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EFFECTS OF Sn CONTENT ON THE CHARACTERISTICS OF 319 ALUMINIUM ALLOY

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Abstract

Some aluminium alloys can be strengthened through ageing process and alloying. The alloying elements will stimulate the formation of precipitates that finely and uniformly distributed. This paper discusses the effect of alloying with Sn on the properties of 319 cast alloys (Al-6Si-2.8Cu), to be used for automotive parts. Observation on the microstructure of the materials was conducted by using light microscopy and SEM (scanning electron microscope) equipped with EDS (energy dispersive spectroscopy).

Research results show that minor addition of Sn up to 0.1 wt. %, increased the peak hardness of the alloys. This is due to enhanced formation of interdendritic structures. However, addition of more Sn seems to give rise to detrimental effects on mechanical properties. Alloys cast in metal mould possess better mechanical properties than those in resin-coated sand mould.

Introduction

One interesting issue in the world today is how to reduce consumption of energy in vehicles. A key factor in achieving the highest possible reduction in energy consumption in vehicles is weight reducing technologies. Studies for the automotive industry have indicated that lighter materials such as aluminium have the potential to substantially improve fuel economy and reduce gasoline consumption over the useable life of a vehicle when substituted for heavier, more traditional materials, such as steel. One foundry alloy that is popular for use in automotive application is 319 aluminium alloy, due to its excellent castability and mechanical properties. Its excellent corrosion resistance and low costs of recycling are also important considerations from an environmental point of view [1].

It is well known that alloying elements possess profound impact on the properties of 319 alloy. Addition of Cu to eutectic Al-Si alloys leads to a slight increase in the alloy fluidity, and a depression in the Si eutectic temperature of ~1.8 °C for every 1 wt% Cu added. Also, some of the mechanical properties obviously benefit from the addition of Cu as an alloying element (such as yield dan tensile strength) [2]. Copper forms an intermetallic phase with Al that precipitates during solidification either as block-like Al_2Cu or in eutectic form as $(Al+Al_2Cu)$. In 319 alloys, the copper intermetallic phase precipitates in these two forms, according to a multicomponent eutectic reaction reported by Mondolfo [3]:

$$L \rightarrow Al + Al_2Cu + \beta\text{-}Al_5FeSi + Si \text{ at } 525\ ^{o}C$$

Iron (Fe) is also one critical alloying elements for 319 alloys. During solidification, it forms several intermetallic compounds. Among these, the formation of hard brittle plates of the β-

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Al_5FeSi phase is particularly deleterious to the alloy mechanical properties [4]. This intermetallic phase also acts as nucleants for the Al_2Cu phase [5]. Magnesium (Mg) is found to considerably enhances the alloy response to artificial ageing, which is believed to be due to the formation of coarse particles of $Al_5Mg_8Si_6Cu_2$ [6].

New advancement to significantly increase the strength of aluminium alloys is through enhancement of precipitates formation within the alloys by addition of minor amount of alloying element. This has been widely studied for Al-Cu system. For example, Al-Cu alloys microalloyed with Cd, Sn and In are known to have a finer dispersion of θ' (Al_2Cu) and exhibit an increased hardening response [7-10]. Various mechanisms have been proposed to account for this effect, i.e., one-dimensional atom probe (1DAP) experiments on an Al-1.7Cu-0.01Sn (at. %) alloy have shown that θ' nucleation is preceded by clustering of Sn atoms and the precipitation of β-Sn. The fine and uniform dispersion of θ' which follows occurs such that the incoherent rim of the precipitates is associated with Sn atoms [11]. Furthermore, Kanno *et al.* [12] have observed In particles in Al-Cu-In alloys and Nie *et al.* [13] as well as Sofyan *et al.* [14-15] have recently discussed the enhanced precipitation of θ' in Al-Cu-Sn/Cd alloys in terms of cluster-assisted nucleation. However, no study has been conducted on the effects of Sn on more complex alloys, such as 319 alloys.

This research investigates the effect of Sn on the ageing response of 319 alloys and the mechanism by which the alloying elements influence formation of precipitates and hardness of the alloys during ageing. Effect of mould material is also studied. Observation on the microstructure of the materials was conducted by using SEM (scanning electron microscope) and light microscopy.

