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Effect of rare earth Pr on microstructure and mechanical properties of Al_2O_3-SiO_2(sf)/Al-Si composites

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Abstract: The Al_2O_3-SiO_2(sf) (volume fraction, 20%)/Al-12.6Si metal matrix composites(MMCs) with or without rare earth Pr addition were fabricated by infiltration squeeze method. Effect of Pr addition on microstructures and fractographs of Al-Si MMCs was investigated by SEM and TEM. Tensile properties at room temperature and 200 ℃ were tested. It is shown that the addition of Pr is favorable to produce uniform microstructures and modify the eutectic Si crystal effectively. Compounds/intermetallics with high content of Pr are formed at the interface between short fiber and matrix. Yield strength($\sigma_{0.2}$), ultimate tensile strength(σ_b) and fracture elongation of Al-Si MMCs are improved by adding suitable amount of Pr. Compared with those values of Al-Si based MMC at 200 ℃, $\sigma_{0.2}$ and σ_b of MMC with 0.29% Pr are increased by 33% and 55%, respectively. The tensile fracture surface of Al-Si MMCs with Pr addition presents ductile fracture features.

Key words: Al-Si alloy; rare earth; metal matrix composites; microstructure; tensile properties

1 Introduction

Because of their high strength, good castability, low thermal expansion and high corrosion resistance, Al-Si alloys are widely applied in the fields of automotive and aircraft, such as engine blocks/heads and gearboxes. However, Al alloys with high content of Si possess poor ductility due to a microstructure composed of plate-like silicon particles and coarse intermetallics embedded in Al matrix[1]. Many ways of grain refining and alloy strengthening are developed for Al-Si alloys[1−4]. Rare earth(RE) is proved to be beneficial to modifying the morphology of primary and eutectic silicon and refining the matrix grain size[5−6]. RE addition in the Al-TM-RE system (TM=transition metals) resulted in the refinement of intermetallic compounds and oxide compounds[7−9]. The role of RE addition was also investigated in Al-Cu-Mg-Ag alloys[10], Al-Zn-Mg alloys[11], AE series alloys[12−13] and Al-Li alloys[14]. Furthermore, the corrosion resistance of Al-Si alloy with RE addition was improved in marine environment[15].

Recently, aluminium-based metal matrix composites(MMCs) have been applied in automotive industry, because of their increased elastic modulus, enhanced wear resistance, and improved high cycle fatigue performance. There are many reports about the effect of RE addition on Al-Si based MMCs. The tensile elongation and tensile strength of in situ TiC/Al-Si+0.5% CeO_2 (mass fraction) composite were much higher than those of the TiC/Al-Si composite, when 0.5% CeO_2 (mass fraction) was added into the composite[16]. With increasing the Ce content, the morphology of primary Mg_2Si particulate in Al-Si-Cu alloy based composite changed from dendritic or irregular to polygonal shape; the eutectic Mg_2Si phase changed from flake-like to chrysanthemum-like; and eutectic Si changed to coral-like morphology[17]. With Sc addition, precipitates of AlScSi (V phase) other than Mg_2Si were seemingly present[18]. The interfacial wettability between reinforcement and Al melt was dramatically improved in Y_2O_3 coated-Al_2O_{3p}/6061Al[19−20]. La presented the same effect in Al_2O_{3p}/A356 MMCs[21].

Crystallized alumino-silicate ($Al_2O_3\cdot SiO_2$) particle [22] or short fibers[23] can reinforce Al-Si MMCs effectively. Improvement of microstructure and wettability are expected for eutectic Al-Si matrix MMCs with RE addition. In this work, rare earth Pr is added into Al_2O_3-SiO_2(sf)/Al-Si composites, and the effect on micro-structures and mechanical properties are investigated.

