Materials and Design 78 (2015) 85–94

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Effect of Sc addition on the microstructure and wear properties of A356 alloy and A356–TiB_2 *in situ* composite

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ARTICLE INFO

Article history:
Received 13 November 2014
Revised 16 April 2015
Accepted 18 April 2015
Available online 18 April 2015

Keywords:
Grain refinement
Si modification
Fading
A356
Scandium
TiB2
Composite
SDAS

ABSTRACT

In this study, the effect of Sc addition on the grain refinement, modification of the eutectic Si, mechanical and wear properties of A356 and A356–10 wt% TiB_2 *in situ* composite has been investigated. The A356–10 wt% TiB_2 composites were prepared by an *in situ* reaction between K_2TiF_6 and KBF_4 salts, which are added in proper stoichiometric ratio to form TiB_2 in the A356 alloy melt at a temperature of 1073 K (800 °C). Al–2 wt% Sc master alloy was added to A356 and A356–10 wt% TiB_2 melt to introduce 0.2 and 0.4 wt% Sc in the alloy and the composite. Addition of Sc reduced the secondary dendrite arms spacing (SDAS) by 50% and changed the Si morphology from needle-like to fine spheroidal particles. Microstructure of Sc modified alloys which were cast for different holding times of 0, 30, 60 and 120 min indicated that there was no fading or poisoning effect on the SDAS and eutectic Si morphology. Hardness was found to increase due to addition of Sc and TiB_2. Pin-on-disk wear tests indicated that Sc addition increase the wear resistance of A356 alloy but reduced the wear resistance of A356–TiB_2 composite.

1. Introduction

Al–Si alloys and Al-matrix composites (AMCs) have received much attention for automobile, aerospace and structural applications due to their high specific strength and specific stiffness, higher hardness and wear resistance and good elevated temperature resistance [1–6]. Currently, AMCs are produced by various processing routes such as casting, powder metallurgy and spray deposition. Addition of fine sized reinforcement is a big challenge in stir casting method when there is lower wettability of the reinforcement phase with the molten matrix. Due to the limitations of *ex situ* processes, *in situ* processes have been developed. In these processes, chemical reactions lead to the formation of thermodynamically stable reinforcing ceramic phase *in situ* in the melt. An *in situ* process for the formation of TiB_2 reinforcement in Al matrix by the chemical reaction of two halide salts (K_2TiF_6 and KBF_4) with the Al melt was invented and patented by the London and Scandinavian Metallurgical Co. in 1993 [1]. The reactions leading to formation of TiB_2 are as follows:

$$3K_2TiF_6 + 13Al \rightarrow 3TiAl_3 + 3KAlF_4 + K_3AlF_6 \quad (1)$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \quad (2)$$

$$AlB_2 + TiAl_3 \rightarrow TiB_2 + 4Al \quad (3)$$

Al composites having *in situ* TiB_2 and TiC reinforcements have gained much attention recently, due to high hardness, modulus and wear resistance [2,5–7]. It has been found that the *in situ* particles also act as nucleation sites during solidification thereby reducing the inter-dendritic arm spacing [7]. Al–TiB_2/TiC composites synthesized by *in situ* processes possess good mechanical and tribological properties [6,8–13]. Kumar et al. [6] studied the effect of 5 and 10 wt% TiB_2 in Al–7Si alloy and reported 50% reduction in wear rate and 40% increase in tensile property for 10 wt% TiB_2. Kumar et al. [6] and Mandal et al. [8] studied the wear behavior of A356–5/10TiB_2 composites and showed that wear resistance improves significantly with the TiB_2 content. Niranjan and Lakshminarayanan [9] and Suresh et al. [10] studied the wear behavior of Al–TiB_2 composite and observed an increase in wear resistance with the TiB_2 content.