Experimental Method

Four Sn-modified alloys were cast by using commercial 319 alloy as the base material and their nominal compositions is presented in Table I. These alloys were melted in a 300 kg – industrial furnace and then cast into two different moulds, metal dan resin-coated sand moulds. Therefore, it is expected that heat transfer in both moulds is different. Gas bubble floatation process using Argon was utilized to remove trapped air from the molten metal. For comparison, two experimental alloys with similar composition were also cast, by using measured quantities of Al-Si master alloy, pure Al, pure Cu and pure Sn. Removal of trapped air in the experimental alloys was conducted by plunging Hexachloroethane (HEC) tablets.

Table 1. Nominal composition (wt. %) of alloys used in this study

Alloys	Si	Cu	Mg	Fe	Mn	Sn	Al
319 base alloy	6.0	2.8	0.15	0.44	0.14	-	remaining
319 + 0.1 % Sn	6.0	2.8	0.15	0.43	0.12	0.1	remaining
319 + 0.5 % Sn	6.0	2.8	0.15	0.38	0.10	0.5	remaining
319 + 1 % Sn	6.0	2.8	0.15	0.41	0.14	1.2	remaining
319 + 2 % Sn	6.0	2.8	0.15	0.44	0.14	2.0	remaining
Experimental alloy	4.1	2.7	0.4	0.20	0.49	-	remaining
Experimental alloy + 1 % Sn	4.0	2.4	0.06	0.24	0.49	1.2	remaining

Samples of each alloy were cut into 10 x 10 mm blocks for hardness testing and microanalysis. After solution treatment at 505 ^{o}C for 1 h and cold water quenching, ageing was conducted at 150 and 200 ^{o}C. Hardening response was monitored by hardness measurements using a 5-kg load Vickers and 31.25-kg load Brinnel. The evolution of microstructure was followed by means of a light microscope and LEO 420 SEM. Samples for microanalysis were prepared by etching with 0.5 % Hidrogen Fluoride.

Results and Discussion

As-Cast Characteristics

Figure 1 shows the effect of Sn content on the as-cast hardness of 319 alloys. It is apparent that addition of small amount of Sn, less than 0.1 wt %, increases the as-cast hardness of 319 alloys. This is similar to the effects of Sn on binary Al-Cu alloys [7]. It is thought that addition a small amount of Sn may induce strain field within the Al matrix. However, when more Sn is added, the atoms tend to form elemental Sn particles, due to immiscibility of Sn in Al. Since Sn is softer than Al, formation of elemental Sn particles decreases the hardness of the alloys.

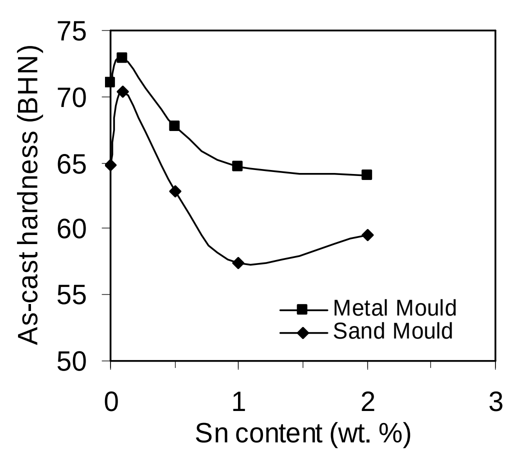


Figure 1. Effect of Sn content and mould material on as-cast hardness of 319 based alloys.

Figure 2 shows comparison of as-cast microstructure of 0.5 % and 2 % Sn added 319 alloys, both in metal and sand moulds. In general, the as-cast microstructure consists of interdendritic structure, which are thought to be Al_2Cu, Mg_2Si, $Al_5Cu_2Mg_8Si_6$ or Al-Fe-Mn-Si [16]. Cast alloys in metal moulds possess finer Al dendritic structure than that in sand mould so that leads to higher hardness of metal mould alloys, as can be seen in Figure 1. The finer structure is due to faster heat transfer in metal mould.

