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ALUMINUM ALLOYS: DEVELOPMENT, CHARACTERIZATION AND APPLICATIONS

Corrosion Resistance and Emerging Technologies

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William Golumbfskie
Naval Surface Warfare Center
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Use of Nano-Structured Silanols on the Solidification of Aluminum-Silicon Based Casting Alloys

Andre Lee[1], Yang Lu[1], Allen Roche[2], and Tsung-yu Pan[2]
[1]Michigan State University, East Lansing, Michigan
[2]Vinci Technology Corporation, Ypsilanti, Michigan

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Abstract

Minor alloying elements had been used to modify the solidification process leading to improve mechanical performance of Aluminum casting alloys. However, difficulties in balancing strength, ductility and the subsequent precipitation strengthening heat treatment remain. In this study, use of nano-structured silanols based on partially-condensed polyhedral oligomeric silsequioxanes (POSS-silanol) was examined. The silanols react with active aluminum surface to form stable Si-O-Al bonds, while cage-like POSS core enables control of subsequent solidification process leading desired mechanical performance. Specifically, trisilanol phenyl POSS modifier was added to the casting alloy A4047. Using standard casting approach, a highly refined fine fibrous of eutectic Al-Si formed instead of the irregular flakes, which lead to a significant improvement in its ductility while improve the tensile strength as compared to the unmodified A4047. This newly developed approach was expanded to other heat-treatable casting aluminum alloys with specific interest on changes in the eutectic Al-Si microstructure.

Introduction

Aluminum (Al) based alloys have structural applications in areas such as automotive, military, aerospace and alternative energy industries, which is directly due to their light-weight and lower life-cycle cost[1,2]. Aluminum-silicon (Al-Si) alloys exhibit narrow solidification range and great fluidity which are important criteria for the selection of aluminum casting alloys. An ultimate goal for the industries is to have alloys with good mechanical properties (e.g. strength and ductility) along with manufacturability. However, the ductility of Al-Si casting alloys is still not high enough as compared to steel. This is mainly because the presence of irregular eutectic silicon crystals in the as-cast condition promotes crack initiation and propagation.

Polyhedral oligomeric silsequioxanes (POSS) are silsequioxane-based nano-structural chemicals[3]. These chemicals are cage like structures with repeated monomer units of RSiO1.5 where Si is the element silicon, O is oxygen and R is hydrocarbon group, e.g. ethyl, isobutyl, phenyl etc. Partial cage-like POSS with multiple silanol (Si-OH) functionalities are produced by replacing a Si atom at the corner of POSS to form silanol bonds. Trisilianol phenyl POSS is used in this study as shown in Figure 1. These silanol bonds have revealed to form thermodynamically stable Si-O-M bonds with metals (e.g. Al).

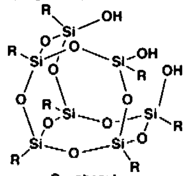


Fig. 1. Partial cage structure of TriSilanolPhenyl POSS

The goal of this study is the development of microstructure refinement by the structural-silanol (e.g. POSS trisilanol) addition, leading to significant mechanical property enhancement for Al-Si based alloys.

Experimental

Materials
Trisilanolphenyl-POSS, obtained from Hybrid Plastics, Inc. (Hattiesburg, MS), was used in this study. A4047 powder -325 mesh (44 µm or less) from Johnson Manufacturing (Princton, IA). Chemical composition (nominal %): 12 Si, balance Al.

Processing
Step 1: Reaction of POSS trisilanol to metal powders. A4047 powder, treatment flux, and 2wt% POSS trisilanol were mixed in ethanol and heated together to 180°C when the acidic ingredients in flux are active. At about 180°C, flux reacts with metal powders to allow the silanols in the POSS solution to attach to the base metal surface. The powder was then washed with hot water to remove unused flux and dried in air.

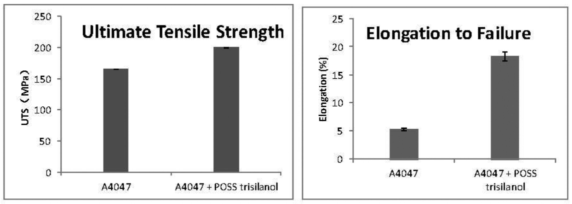
Step 2: Casting. Metal powders was melted with the casting flux and covered with argon gas. Temperature is set at 815°C. Molten melt was poured by gravity to a permanent graphite mold to form a rectangular ingot of 25 mm x 50 mm x 12 mm in size, and cooled in air.

Characterization
Metallographic samples were prepared by grinding with SiC paper and then polishing with 0.3 µm alumina slurry and 0.05 µm colloidal silica suspensions. Optical micrographs were taken with an Eclipse MA200 microscope with the magnification up to 1,000X. Scanning electron microscopy (SEM) was performed with a LEO 1450VP SEM.