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2 Experimental

The 20% (volume fraction) Al_2O_3-SiO_2(sf)/Al-Si MMCs were fabricated by infiltration squeeze method. The matrix material used was eutectic Al-Si alloy containing 12.6% Si with elemental compositions listed in Table 1. The perform was made of low-cost alumina silicate (Al_2O_3-SiO_2) short fibers crystallized at 800−1 100 ℃, with diameter of 8−10 μm and length of 60−120 μm. In order to add a certain amount of rare earth Pr in the matrix alloy, pure Pr metal was sliced into small pieces and wrapped in aluminum foil. Then the wrapped small pieces of Pr were deposited into the melt after the temperature of Al-Si alloy melt was raised up to 1 200 ℃. 2 g pure Al per 1 kg Al-Si alloy was added to compensate its evaporation. Followed by stirring for 5 min, the matrix alloy melt was poured into fiber perform at 800 ℃ under 50 MPa. The addition amounts (mass fraction) of Pr in the MMCs are 0, 0.19%, 0.29%, 0.44% and 0.73%, respectively.

The microstructure observation and analysis of Al-Si MMCs were performed on scanning electron microscope (SEM, LEO 1530 VP equipped with an KEVEX Sigma EDXS), transmission electron microscope (TEM, HITACH 800 attached EDAX PV9100/75). Tensile testing was carried out on Gleeble-1500 machine with a displacement speed of 0.5 mm/min. Dog-bone shaped coupons with 2 mm in thickness, 4 mm in width and 20 mm in gauge length were machined from the MMCs materials.

3 Results and discussion

3.1 Microstructure

Less shrinkage pores in Al_2O_3-SiO_2(sf)/ A1-Si alloy composites can be observed. In some area, the agglomeration of alumina-silicate short fibers is seen in Al-Si MMCs without rare earth Pr (Fig.1(a))), while Al_2O_3-SiO_2 short fibers are distributed uniformly in the Al-Si matrix with addition of Pr (Figs.1(b) and (c)). In the Al-Si MMCs without Pr addition, the eutectic Si includes stick-like or sheet-like morphologies with length of about 30 μm. With increasing the addition of Pr, the amount of sheet or stick-like eutectic Si decreases. When the addition of Pr rises up to 0.73%, the morphology of eutectic becomes equiaxied and stick/ sheet-like morphology almost disappears.

From the back scattering electron images of Al-Si MMCs, it is shown that the distribution of Pr in composites is heterogeneous. Mostly, the Pr is rich at the boundary among alumina-silicate short fibers (Fig.2(a)). Some short fibers are even wrapped by a Pr-rich zone (Fig.2(b)). EDS spectrum from area “A” in Fig.2(b) is presented in Fig.2(c). It is shown that the Pr content in this area is high. From TEM observation, an enriched Pr phase (Fig.3(a)) and a pure Si phase (not shown here) are formed at the interface between alumina-silicate short fiber and matrix. In situ EDS analysis from the enriched Pr phase shows that molar fraction of elements are: O 6.02%, Al 41.38%, Si 28.75% and Pr 23.65%. The selected area diffraction pattern from this phase is shown. According to Powder Diffraction Files and the calculated lattice parameters, the enriched Pr phase is one of the following phases or a mixture of them: PrAl (Sys: orthorhombic, PDF 65-1395), $PrAl_3$ (Sys: hexagonal, PDF 29-0073), $PrAl(OH)(SiO_4)_2$ (Sys: unidentified, PDF 37-0064), and $Pr_2(Si_2O_7)$ (Sys: Tetragonal, PDF 76-0725). Among them, the Pr-enriched phase is most probably PrAl phase modified by other elements. Dislocations near the interface of as-cast Al-Si composites

Table 1 Elemental compositions of Al-Si alloy (mass fraction, %)

Si	Cu	Fe	Mg	Mn	Others	Al
12.60	0.15	0.30	0.24	0.22	0.72	Bal.