Age Hardening Response

Natural Ageing Age hardening curves of the alloys following ageing at room temperature are presented in Figure 3. An incubation period of about 20 – 50 hours was observed in all alloys, which then followed by an increase in hardness. The base 319 alloy shows significant decrease in hardness upon quenching. This behaviour is common in Al-Si-Cu alloys which are sensitive to quenching stress [8]. However, with minor alloying of Sn, hardness reduction during initial period in ageing diminishes. It is thought that the presence of Sn in Al matrix cause compressive lattice strain, so that tensile stress produced during quenching is nullified and no further stress relieve occurs upon subsequent ageing process. It is noted that the optimum amount of Sn addition for higher ageing response is 0.1 wt. %.

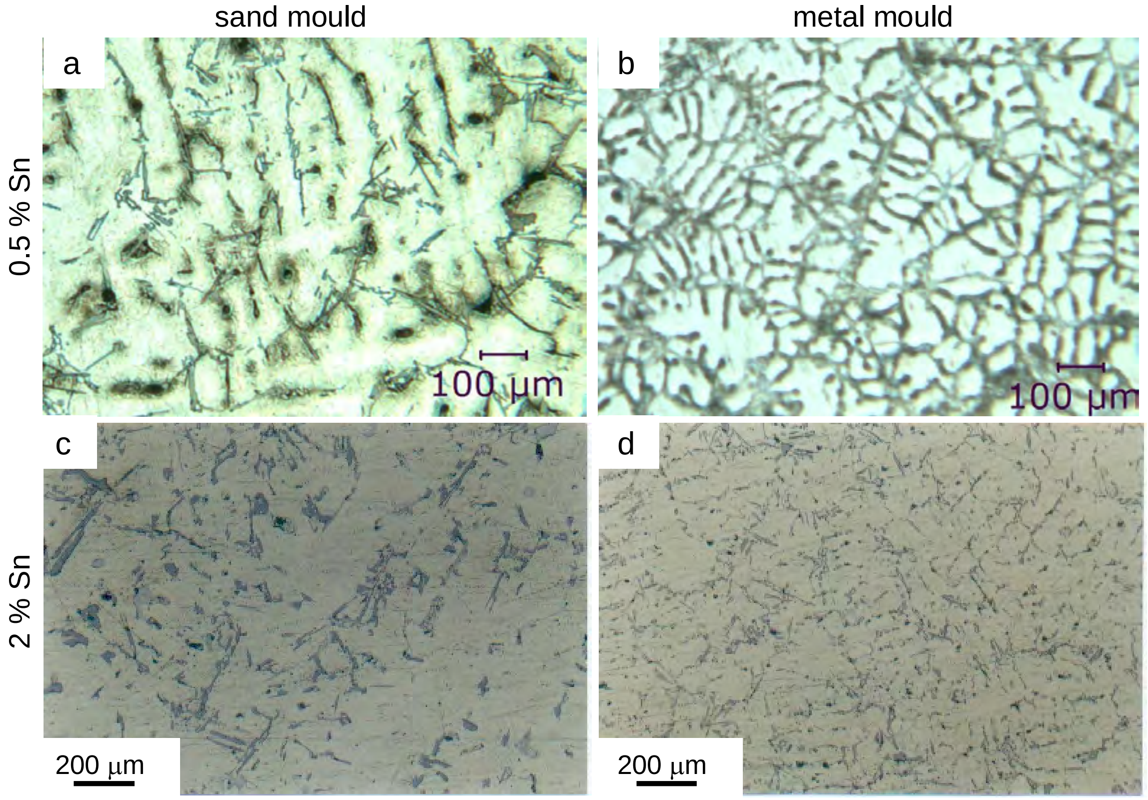
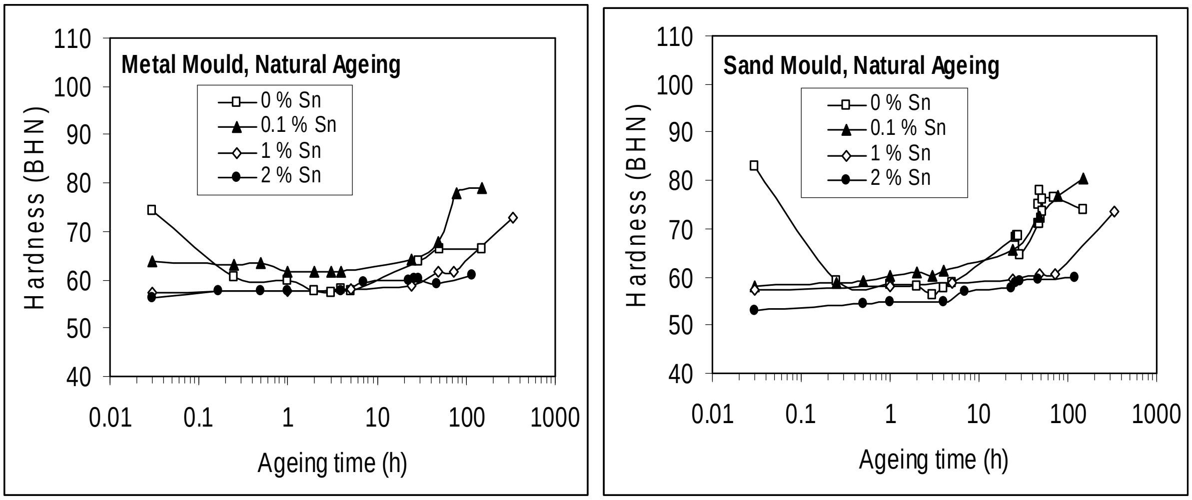


