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Microstructural Evolution and Intermetallic Formation in an Al Casting Alloy Due to Addition of Grain Refiner and Modifier

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Abstract: An alloy of Al-8Si-0.8 Fe was cast in a metallic die and its microstructual changes due to addition of Ti-B refiner and Sr modifier were studied. Apart from usual refinement and modification of the microstructure, some mutual influences by either of the additives took place and no mutual poisoning effects by these additives, in combined form, were observed. It was noticed that the dimensions of the iron rich intermetallics were influenced by the additives causing them become larger in dimensions. The needle shaped intermetallics which were obtained from addition of the refiners became thicker and longer on adding the modifiers. It was also found that the preferred nucleation of α-Al and eutectic silicon phases occurred on different types of intermetallic compounds. The more iron content of the intermetallic compounds the more changes in their dimensions occurred. Formation of the shrinkage porosities was also observed.

Key words: Aluminum; Casting Alloy; Morphology; Intermetallic.

INTRODUCTION

Al-Si based casting alloys are of the most widely used materials with a combination of fascinating properties such as good castability, high strength to weight ratio, low coefficient of thermal expansion, high thermal conductivity, good resistance to corrosion and wear. These advantages have led automotive industries to employ such materials for manufacturing of various parts like pistons, cylinder blocks, cylinder heads and valve lifters (ASM, 1993; Lu, 2006; Prasada, 2004). To further improve the properties and the performance of these alloys some changes are imposed on the microstructure of the material through adding grain refiners (Mohanty, 1996; Cibula, 1950; McCartney, 1989; Prasada Rao, 2006) and modifiers (Lu, 2006; Suarez-Pena, 2006) during casting processes. When the hypoeutectic Al-Si alloy is left without modification and refinement, the large platelets of the eutectic silicon phase would form with needle shaped morphologies within a coarse columnar grain structure (ASM Specialty Handbook, 1993). Addition of the refiners and the modifiers helps the alloy achieve a refined equiaxed grain structure containing fine spherical eutectic silicon particles. In recent years, many research works have been conducted on Al-Si alloys to optimize their microstructural features. Different kinds of grain refiners and modifiers have been practiced among which Ti-B and Sr compounds have been recognized to be the best grain refiners and modifiers, respectively. The effects of addition of each of the grain refiners and the modifiers separately and simultaneously on the microstructure of the Al-Si alloys have been investigated (Lu, 2006; Prasada, 2004; Li, 2002; Liao, 2003; Suarez-Pena, 2006; Liao, 2007). In some cases the combined additions of the two have been reported to end up mutual poisoning of the grain refinement and modification effects (Li, 2002; Suarez-Pena, 2006).

Iron is one of the main impurities in aluminum cast alloys which is dominantly present in the form of β-AlFeSi, (Al_5FeSi) intermetallics due to its low solid solubility in aluminum (Suarez-Pena, 2006). These intermetallics have been reported in Al-Si alloys containing 0.2 to 1.2 wt% Fe. They normally are long and needle shaped coming with large eutectic silicon platelets during solidification. The lengths of the intermetallics depend on the iron content of the alloy. They are usually hard and brittle having a low cohesion with the matrix (Narayan, 1994). There is always possibility of iron pick up during melting and casting of Al-Si based alloys.

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The main sources of iron contamination are raw materials and the dissolution of the iron tools often used for melting and casting (Sreeja Kumari, 2007). The other type of the iron rich intermetallics is Al_8Fe_2Si, so-called α-AlFeSi which usually looks smaller than the β-phase with morphology of Chinese scripts having much less deleterious effects on the mechanical properties and fracture toughness of the alloy (Gruzleski, 2000).

In this study the microstructural features of an Al-8Si-0.8Fe alloy were examined after the separately addition of the grain refiners and the modifiers. Both the grain refiners and the modifiers were also added together for the purpose of studying their mutual effects. The focus was made on the morphological changes of the iron rich intermetallics with respect to the additives. This has probably been studied only marginally in terms of Al-Si cast alloy systems.