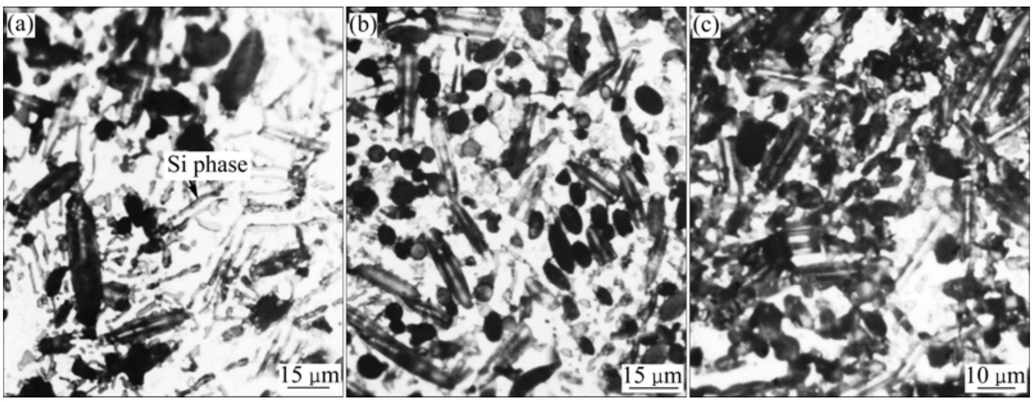

Fig.1 Optical microstructures of Al-Si MMCs with different Pr additions: (a) 0% Pr; (b) 0.19% Pr; (c) 0.73%Pr

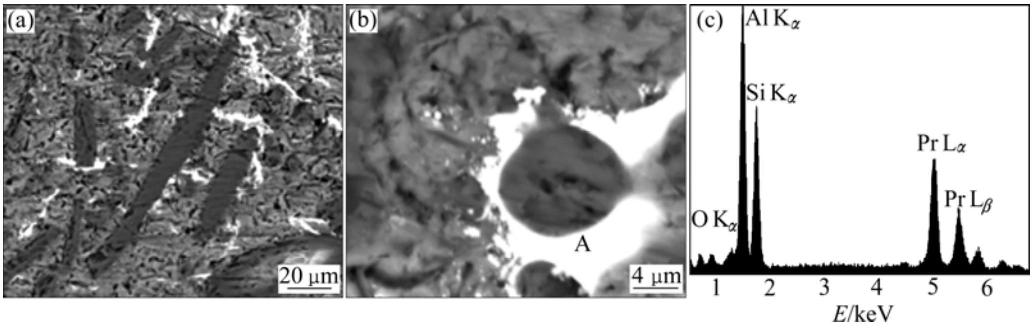

Fig.2 Back scattering electron(BSE) images of Al-Si MMC with 0.73% Pr: (a) Microstructure in lower magnification; (b) Microstructure in higher magnification; (c) EDS spectrum from Zone "A" in (b)