Figure 2. As-cast microstructure of 319 alloys with (a) 0.5 % Sn in sand mould, (b) 0.5 % Sn in metal mould, (c) 2 % Sn in sand mould, and (d) 2 % Sn in metal mould.



(a) (b)

Figure 3. Hardness response of 319-based alloys cast in (a) sand mould, and (b) metal mould, upon ageing at room temperature.

Artificial Ageing Figure 4 and 5 show the age hardening response of 319 based alloys aged at 150 °C and 200 °C, respectively. Again, an incubation period for ~ 1 h is detected in all alloys, which then followed by an increase to peak hardness. Addition of Sn seems to not affect the time needed to reach peak hardness. It is confirmed that 319 alloys modified with 0.1 % Sn reveals optimum hardness. Alloying 319 alloy with more than 0.1 % Sn leads to decrease in peak hardness, which is similar with the trend in as-cast hardness.

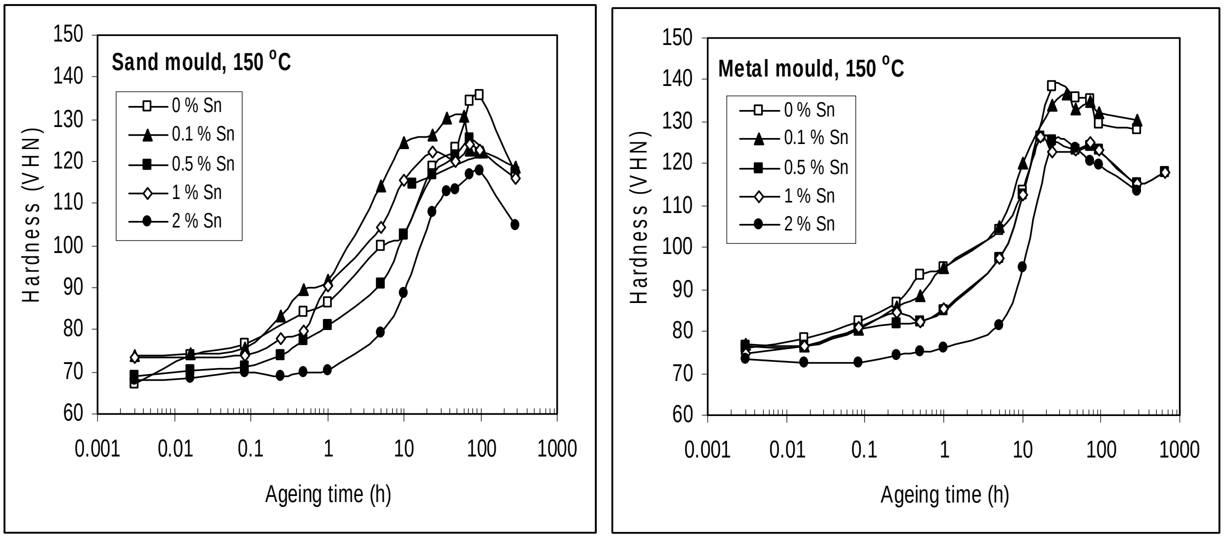


Figure 4. Hardness response of 319-based alloys cast in (a) sand mould, and (b) metal mould, upon ageing at 150 ^{o}C.

