Research Article

Effect of Solidification Rate and Rare Earth Metal Addition on the Microstructural Characteristics and Porosity Formation in A356 Alloy

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The present study was performed on A356 alloy with the main aim of investigating the effects of La and Ce additions to 356 alloys (with and without 100 ppm Sr) on the microstructure and porosity formation in these alloys. Measured amounts of La, Ce, and Sr were added to the molten alloy. The results showed that, in the absence of Sr, addition of La and Ce leads to an increase in the nucleation temperature of the α -Al dendritic network with a decrease in the temperature of the eutectic Si precipitation, resulting in increasing the freezing range. Addition of 100 ppm Sr results in neutralizing these effects. The presence of La or Ce in the casting has a minor effect on eutectic Si modification, in spite of the observed depression in the eutectic temperature. It should be noted that Ce is more effective than La as an alternate modifying agent. According to the atomic radius ratio, $r_{\text{La}}/r_{\text{Si}}$ is 1.604 and $r_{\text{Ce}}/r_{\text{Si}}$ is 1.559, theoretically, which shows that Ce is relatively more effective than La. The present findings confirm that Sr is the most dominating modification agent. Interaction between rare earth (RE) metals and Sr would reduce the effectiveness of Sr. Although modification with Sr causes the formation of shrinkage porosity, it also reacts with RE-rich intermetallics, resulting in their fragmentation.

1. Introduction

The main role of rare earth (RE) metals as modifiers is to change the mode of growth of the eutectic silicon. Lanthanum is the most powerful of its kind. Microadditions of RE should be enough to modify the eutectic Si particles provided that a critical cooling rate is reached. RE-treated alloys can maintain the modified structure much longer than Na-treated alloys. A reliable and persistent eutectic modification effect can be obtained with rare earth element addition [1–4]. However, the minimum amount of rare earth elements necessary to obtain proper modification is exceptionally large. Kim and Heine [5] showed that both as-cast grain size and secondary dendrite arm spacing were decreased by adding cerium (Ce) and lanthanum (La) metals.

Aguirre-De la Torre et al. [6] investigated the mechanical properties of A356 aluminum alloy modified with La/Ce.

It was suggested that an increase in the mechanical performance of the alloy could be achieved by a homogeneous dispersion of fine particles containing La/Ce phase. The work of Nogita et al. [7] on eutectic modification of Al-Si alloys with rare earth metals reveals that the impurity induced twinning model of modification, based on atomic radius alone, is inadequate and other mechanisms are essential for the modification process. Furthermore, modification and the eutectic nucleation and growth modes are controlled independently of each other.

Kinetic nucleation of primary α -Al dendrites in Al-7% Si-Mg cast alloys with Ce and Sr additions was analyzed by Chen et al. [8]. The results show that the values of activation energy and nucleation are decreased and the nucleation frequency is increased with the addition of Ce and Sr to the alloys. The nucleation temperatures of primary α -Al dendrites are decreased with the additions of Ce and Sr.

TABLE 1: Chemical composition of the base A356 alloy.

Alloy	Elements (wt.%)					
	Si	Cu	Mg	Fe	Zn	Al
A356	7.2	<0.20	0.35	<0.20	<0.10	Bal

An elaborate review was carried out by Alkahtani et al. [9] on the modification mechanism and microstructural characteristics of eutectic Si in Al-Si casting alloys. Although all rare earth elements have some effect on the eutectic silicon as they are within the atomic radii range predicted by models to be effective in producing growth twins in an Al-Si alloy ($r/r_{\text{Si}} = 1 : 65$), however, they only result in a minor refinement of the plate-like silicon morphology.

El Sebaie et al. [10, 11] studied the effects of mischmetal (MM), cooling rate, and heat treatment on the eutectic Si particle characteristics of A319.1, A356.2, and A413.1 Al-Si casting alloys. Measurements of the eutectic Si particles revealed that addition of mischmetal led to partial modification, while full modification was achieved with the addition of Sr in the as-cast condition, at both high and low cooling rates. The interaction between Sr and mischmetal weakened the effectiveness of Sr as a Si particle-modifying agent. This effect was particularly evident at the low cooling rate.

The present study was undertaken to investigate the combined effect of solidification rate and addition of rare earth metals with or without Sr on the characteristics of the eutectic Si structure as well as on porosity formation in cast A356 alloy.