Cylindrical tensile specimens of Al-based alloys were machined from ingots with a gauge diameter of 4 mm and gauge length of 30 mm, according to ASTM-E8 standard for room temperature testing.

Results and Discuss

Mechanical Properties
A4047 powders with and without POSS trisilanol added were used to make ingots for mechanical property measurement. The set of the ingots was made from same powder without POSS trisilanol added, and was benchmarked as control samples. Tensile tests were conducted on the tensile bars machined from the ingots as described earlier. The ultimate tensile strength (UTS), and elongation to failure are summarized in Figure 2.



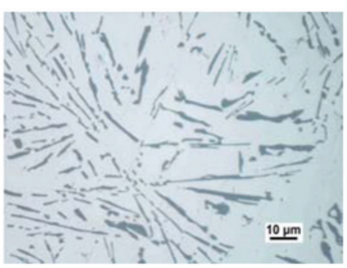
(a) (b)

Fig. 2. Ultimate tensile strength (a) and elongation to failure (b) of ingots made of -325 mesh A4047 powder without and with POSS trisilanol addition

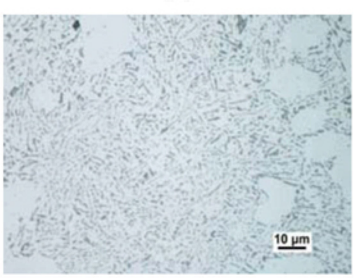
Elongation to failure is increased with POSS trisilanol addition, with percentage increase to 250% over the control sample (without POSS trisilanol added). However, very surprisingly, the ultimate tensile strength does not decrease with the increase of elongation. Instead, it is slightly higher with POSS trisilanol addition. This is opposite to the common practice of material development – increasing elongation (ductility) usually causes the decrease in the strengths as a consequence. With addition of POSS trisilanol, elongation is increased to 18% for the ingots made of -325 mesh A4047 powders with POSS trisilanol added. They were remarkable results even without any heat treatment.

Microstructure

The improved elongation of samples with POSS trisilanol addition can be explained by the microstructure. Figures 3 (a) and (b) are the optical micrographs of the ingots made of 325 mesh A4047 powders without and with POSS trisilanol addition, respectively. A4047 has a near-eutectic Al-Si composition with primary Al phase and eutectic Si-Al phase. Figure 3 (a) displays the microstructure of A4047 without POSS trisilanol, which is typical from a slow-cooled ingot with Al dendrite and lamellar Si cuboids[4]. With the addition of POSS trisilanol, under the same casting and cooling configurations, the Si platelets are broken down to very fine spheroidized phase, as shown in Figure 3 (b).



(a)



(b)

Fig. 3. Optical micrograph of an ingot made of 325 mesh A4047 powders without POSS trisilanol in (a) and with POSS trisilanol in (b).

POSS trisilanol addition has similar effect on the refinement of primary aluminum phase. The effect of POSS trisilanol addition in spheroidizing Si cuboids is very similar to that by the addition of Sr or Na [5-7], and in decreasing the size of primary Al phase as by the addition of Ti and B [8]. It is likely that the change of microstructure of Al-Si eutectic constituent from irregular to fibrous in A4047 is favorable to the dramatically 250% increment in ductility.

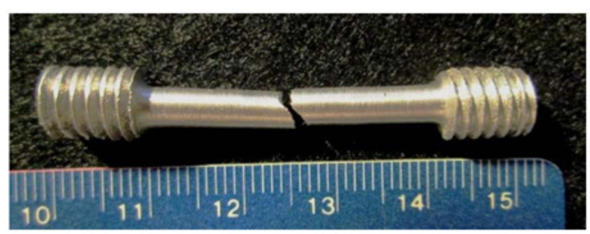
Fracture Surfaces

Si platelets shown in Figure 3(a) contribute to the brittle fracture and low ductility as the crack propagate through the interface between Si platelet and the primary Al phase. In contrast, continuous Al matrix with dispersed Si cuboids, shown in Figure 3(b), resulted in higher ductility when the crack propagated through the mixture of ductile primary Al and Si phases. Fractured samples made of 325 mesh A4047, after tensile testing, without and with POSS trisilanol were photographed are shown in Figures 4 and 5, respectively.

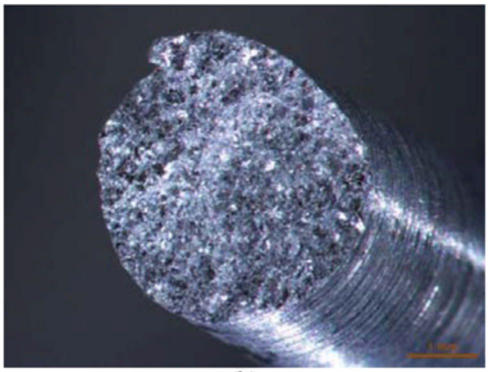
The subfigures (a) in Figures 4 and 5 are the photographs of fracture specimens after tensile testing from ingots without and with POSS trisilanol addition, respectively. Control sample (without POSS trisilanol added) has 5% elongation to failure, in Figure 4(a), shows very little deformation at the fracture. POSS trisilanol-added sample, shown in Figure 5(a), with 18% elongation to failure, clearly shows a necking phenomenon at the fracture point.