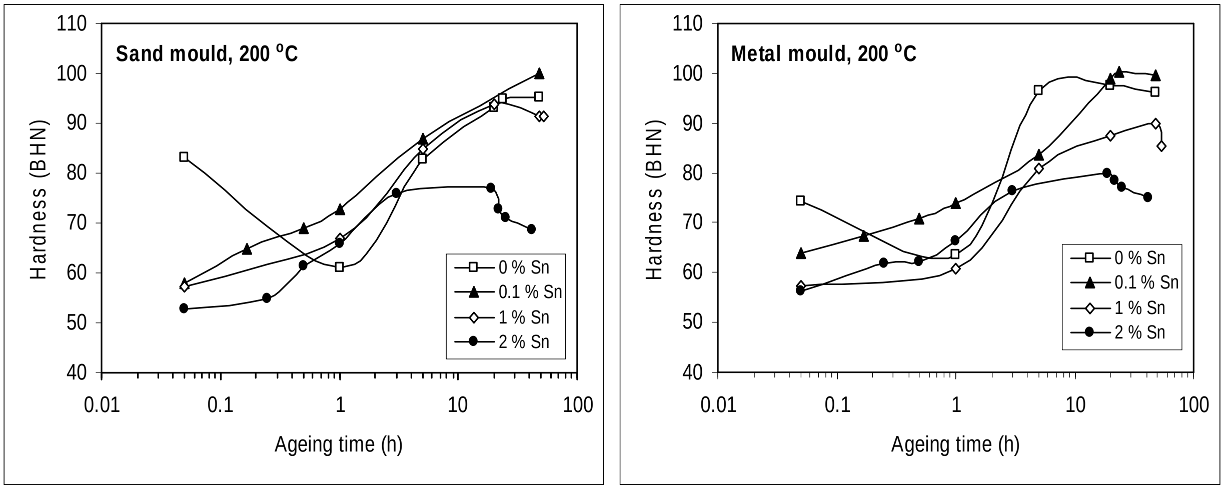


Figure 5. Hardness response of 319-based alloys cast in (a) sand mould, and (b) metal mould, upon ageing at 200 ^{o}C.

Comparison between Commercial and Experimental Alloys The main difference in processing commercial and experimental alloys is in degassing process. Commercial alloys were degassed by gas bubble floatation process while experimental alloys by plunging hexachloroethane (HEC) tablets. This results in higher volume of porosity in the experimental alloys than that in the commercial alloys. Comparison between hardening response of the two alloys is presented in Figure 6. Open and closed marks are for the experimental and commercial alloys, respectively. The as-quenched hardness of experimental alloys is lower for both the base and the 1.2 % Sn added alloys. The lower Si content in these alloys (see Table 1) seems to be the reason for this. Lower Si content leads to fewer interdendritic structures, which contributes to the hardness of the alloys. However, in general, hardening response of both alloys is very similar, either for natural or artificial ageing at 150 ^{o}C. This indicates that precipitation mechanism occurs in both alloys is similar, regardless the presence of porosity.