2. Experimental Procedure:

Al-8Si alloy was initially made by the controlled melting of the aluminum ingot of 99.5% purity together with an aluminum master alloy of Al-38Si into a graphite crucible, using an electrical resistance Ni-Cr furnace. Casting then was carried out in sand molding. The nominal composition of the alloy which was such selected that a hypoeutectic aluminum alloy containing nearly 8wt% Si to be achieved, is tabulated in Table 1. Each time, a portion of 500g of the resulting hypoeutectic cast alloy was melted at 720°C into a graphite crucible in a resistance muffle furnace. The melt was then degassed with a commercial hexachloroethane degasser. Any of the grain refiner or the modifier was added into the melt in the form of chips the mixture being stirred gently for about 30 seconds by a graphite rod. The grain refiner used was M51 (Al-5Ti-1B) and the modifier was Al-10Sr master alloy. The combined addition of the refiner and the modifier were also practiced. After 5 minutes holding time, the melt was poured into a preheated metallic die of 50×50×60 mm dimensions at temperature of 220°C. Different amounts of refiner (0.8% Al-5Ti-1B), modifier (0.1% Al-10Sr) and refiner + modifier (1% Al-5Ti-1B + 0.5% Al-10Sr) were added into the melt, so four alloys were obtained the last one being the untreated Al-8Si-0.8Fe alloy. Perpetual possibility of oxidation, evaporation and fading of the additives made it difficult to fully control their exact amount to be added in the final castings. The samples were made from middle part of the cast blocks for metallography. Microstructural features were examined utilizing scanning electron microscope (SEM) model LEO 1455 VP equipped with EDX. For the optical metallography the samples were first polished and then etched using any of the following, subject to the requirement: Keller's reagent, Poulton's reagent, the 0.5% HF solution, the solution of 25 ml distilled water + 15g NaOH, and the solution made up of 25ml distilled water + 5ml HF + 25ml HNO_3 + 75ml Hcl.

Table 1: Chemical composition of the as cast alloy.

Si	Fe	Cu	Mg	Zn	Ni	Pb	Sn	P	As	Al
7.7383	0.7587	0.0112	0.0038	0.0015	0.0109	<0.0010	<0.0010	0.0030	<0.0010	91.46

RESULTS AND DISCUSSION

3.1. Effects of Grain Refiner:

Figures 1(a), 2(a) and 3(a) are optical micrographs of the untreated alloy etched with different etchants. The effects of grain refiner on the α-Al are observed in Figures 1(b), 2(b) and 3(b). It is seen that the grain size is considerably reduced and a finer grain structure is obtained. It is also revealed that the dendrites have become smaller with a more uniform distribution compared to the untreated microstructure. Fig 3(b) indicates that the large dendritic α-Al grains are changed to the fine and relatively equiaxed ones. The refinement effects can be attributed to the presence of the fine TiB_2 particles in the melt on which the heterogeneous nucleation of α-Al takes place. The higher refiner content would provide the melt with more nucleation sites during solidification (Lu, 2006) resulting in an increased number of smaller α-Al grains. Consequently, due to the presence of the grain refiner, the silicon particles which are formed between the refined and uniformly distributed α-Al dendrites would have a small size and uniform distribution.

3.2. Effects of Modifier:

Usually, the as cast microstructure of a hypoeutectic Al-Si based alloy consists of long and coarse needle/plate like eutectic silicon particles located in the regions between coarse α-Al dendrites, as shown in Figs 2(a) and 3(a). In order to improve the mechanical properties of the alloy, such a microstructure should be modified containing fine, well distributed eutectic silicon particles with spherical morphologies. Fig 1(c) illustrates that the modification of the microstructure occurred due to adding strontium as the modifier.

A further modification of the morphology of the silicon particles which were converted to fine rounded, uniformly distributed particles by Sr addition is evident in Figs 2(c) and 3(c). A comparison of Figs 2(c) and 3(c) with Figs 2(a) and 3(a) reveals that α-Al dendrites changed in both dimensions and distribution being refined and uniformly distributed. The refinement effect of Sr on α-Al dendrites are controversial as some researchers have reported that Sr acted as a refiner but others believed that the addition of strontium caused coarsening of α-Al (Liao, 2003).