Recently, researchers added exotic metals like La, Nd, Sc for the grain refinement of Al alloys [14–25]. Chen et al. [14] studied the combined effect of grain refinement and modification by adding La and B grain refiners and Sr as Si modifier and observed LaB_6 particle acts as nucleation site for α-Al and suppressed the poisoning between B and Sr. Bolzoni et al. [15] and Nowak et al. [16] studied

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http://dx.doi.org/10.1016/j.matdes.2015.04.026
0261-3069/

the grain refinement of Al–Si alloys with Nb–B addition and observed effective grain refinement and in-situ formed Al_3Nb and NbB_2 intermetallic particles are the heterogeneous nuclei responsible for the grain refining of Al cast alloys. Al–Sc alloys have good mechanical properties at ambient and elevated temperatures due to the hardening effect of nanocrystalline Al_3Sc precipitates [17]. Recently, there has been an increased interest in the study of the effect of Sc on microstructure and properties of Al and Al–Si alloys [18–30]. It has been shown by Fatih et al. [18] in case of Al–20Si hyper-eutectic alloys that the size of both eutectic as well as primary Si reduces due to Sc addition, results in enhanced mechanical properties of the alloy. They proposed that Sc addition modifies the Si particles by an impurity induced twinning (IIT) mechanism. Prukkanon et al. [19] have reported that a 0.2 wt% Sc addition in Al–7 wt% Si alloy modified the eutectic Si by changing its morphology into rounded and fibrous shapes and the addition of Zr together with Sc increased the effectiveness of Si modification. Kim et al. [20] studied the effect of 0.4 wt% Sc in Al–8.5 wt% Si alloy and observed a 60% increase in the tensile strength and 50% increase in elongation due to Sc addition. Kim et al. [21] studied the effect of Sc and Sr in Al–20 wt% Si alloys. They observed no significant difference in the primary and eutectic Si morphologies with the addition of Sc and Sr. They have shown that Sr is present uniformly on the surfaces of primary Si and eutectic Si, which results in modification by IIT mechanism. Prukkanon et al. [22] carried out fluidity tests on Sc modified A356 alloy and found that the addition of 0.2 and 0.4 wt% increased the fluidity by more than 40%. Rajinikanth et al. [23] have studied the effect of 0.25 wt% Sc addition in Al–2Si alloy subjected to high pressure torsion test at 6 GPa pressure. They reported that Sc addition resulted in a 60% reduction in grain size and a 15% improvement in tensile property. Patakham et al. [24] reported that Sc addition results in refinement of α-Al and modification the eutectic Si but the grain refinement efficiency of Sc was considerably lower than that of conventional Al–Ti grain refiner. Zhang et al. [25] have studied the effect of Sc in Al–7Si alloy and found Sc atoms segregated in the inter-dendritic region and a Fe-rich phase precipitated on the $AlSc_2Si_2$ V-phase along the grain boundary. It is known that during the precipitation hardening treatment of Al–Sc alloys, various precipitates such as Al_3Sc, AlSc and Al_2Sc are formed. It is known that the Al_3Sc phase can act as a grain refiner, a dispersoid and a precipitation hardening agent [26–30]. Kori et al. [31] have studied the combined effect of grain refiner and modifier addition in Al–7Si alloy using several grain refiners and modifiers and concluded that Al–1Ti–3B refiner and 0.02 wt% Sr addition avoided the fading and poisoning effects and gave the best results. Li et al. [32] reported Al–3Ti–1B–0.2C master alloy shows better grain refining efficiency in A356 alloy compared to the Al–5Ti–1B master alloy. Also reported fading is not observed for 60 min holding of the melt. The combined effect of grain refinement and modification in Al–Si–Mg alloy was studied by the addition of Ti and B refiners and Sr as modifier and observed an improvement in tensile and impact properties [33,34]. Several studies exist in literature on grain refinement and the eutectic Si modification in A356/Al–7Si alloys by addition of Al–Ti–B or Al–Ti–C based grain refiners and Sr as Si modifier and their effect of mechanical and wear properties [31,35–37,6,38–40]. Wang et al. [11] studied the effect of Sr on A356–3 wt% TiB_2 composite prepared by re-melting and dilution of A356–5 wt% TiB_2 composite and observed an improvement in mechanical property.