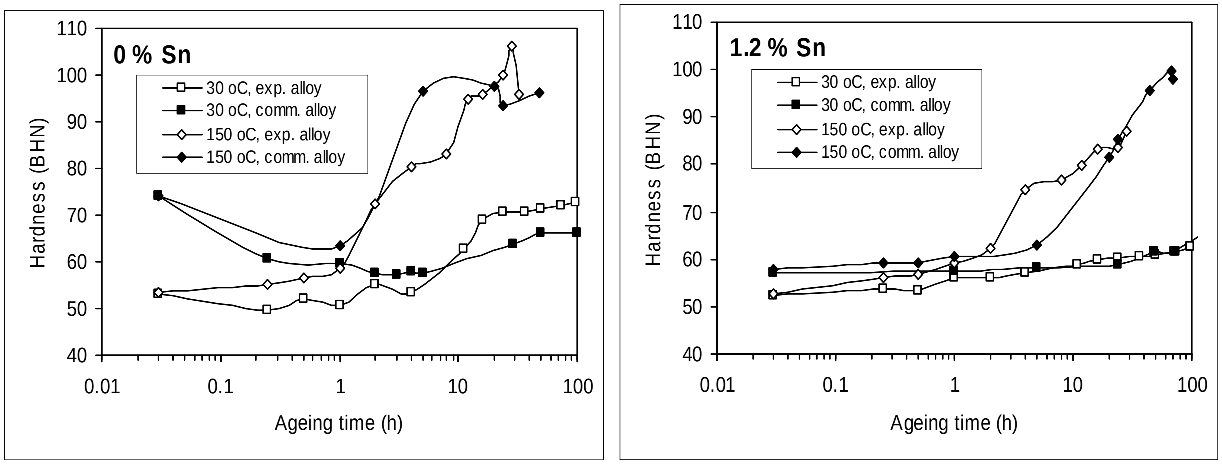


Figure 6. Comparison of hardness response between commercial and experimental 319-based alloys with composition of (a) 0 % Sn (base alloy), and (b) 1.2 % Sn.