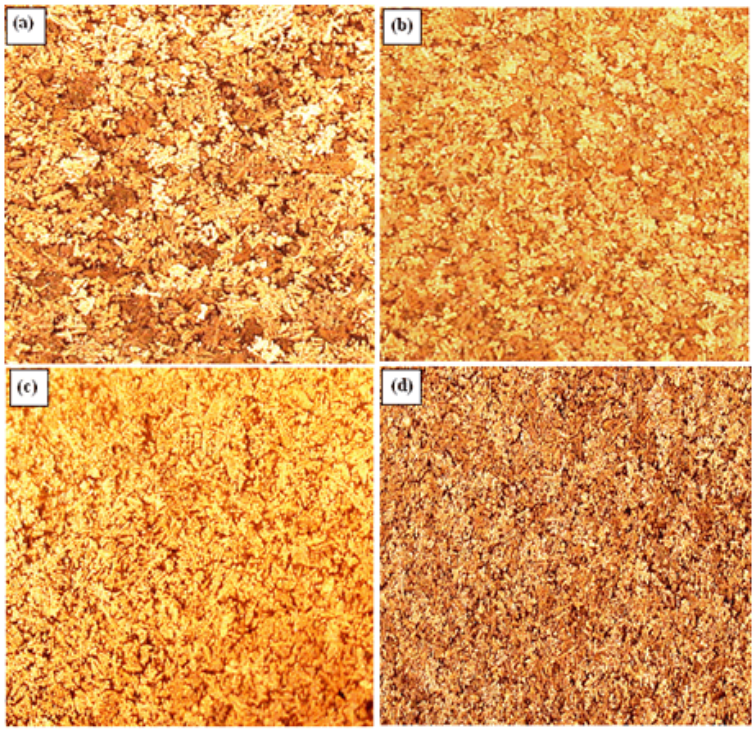


Fig. 1: Optical micrographs of (a) untreated alloy, (b) treated alloy with 0.8% refiner, (c) treated alloy with 0.1% modifier and (d) treated alloy with 1% refiner + 0.5% modifier, 10x (Poulton's regent).

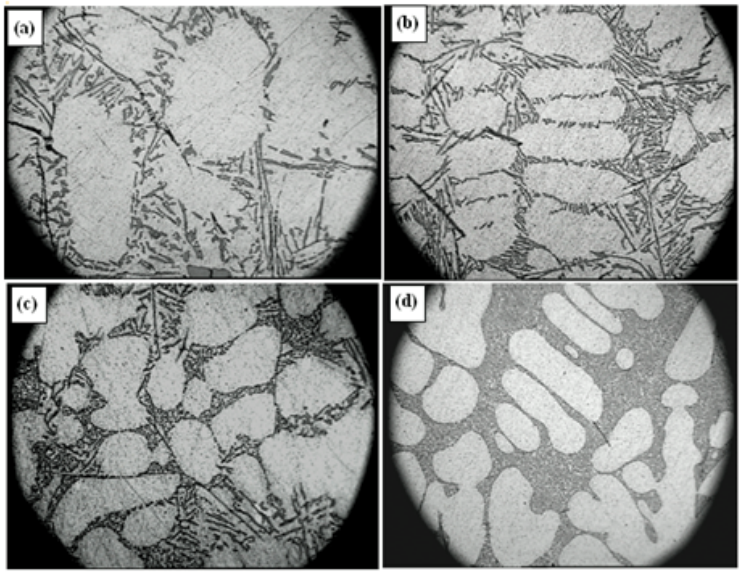


Fig. 2: Optical micrographs showing morphology changes in constituent phases of (a) untreated alloy, (b) treated alloy with 0.8% refiner, (c) treated alloy with 0.1% modifier and (d) treated alloy with 1% refiner + 0.5% modifier, 400x (Keller's reagent).