A356 alloy is used to manufacture automotive cylinder blocks and gear box casings and A356–10 wt% *in situ* TiB_2 composite is a potential candidate for cylinder liner applications because of its high strength and wear resistance. This study was carried out on commercial A356 alloy for several reasons. There are only few studies on Sc addition to commercial A356 alloys. A few studies have been done using Al–7Si–0.3 Mg alloys, but the presence of other elements such as Fe, Ti (from grain refiners), Cu and Mn can interact with Sc and affect the Si modification and the resulting properties. Thus, a study on commercially used A356 alloy is necessary. There is also no study on the fading effect (settling or dissolution of the grain refiner with holding time, which reduces the grain refiner efficiency) on A356 alloy with Sc addition, which is important in industrial practice. It is also found that there is no study on the effect of Sc on microstructure and properties of A356–TiB_2 composites. The last reason is that there is no report on the effect of Sc addition on the wear properties of A356 and A356–TiB_2 composites. So, the aim of the present work was to study the effect of Sc on the microstructure and wear properties of commercial alloy A356 and A356–10 wt% *in situ* TiB_2 composites.

2. Experimental details

An Al–2 wt% Sc master alloy was added to A356 melt at 1003 K (730 °C) to synthesize 0.2 and 0.4 wt% Sc modified A356 alloys. The dilution of Si in A356 alloy, due to the addition of master alloy was compensated by Al–11Si (LM6) alloy. The melt was degassed by hexa-chloro ethane. Magnesium was added to the degassed melt to compensate for dilution and the melt was cast into a 40 mm diameter steel mold preheated to 473 K (200 °C).

The A356–10 wt% TiB_2 composites (here after referred as A356–TiB_2 composite) were processed by adding a mixture of K_2TiF_6 and KBF_4 in the required stoichiometric ratio to the A356 melt at a temperature of 1073 K (800 °C). The salts were preheated to 473 K (200 °C) and added to the molten melt at 1073 K (800 °C) and stirred at regular intervals of 10 min for an hour. This ensured that the exothermic reaction between the salts and molten aluminum goes to completion and the *in situ* formed TiB_2 particles were uniformly distributed in the melt. Al–2 wt% Sc master alloy was added to the composite to produce A356–TiB_2 composite with 0.2 and 0.4 wt% Sc. Degassing and addition of Mg was done in the same manner as described for the alloys.

In order to determine the fading characteristics of Sc, the degassed A356 melt after the addition of Sc was held at 1003 K (730 °C) for different time intervals of 5, 30, 60 and 120 min in the furnace and then poured into graphite molds having 1 in. diameter. The microstructures from a region, which is 1 in. thick from the bottom of the casting was compared to see the effect of holding time on the SDAS and Si morphology.

The samples of the alloy and composites were ground using emery paper, polished using diamond paste (up to 0.5–1 μm) and etched with Keller's reagent for microstructure and hardness analysis. Optical Microscopy was carried out using Olympus GX51 microscope. The grain size was measured by measuring the secondary dendrite arm spacing (SDAS) by linear intercept method in several regions where secondary dendrites were observed lined up in an array. FEI Quanta 200 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) was used for microscopy and composition analysis. In order to confirm that there was complete formation of TiB_2 without any residual Al_3Ti, a small amount of the composite was dissolved in NaOH solution to dissolve the Al and Si and the residual powders were collected after 5 h, dried and analyzed using X ray diffraction (XRD).

Vickers hardness was measured on polished samples using a micro Vickers hardness tester (Model 420 MVD, Wolpert Wilson Instruments, USA) with a 10 s dwell time and a load of 500 g. Wear properties were measured using a pin-on-disk wear tester according to ASTM G99 standard. The sliding velocity and track diameter were kept constant at 1 m/s and 45 mm, respectively. The tests were carried out at normal loads of 50, 75 and 100 N. Weight loss was measured after a sliding distance of 500 m,