Further indications of brittle failure of sample without POSS trisilanol added are evidenced by the shining surface (due to high Si content) in the stereo photograph of figure 4(b), large cleavage in the secondary electron micrograph (Figure 4(c)), and high Si content on the facture surface, analyzed by EDS (Figure 4(d)). In comparison, failure sample with POSS trisilanol addition shows dull facture surface in Figure 5(b), denser cleavage in Figure 5(c) and higher Al, less Si contents from EDS, shown in Figure 5(d).

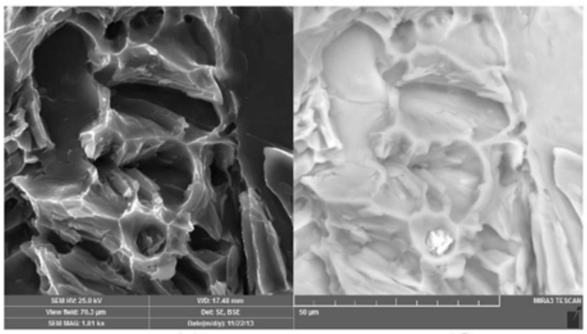
To summarize, intergranular-like cracks and cleavage-like brittle fracture are observed on the fracture surface of A4047 in Figure 4 (b). However, the cleavage-like facet becomes smaller or the larger cleavage-like facet is replaced by dimples with the addition of POSS trisilanol in Figure 5 (b), which makes the surface much more rougher and thus results in higher elongation to failure.



(a)

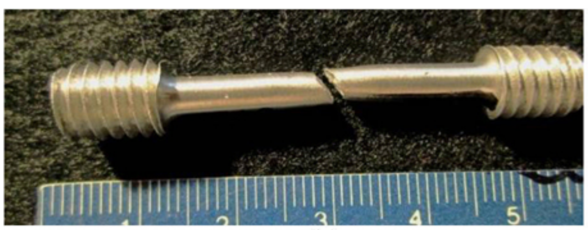


(b)

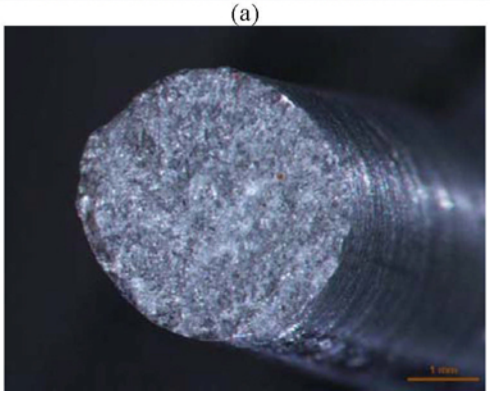


(c) (d)

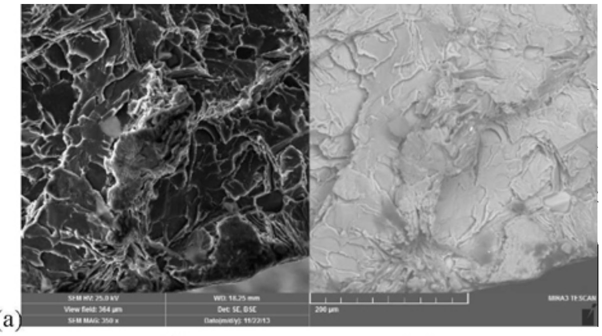
Fig. 4. Fractured sample of a tensile bar made of 325 mesh A4047 powder without POSS trisilanol. (a) Photograph of fractured sample (b) Stereo photograph of fracture surface (c) Secondary electron micrograph of fracture surface. (d) Back-scattering micrograph of fracture surface.



(a)



(a)



(b) (c)

Fig. 5. Fractured sample of a tensile bar made of 325 mesh A4047 powder with POSS trisilanol. (a) Photograph of fractured sample (b) Stereo photograph of fracture surface (c) Secondary electron micrograph of fracture surface. (d) Back-scattering micrograph of fracture surface.

Conclusions

The POSS trisilanol approach is to add large-volume of nanoscale Si-O cage compounds in a metal matrix using in-situ chemical reaction. A "two step" process developed in this study enabled the in-situ reaction of POSS trisilanol chemicals with metal ions. Trisilanol POSS-treated Al-Si based alloys exhibited the microstructure of refined primary Al phase and eutectic colonies. This modified microstructure associated with the enhanced ductility without decreasing in strength with POSS trisilanol addition.

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