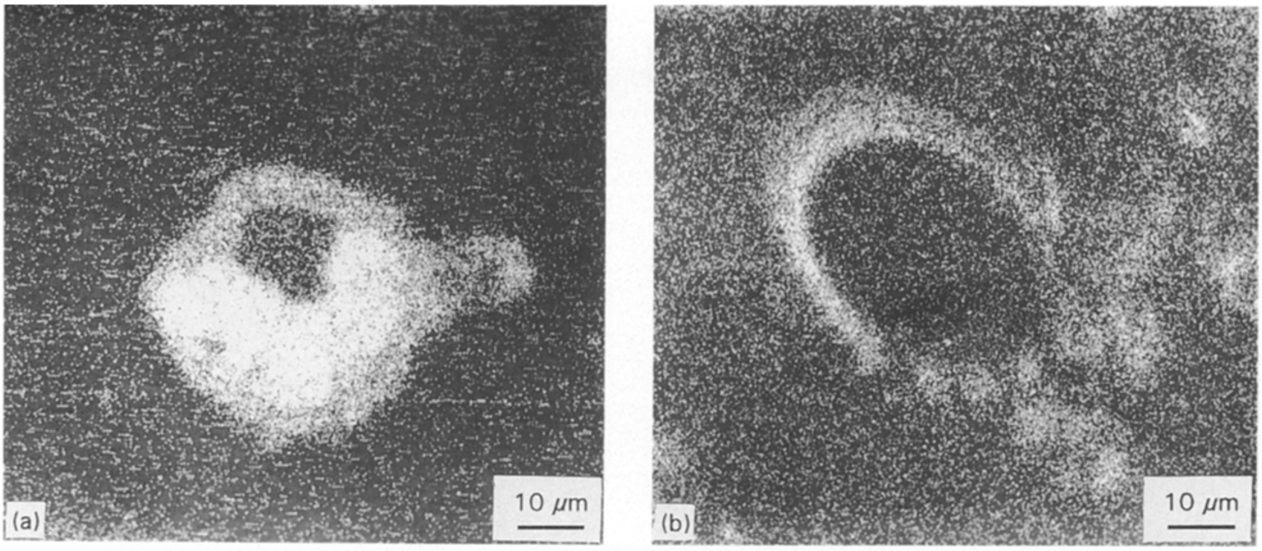

Figure 3 Elemental magnesium X-ray map for (a) amorphous alumina–silica short fibres and (b) crystallized alumina–silica short fibres, heated at 1513 K for 2 h.

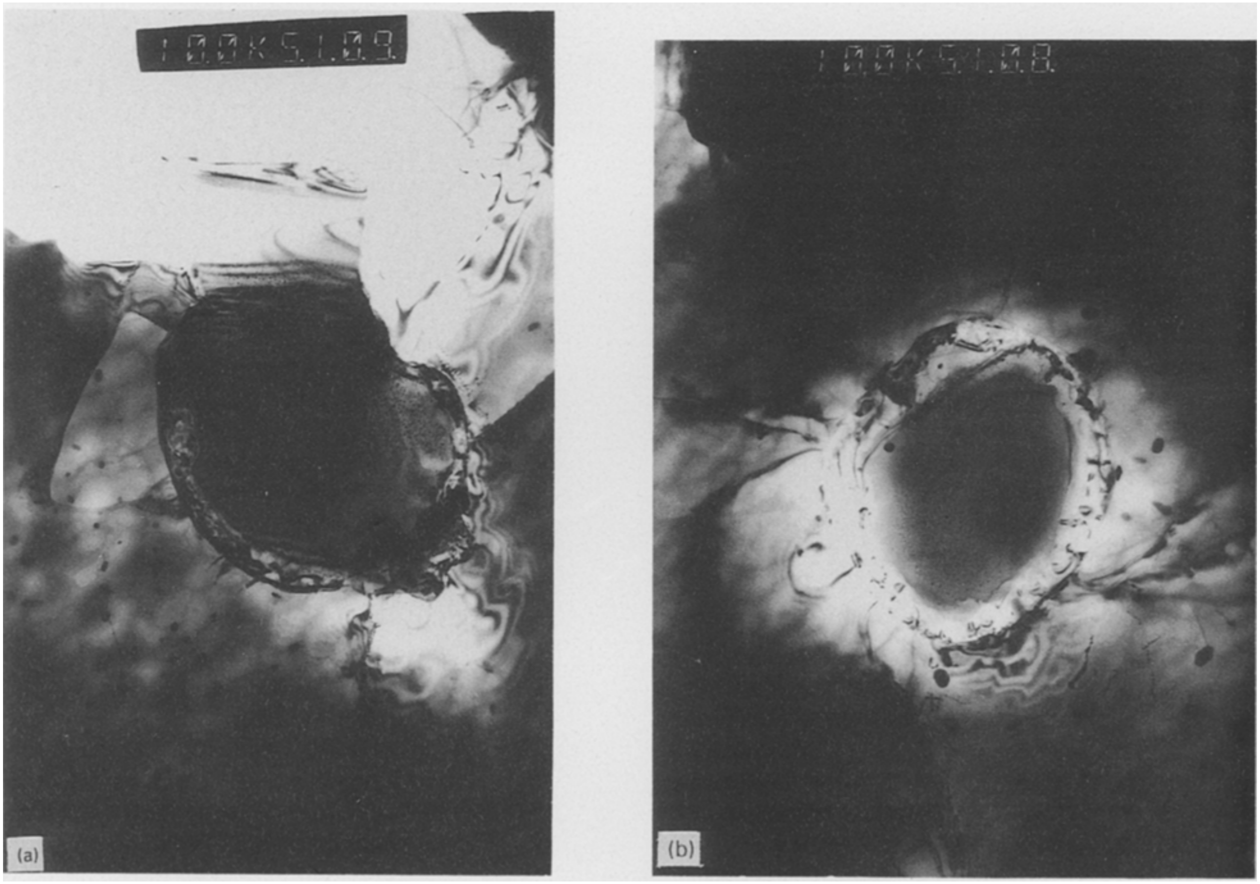

Figure 4 Transmission electron micrographs of amorphous alumina–silica short-fibre-reinforced Al–Si alloy: (a) interface between fibre and matrix; (b) the distribution of the dislocations around the fibre.

analysis of the possible production also verified the results of X-ray diffraction.

$$\begin{aligned} 2\mathrm{MgO} + \mathrm{SiO_2} &= 2\mathrm{MgO}\cdot\mathrm{SiO_2} \\ \Delta G^\circ &= -\ 15120\ \mathrm{cal} \qquad (5) \end{aligned}$$

$$\begin{aligned} \mathrm{MgO} + \mathrm{SiO_2} &= \mathrm{MgO}\cdot\mathrm{SiO_2} \\ \Delta G^\circ &= -\ 8900 + 1.1T\ \mathrm{cal} \qquad (6) \end{aligned}$$

$$\begin{aligned} \mathrm{MgO} + \mathrm{Al_2O_3} &= \mathrm{MgO}\cdot\mathrm{Al_2O_3} \\ \Delta G^\circ &= -\ 5200\ \mathrm{cal} \qquad (7) \end{aligned}$$

Conclusion

Thus, by studying the surface of fibres before and after heat treatment and the interface between the short fibres and the matrix metal, a new type of reinforcement applicable to composite material has been found. (Fig. 4). The crystallized alumina–silica short fibre had a remarkable stability in chemical reaction with the matrix metal. Composite materials reinforced by the crystallized alumina–silica short fibre have excellent tensile and fatigue properties.

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