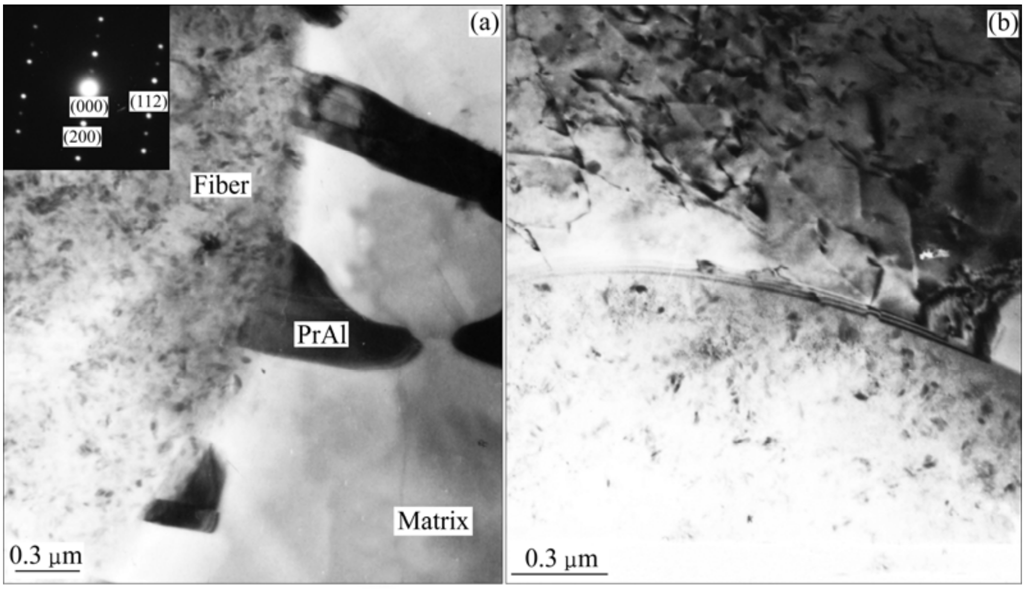

Fig.3 TEM images of interface of as-cast Al-Si MMCs with Pr addition: (a) Bright field image; (b) Dislocation structure near interface (Insert: SAD pattern)

with Pr addition is also presented in Fig.3(b).

It is well known that a very small amount of earth addition in Al-Si alloys and Al-Si based MMCs is enough to change their microstructure. The roles of rare earth addition in Al alloy and MMCs are identified by many reports. Because of lower electronegativity of rare earths such as La and Ce, they tend to absorb onto the growth front of Si crystal and therefore effectively poison the growth steps, resulting in the isotropic growth of Si crystals[5−6]. No matter the ways of rare earth addition, for example, in the form of pure RE metal, RE mishmetal, Al-RE master alloy or RE oxides, the segregation of RE around eutectic Si or reinforcements is observed[5−6, 16−17, 21, 24]. RE enriched phases are also formed at the interface between reinforcements and matrix, for instance, Y_2Al phase in the Y_2O_3 coated Al_2O_3/Al composite[18−19], and needle-like Ce-enriched phase in aluminum borate whisker-reinforced magnesium alloy (MB8) composite[24].

In the element periodical table, Pr is located close to La and Ce, and its electronegativity and atomic radius are similar to Ce and La. Like Y_2O_3 coated-Al_2O_{3p}/6061Al[19−20], wetting angle between Al-Si alloy melt and alumina-silicate short fiber is expected to decrease. Moreover, pressure distribution in the preform is more uniform, thus local deformation of perform is suppressed. By comparing Figs.1(b)−(c) with Fig.1(a), addition of Pr in the matrix is favorable to produce more uniform microstructure in the studied Al-Si MMCs.

Rare earth Pr has lower solubility in Al alloys. During solidification, it will segregate to grain boundary and short fiber interface by redistribution. The following points should also be noticed: La, Pr, Ce and Nd decrease surface tension slightly; in Al alloys with RE addition, all the melts remain strongly micro-heterogeneous even at high overheating above liquidus line; and the viscosity of Al-Pr melt increases with amount of Pr at about 1 000 ℃[25]. According to the

Pr-Al binary phase diagram, there are phases of Pr_3Al, Pr_2Al, PrAl, $PrAl_2$, $PrAl_3$, Pr_3Al_{11}[26]. From these factors and the addition amount of Pr in this work, it is possible that the precipitation of enriched Pr phase is formed at the interface between alumina-silicate short fibers and Al-Si matrix.

3.2 Tensile proprieties and fractograph

The yield strength, ultimate tensile strength, fracture elongation at room temperature and high temperature (200 ℃) of Al-Si MMCs with more than 0.19% Pr addition are higher than those of the MMCs without Pr addition (Figs.4(a) and (b)). The ultimate strength reaches the peak at w(Pr)=0.29%. Compared with those values of Al-Si based MMC at 200 ℃, $\sigma_{0.2}$ and σ_b of MMC with 0.29% Pr are increased by 33% and 55%, respectively. From Fig.3(b), high density of dislocations is observed in the matrix close to interface in as-cast MMCs. This indicates that large residual thermal stress exists in the MMCs because of thermal mismatch between short fibers and matrix. The more the tensile thermal stress in the matrix is, the less the external applied stress to move dislocations is[23]. When tension test was carried out at higher temperature, tensile thermal stress in the matrix relaxes to some extent. This is probably the reason why the yield stress of Al-Si MMCs studied in this work does not decrease.