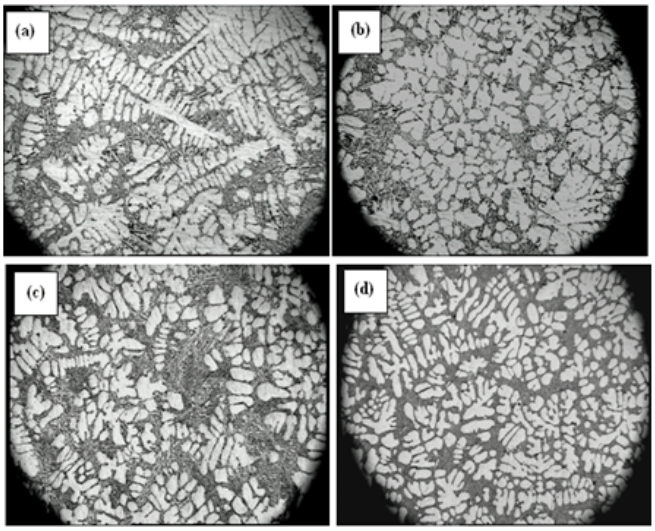


Fig. 3: Optical micrographs showing morphology changes in constituent phases of (a) untreated alloy, (b) treated alloy with 0.8% refiner, (c) treated alloy with 0.1% modifier and (d) treated alloy with 1% refiner + 0.5% modifier, 100x (0.5% HF solution).

3.3. Effects of Simultaneous Additions of Refiner and Modifier:

There are too many reports in the literatures about the simultaneous effects of grain refiner and modifier additions on the Al-Si based alloys (Prasada, 2004; Li, 2002; Liao, 2007). Some research works have reported that the addition of the refiner and the modifier at the same time had a positive effect (Lu, 2006) while others have emphasized on the mutual poisoning effect of Ti-B and Sr additions on refinement and modification of the Al-Si based alloys (Lu, 2006; Li, 2002; Suarez-Pena, 2006).

However, there is not a complete agreement on the conclusion that what the combined effects of these two additives are. The influence of simultaneous additions of the refiner and the modifier can be inferred from Figs 1(d), 2(d) and 3(d) in which the occurrence of refinement of α-Al phase, due to the presence of Ti-B, and also the modification of the eutectic silicon particles in both morphology and size distribution are revealed. In the present study, the addition of Ti-B and Sr in combined form led to both refining of α-Al and modification of the eutectic silicon particles without observation of mutual poisoning effects in the Al-8Si-0.8Fe alloy. This finding is in accordance with results of Lu and Dahle (Lu, 2006) who studied the combined effects of Sr and 5Ti-1B additions on the alloy Al-10Si-0.3Mg alloy system.

3.4. Effects of Refiner and Modifier on Iron Rich Intermetallics:

Iron, as a very harmful impurity, is the most common undesirable adding element in aluminum cast alloys. It can basically form two types of intermetallics of β-AlFeSi and α–AlFeSi (ASM., 1993). The latter was not detected in this research, possibly due to the lack of the stabilizing elements such as Mn and Cr (Wang, 2004; Murali, 1994) in the composition of the base alloy. These platelet phases, which appear as needles in the microstructure, act as stress raisers which contribute to the brittleness of the material. In addition to this effect on mechanical properties, large iron rich needles which form earlier in the solidification process tend to prevent the flow of liquid metal through the feeding channels and may cause unsoundness (Couture, 1981). The β-AlFeSi intermetallics are usually observed in the primary and the secondary forms (Suarez-Pena, 2006) the primary one being white, long and thick with a needle-shaped morphology that is formed at high temperatures. These particles are the preferred sites for nucleation of α-Al phase during solidification being known to be trapped in the colonies of the α-Al dendrites.