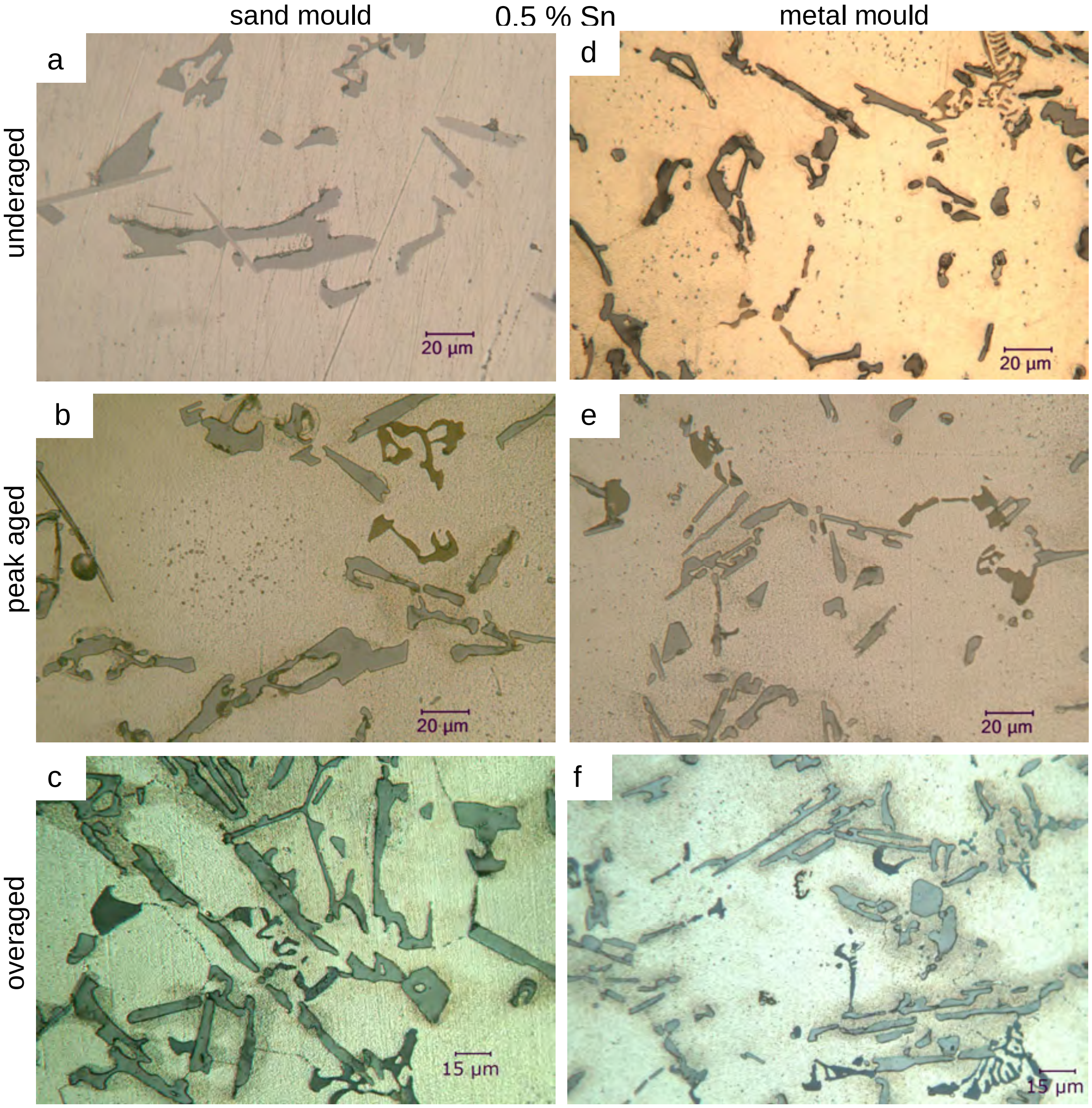


Figure 7. Evolution of microstructure of 0.5 % Sn modified 319 alloys cast in (a – c) sand mould, and (d – f) metal mould, during ageing at 200 ^{o}C.

Microstructural Analysis

As-quenched microstructures (not shown here) revealed slightly finer interdendritic structure, indicating that dissolution of the structure may occur during solution treatment. A series of microstructural evolution of 319 alloys added with 0.5 % Sn, for both sand and metal moulds, during ageing at 200 ^{o}C, is presented in Figure 7. All micrographs have the same magnification as shown by the scale bar. It is confirmed that alloys cast in metal moulds have relatively finer interdendritic structure that that of the sand mould. With further ageing, growth of interdendritic structure seems to apparent. However, fine and nanoscale precipitates were not detected here due to the limitation of light microscopy.

To retrieve the presence of Sn, microanalysis by using EDS/SEM was conducted. Figure 8 shows SEM micrograph of a 2 % modified Al-Si-Cu alloy cast in metal mould and peak-aged at 150 ^{o}C. Composition of each position in Figure 8 is presented in Table 2. White round particle (position 1) is confirmed to be Sn-rich with a small amount Si, while bright interdendritic structure (positions 3 and 4) seems to be Al-Fe-Mn-Si, similar to findings by Cayron [16]. Position 5 and other grayish structures apparently are Al-Si eutectic with a slight enrichment of Sn. The association of Sn in relation with the Al-Si eutectic structures was confirmed in several places and may indicate that Sn plays a role in the formation of these structures. As has been well known, Sn atoms have high binding energy with vacancy due to its large atomic size. The vacancy associated with Sn may facilitate formation of eutectic structures through enhanced diffusion process. More work is needed to confirm this. Microstructure of 0.1 % - added Sn alloy (not shown here) possesses the finest eutectic structure among other Sn-added alloys. However, addition of Sn more than 0.1 % seems to not lead to promotion of eutectic, because Sn tends to form elemental particles due to its miscibility in Al. These particles are soft, so that leads to detrimental effect to the properties of bulk 319 alloys. Therefore, the 0.1 % Sn-added Al-Si-Cu alloy are potential to be exploited to have higher mechanical properties for automotive application.

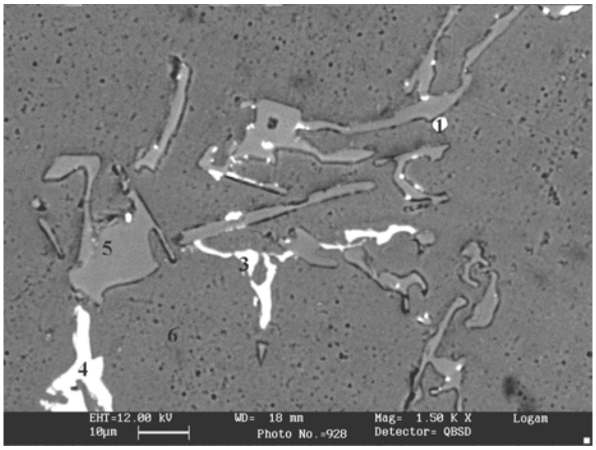


Figure 8. SEM micrograph of a 2 % - Sn added 319 alloys peak-aged at 150 ^{o}C.