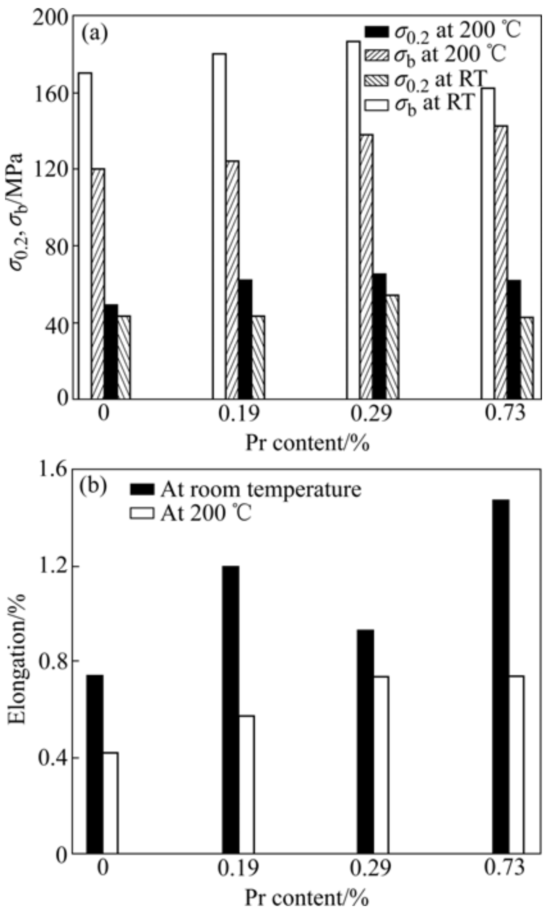

Fig.4 Tensile properties of Al-Si MMCs with different Pr contents: (a) Yield strength and ultimate strength; (b) Elongation

The tensile fracture surfaces of Al-Si MMCs with different amount addition of Pr were observed by SEM (Figs.5 and 6). There are higher amount of pulled out-short fiber on the fracture surface in the MMCs without Pr addition, while short fibers fracture in those MMCs with Pr addition (Figs.5(b) and (c) and Figs.6(b) and (c)). These mean that Pr addition enhances the adhesion between short fiber and matrix and prove the benign effect of rare addition on the interface adhesion of

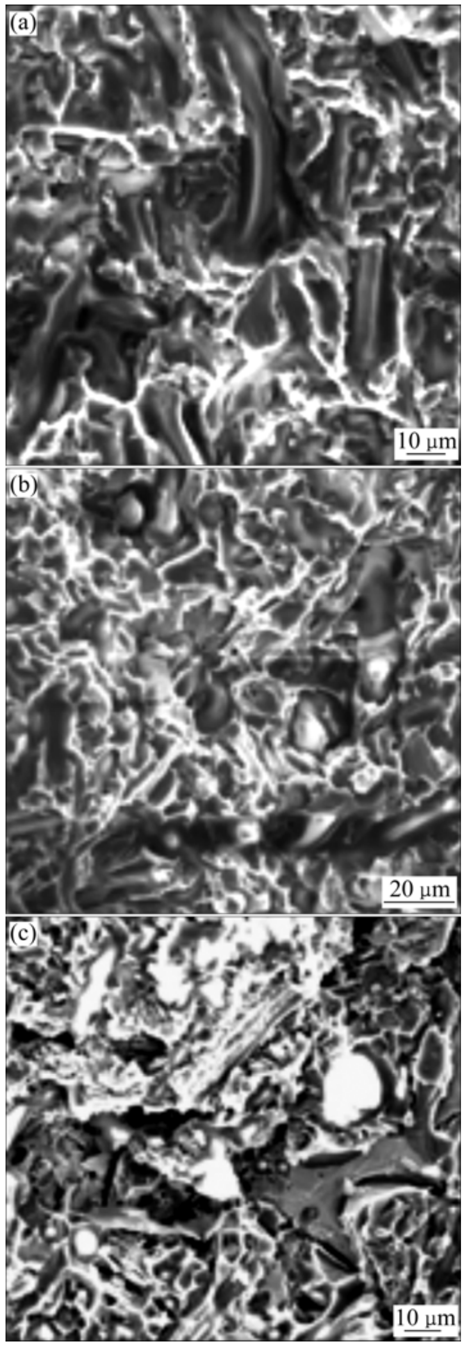

Fig.5 Fractographs of Al-Si MMCs under tension at room temperature: (a) 0% Pr; (b) 0.29% Pr; (3) 0.73% Pr