The secondary β-AlFeSi phase, however, is formed around the eutectic silicon particles at lower temperatures being smaller than the primary intermetallic. The two types of β-phase can be recognized by their morphologies and formation sites. Figures 4-6 are the evidences of the presence of these intermetallics in the treated alloys which are easily distinguished from the α-Al and the eutectic silicon particles. The iron rich intermetallic particles are also evident in the untreated alloy (Fig 4(a)). The effects of the refiner, on its own, on the morphology of the intermetallics are shown in Fig 4(b).

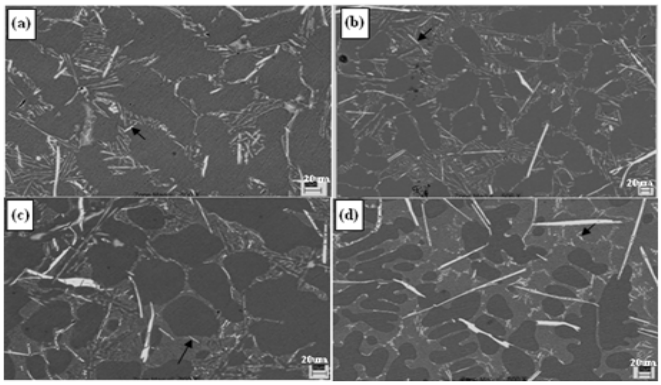


Fig. 4: Back scattered electron microscope (BSE) images of iron rich intermetallics in (a) untreated alloy, (b) treated alloy with 0.8% refiner, (c) treated alloy with 0.1% modifier and (d) treated alloy with 1% refiner + 0.5% modifier. The longer white bars are primary β-phase and the small bars pointed by arrows are secondary β-phase intermetallics.

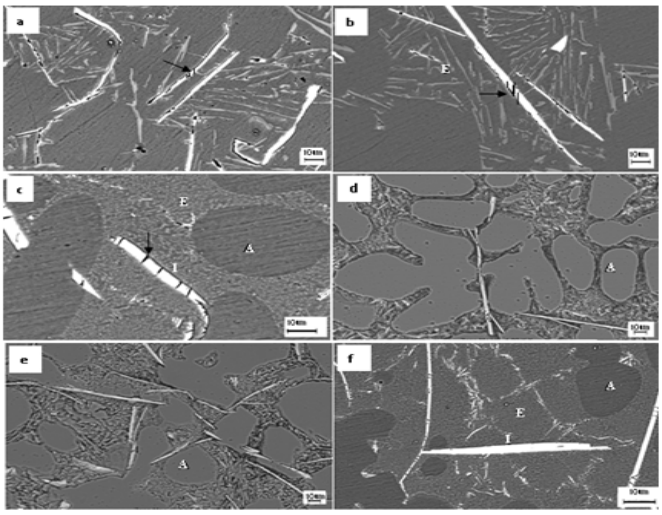


Fig. 5: Back scattered electron microscope (BSE) images showing morphologies of iron rich intermetallic phases (denoted by I), shrinkage cavities (denoted by arrow), α-Al phase (denoted by A) and eutectic silicon (denoted by E) in (a) untreated alloy, (b) treated alloy with 0.8% refiner, (c) treated alloy with 1% refiner + 0.5% modifier, (d) treated alloy with 0.1% modifier, (e) treated alloy with 1% refiner and (f) treated alloy with 0.5% modifier.

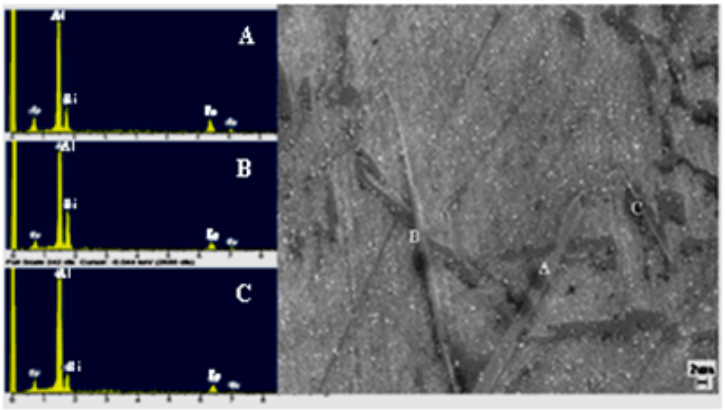


Fig. 6: EDX quantitative analysis taken from three intermetallic needle-shaped particles with different dimensions indicated in the SEM image on the right hand side as A, B and C regions and the relationship between the dimensions of each particle and its iron content tabulated in the table below.