Table 2. Microanalysis result on positions shown in Figure 7.

Position	Content (wt. %)						Colour	Possible phase
	Al	Si	Cu	Fe	Mn	Sn		
1	32.5	0.4	-	-	-	66.51	White	Elemental Sn
3	67.1	8.3	6.0	16.3	2.2	-	White	Al-Fe-Mn-Si
4	65.6	9.2	6.0	16.8	2.4	-	White	Al-Si eutectic
5	15.2	82.1	-	-	-	2.6	Greyish	Si-rich dendrites
6	93.2	2.5	2.9	-	-	-	Grey	Al matrix

Conclusions

1. Addition of 0.1 % Sn into 319 alloy is effective in improving properties of Al-Si-Cu alloy. This may be due to the facilitation of Al-Si eutectic formation, due to its high binding energy with vacancy, which may enhance diffusion process.
2. Addition of more than 0.1 % Sn into 319 alloys seems to lead to detrimental effects because of the tendency of Sn to form elemental particles which possess low hardness.
3. Sn-modified 319 alloys are sensitive to age hardening, so that potential to be strengthen for automotive purpose.
4. Microstructure of Sn-modified 319 alloys consists of Al dendrites with second phase particles, such as: elemental Sn, Al-Fe-Mn-Si and Al-Si eutectic. Most of the Al-Si eutectic is associated with Sn, which may indicate that Sn plays a role in the formation of the structures.
5. Alloys aged in metal moulds seem to have higher mechanical properties due to faster heat transfer which then lead to finer dendritic structures.
6. Experimental alloys were successfully cast to have similar properties with the commercial alloys, however, removal of porosity remains a major concern.

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References

1. J.E. Hatch (ed.), *Aluminium: Properties and Physical Metallurgy* (Ohio, OH: American Society for Metals, 1984), 143.
2. M.A. Moustafa, F.H. Samuel, H.W. Dotty and S. Valtierra, *Int. J. Cast Metals Res.*, 14 (2002), 235.
3. L.F. Mondolfo, *Aluminum Alloys: Structure and Properties* (London: Butterworths, 1976).
4. A. Couture, *AFS Int. Cast Metals J.*, (1981), 9.
5. P.N. Crepeau, *AFS Trans.* 103 (1995), 361.
6. P. Ouellet, F.H. Samuel, *J. Mat. Sci*., 34 (1999), 4671.
7. H.K. Hardy, *J. Inst. Met*., 80 (1951-52), 483.
8. I.J. Polmear and H.K. Hardy, *J. Inst. Met.*, 81 (1952-53), 427.
9. J. M. Silcock, T. J. Heal and H. K. Hardy, *J. Inst. Met.*, 82 (1953-54), 239
10. J.M. Silcock, T.J. Heal and H.K. Hardy, *J. Inst. Met*, 84 (1955-56), 23.
11. S.P. Ringer, K. Hono, and T. Sakurai, *Metall. Mater. Trans. A*, 26A (1995), 2207
12. M. Kanno, H. Suzuki, and O. Kanoh*J. Japan Inst. Light Metals*, 44 (10) (1980), 1139.
13. J.F. Nie, B.C. Muddle, H.I. Aaronson, S.P. Ringer, and J.P. Hirth, *Metall. Mater. Trans. A*, 33A (2002), 1649.
14. B.T. Sofyan, K. Raviprasad and S.P. Ringer, *Micron*, 32 (8) (2001), 851.
15. B.T. Sofyan, I.J. Polmear and S.P. Ringer, *Mater. Sci. Forum*, 396 – 402 (2002), 613.
16. C. Cayron, "TEM Study of Interfacial Reactions and Precipitation Mechanisms in Al_2O_3 Short Fibers or SiC Particles Reinforced Al-4Cu-1Mg-0.5Ag Squeeze-Cast Composites" (PhD. Thesis, Ecole Polytechnique Federale de Laussane, France, 2000)