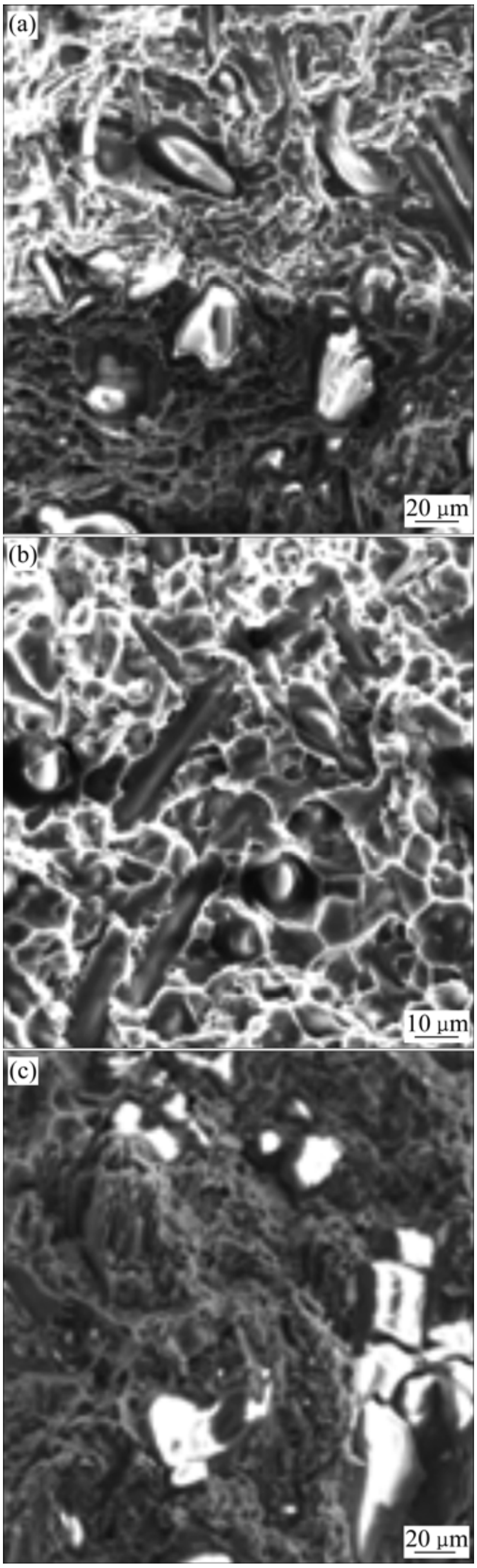

Fig.6 Fractographs of Al-Si MMCs under tension at 200 ℃: (a) 0% Pr; (b) 0.29% Pr; (c) 0.73% Pr

MMCs. In the Al-Si MMCs with Pr addition, many fine dimples are observed in the matrix, and this is responsible for the eutectic Si crystal modification and much more uniform microstructure.

4 Conclusions

1) Addition of Pr in the matrix is favorable to produce more uniform microstructures in the studied Al-Si MMCs. The distribution of Pr in composites is heterogeneous. Mostly, it is rich around the interface between alumina-silicate short fibers and matrix.

2) Addition of Pr in Al-Si MMCs can modify the eutectic Si crystal effectively. Compounds or intermetallics with a high content of Pr are formed at the interface between short fiber and matrix, and this is beneficial to improving wettability and adhesion between short fiber and matrix.

3) Yield strength, ultimate tensile strength and fracture elongation of Al-Si MMCs are improved by adding suitable amount of Pr. Comparing with those of Al-Si based MMC at 200 ℃, $\sigma_{0.2}$ and σ_b of MMC with 0.29% Pr are increased by 33% and 55%, respectively. With Pr addition of 0.29% and 0.73%, the tensile fracture surface presents ductile fracture feature.

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