Element content Intermetallic	Al (wt%)	Si (wt%)	Fe (wt%)
A	60.54	19.54	19.92
B	55.91	32.30	11.79
C	78.45	14.22	7.73

As seen in this figure, a moderate refinement of the intermetallics was attained and the number of the primary β-phase particles decreased. In contrast, the number of the secondary β-phase particles, which were finely dispersed, increased. The same effects have been reported by Suarez *et al*. (2006). The effect of the modifier on the morphology of the intermetallics is shown in Fig 4(c).

As indicated, unlike the effect of the refiner, the number of primary *β*-phase particles increased here without any increase in the number of the secondary phase particles. This might be firstly because adding Sr causes the saturation of the alloying elements in the melt, thereby accelerating the nucleation of primary intermetallics. Secondly, Sr reduces eutectic temperature and increases under-cooling leading to an increase in the duration of both nucleation and growth (Tenekedjiev, 1995). The third reason might be addressed to the shifting of the eutectic transformation point in the equilibrium phase diagram to the right hand side, due to addition of Sr and therefore, more time being available for nucleation and growth of the primary β-phase particles to occur (Pero-Sanz, 2000).

The morphology change in the intermetallics with simultaneous addition of the refiner and modifier can be seen in Fig 4(d). A comparison between the BSE images in Fig 4 reveals that there are a large number of thick and long primary β-phase particles in the microstructure shown in Fig 4(d) which is associated to the addition of strontium, although, the smaller secondary β-phase particles distributed among the eutectic silicon phase also exist. The obvious difference in dimensions of the primary β-phase particles in figures 4(c) and 4(d) is considered to be because of the modifier content which was increased from 0.1% in the former to 0.5% in the latter. The formation of shrinkage porosities also occurred across the long intermetallic compounds with the appearance of small cracks, as observed in Figs 5(a, b and c). Eklund (1991) reported that intermetallic compounds in the as cast aluminum alloys may frequently appear in contact with porosity. He showed that compounds of the AlFeSi and AlFeMnSi type favor the formation of shrinkage porosity by blocking the inter-dendritic feeding channels of hypoeutectic Al-Si alloys. It is therefore important to know how to avoid, or at least control, the precipitation of iron containing intermetallic compounds during alloy solidification (Eklund, 1991). Moreover, these small cracks can appreciably deteriorate mechanical properties of the alloy. Differences between the thermal volume contractions of the constituent phases and the intermetallic compounds might contribute to the formation of such cracks at higher temperatures.

As mentioned above, the large intermetallic compounds are the preferred nucleation sites of the α-Al. The α-Al phases which were nucleated and grown on the primary β-AlFeSi intermetallics, are shown for different alloys in Fig 5(d, e and f). The iron rich intermetallic compounds that are precipitated at high temperatures not only contribute to heterogeneous nucleation of α-Al at the temperature zone of liquid + solid, but also because they are rich in silicon too, once they are formed, the adjacent area would be depleted from Si and thus, facilitating the formation conditions for the α-Al phases.

On the other hand, since the secondary β-AlFeSi intermetallic compounds are formed at lower temperatures at or during eutectic transformation, they are considered to be preferred sites for the nucleation of the eutectic silicon phase. This is clearly shown in Fig 5(a, b, c and f) where the finely dispersed eutectic silicon phases are attached to the sides of the β-AlFeSi intermetallics. This is also possible that both the α-Al and the eutectic silicon phases nucleate and grow on the longer secondary β-phase particles, as observed in Fig 5(c and f).

It is believed that the dimensions of the iron rich intermetallics increase with their iron content (Sreeja Kumari, 2007). The effect of iron content on the dimensions of intermetallics was also studied. SEM study and EDX quantitative analysis were performed on three different intermetallics, in order to realize the correlation between their dimensions and the iron contents. The results are shown in Fig 6 where it is indicated that the tinier intermetallic particle has relatively lower iron content. It is to be mentioned that the morphologies of the iron rich intermetallic compounds are basically modified by the addition or presence of elements such as Mn and Cr (Murali, 1994; Couture, 1981; Tenekedjiev, 1995). Since these elements were absent in the compositions of the alloys under investigation, no change in the morphologies of the intermetallics occurred.

Conclusions:

1. Refinement and modification of the phases in Al-8Si-0.8Fe were obtained with the addition of Ti-B and Sr, respectively.
2. Some efinement of the α-Al grains by Sr addition and some moderate refinement of the eutectic silicon phase by the addition of Ti-B were also obtained when they were added separately. No poisoning effects due to simultaneous addition of these additives were observed.
3. The precipitation of the primary and secondary β-phase iron rich intermetallics with needle or platelet morphologies occurred and the shrinkage porosities were formed across the length of the larger and longer iron rich intermetallic compounds.
4. The primary β-phase intermetallics were the preferred locations for formation of α-Al, while the eutectic silicon phase nucleated on the secondary β-AlFeSi intermetallics.
5. With increasing the iron content of the intermetallic needle-shaped particles they were formed in larger dimensions.
6. The addition of refiner slightly reduced the number of primary β-AlFeSi intermetallics, whereas, the number of the tinier secondary β-AlFeSi phases increased being dispersed more uniformly.

REFERENCES

ASM Specialty Handbook, 1993. "Aluminum and Aluminum alloys", 220.

Cibula, J., Inst. Met., 1949-1950: 76-321.

Couture, A., 1981. AFS Inter. Cast Metals J., 6(4): 9-17.

Eklund, J.E., 1991. Ph.D. thesis, Helsinki University of Technology.

Gruzleski, J.E., 2000. DesPlaines (IL): AFS; 215.

Lu, L., A.K. Dahle, 2006. Mater. Sci. Eng., A 435-436: 286.

Li, J.G., B.Q. Zhang, L. Wang, W.Y. Yang, H.T. Ma, 2002. Mater. Sci. Eng., A 328: 169.

Liao, H., G. Sun, 2003. Scripta Mater., 48: 1035.

Liao, H., M. Zang, Q. Wu, H. Wang, G. Sun, 2007. Scripta Mater., 57: 1121.

Mohanty, P.S., J.E. Gruzleski, 1996. Acta Mater., 44-3749.

McCartney, D.G., 1989. Int. Mater. Rev., 34-247.

Murali, S., K.S. Raman, K.S.S. Murthy, 1994. Mater. Charact., 33-99.

Narayan, L.A., FH. J.E. Samuel, 1994. Gruzleski, Metall. Mater. Trans., A 25: 1761.

Prasada, A.K., K. Das, B.S. Murty, M. Chakraborty, 2004. Wear, 257: 48.

Prasada, A.K. Rao, K. Das, B.S. Murty, M. Chakraborty, 2006. Wear, 261: 133.

Pero-Sanz, J.A., 2000. Ciencia e Ingenieria de Materiales. 4a edicio´n. Madrid: CIE Inversiones Editoriales-Dossat; 133.

Suarez-Pena, B., J. Asensio-Lozano, 2006. Mater. Charact., 7: 218.

Suarez-Pena, B., J. Asensio-Lozano, 2006. Scripta Mater., 54: 1543.

Sreeja, S.S., Kumari, R.M. Pillai, T.P.D. Rajan, B.C. Pai, 2007. Mater. Sci. Eng., A 460-461: 561.

Tenekedjiev, N., H. Mulazimoglu, B. Closset, JE. Gruzleski, 1995. Des Plaines, IL, USA: AFS; 13.

Wang, F., Z. Zhang, Y. Ma, Y. Jin, 2004. Mater. Lett., 58-2442.