2. Experimental Procedure

Table 1 lists the chemical composition of the base A356 alloy used in the present study. The as-received ingots were melted using an electrical resistance furnace at 750°C. The molten metal was degassed using pure, dry argon, injected into the melt by means of a graphite rotary impeller (at a speed of 130 rpm). Prior to degassing, measured amounts of Sr, La, and Ce were added. The three elements were introduced into the molten alloy in the form of Al-10% Sr, Al-20% La, and Al-20% Ce master alloys. At the end of the degassing period, the molten alloy was poured into three different molds which provided different solidification rates:

- (1) A graphite mold preheated at 600°C used for carrying out thermal analysis for obtaining the solidification curve (see Figure 1(a)) [12]
- (2) A variable angle metallic mold (0°, 5°, and 15°) heated at 350°C (see Figure 1(b))
- (3) A step-like metallic mold heated at either 200°C or 400°C (see Figure 1(c))
- (4) Setup for measuring the solidification curves in the variable angle mold (see Figure 1(d))

For each pouring/casting, samplings for chemical analysis were also taken, to determine the exact composition of the melt. Chemical analyses were carried out at General Motors facilities in Warren, MI, and the results are listed in Table 2. Samples for metallography were also sectioned from all

castings. These samples were individually mounted in bakelite using a Struers LaboPress-3 machine, subjected to grinding and polishing procedures using a TegraForce-5 machine, and subsequently polished to a fine finish using 1 μm diamond suspension. The polished samples were examined using an Olympus PMG3 optical microscope-Clemex Vision PE image analysis system. The secondary dendrite arm spacing (SDAS) values were measured using the line intercept method shown in Figure 1(e). Table 3 summarizes the measured SDAS values obtained from the examined samples. Phase identification was carried out using an electron probe microanalyzer (EPMA) in conjunction with energy dispersive X-ray (EDX/EDS) analysis and wavelength dispersive spectroscopic (WDS) analysis where required, integrating a combined JEOL JXA-8900I WD/ED microanalyzer operating at 20 KV and 30 nA, where the size of the spot examined was $\sim 2 \mu\text{m}$.

3. Results and Discussion

3.1. Thermal Analysis. Solidification kinetics of an unmodified and Sr-modified near-eutectic Al-Si alloy were analyzed by Aparicio et al. [13] who found that there are changes in the solidification rate during eutectic nucleation followed by similar solidification rate evolutions during growth, suggesting that this parameter is governed principally by the heat extraction conditions. The work of Hengcheng et al. [14] on the effects of Sr and solidification rate on eutectic grain structure in an Al-13 wt.% Si alloy revealed that the characteristic temperature of eutectic nucleation (T_N), the minimum temperature prior to recalescence (T_M), and the growth temperature (T_G) during cooling as determined by quantitative thermal analysis are continuously decreased with increasing Sr content. As mentioned previously, Nogita et al. [15] reported that all rare earth elements had some effect on the eutectic silicon; however, europium was the only element to cause fully modified, fine fibrous silicon, whereas the other elements only produced a minor refinement of the plate-like silicon morphology.

Ferdian et al. [16] studied the effect of cooling rate on the eutectic modification in A356 alloy. Figure 2 shows the parameters taken from thermal analysis cooling curves for characterizing the (Al)-Si eutectic arrest which, according to the authors, comprises the minimum eutectic temperature ($T_{e,\text{min}}$), maximum eutectic temperature ($T_{e,\text{max}}$), and recalescence (ΔT_e). In case of no recalescence, $T_{e,\text{max}}$ was obtained as the temperature for which the absolute value of the cooling rate (time derivative of the cooling curve) was the highest. $\Delta T_d = T_R - T_{e,\text{max}}$ is the eutectic depression, where T_R is the equilibrium eutectic temperature calculated using (1) which was obtained by updating the equation proposed by Mondolfo [17].

$$T_R \text{ (}^\circ\text{C)} = 577 - \frac{12.5}{w_{\text{Si}}} \cdot (4.59 \cdot w_{\text{Mg}} + 1.37 \cdot w_{\text{Fe}} + 1.65 \cdot w_{\text{Cu}} + 0.35 \cdot w_{\text{Zn}} + 2.54 \cdot w_{\text{Mn}} + 3.52 \cdot w_{\text{Ni}}) \quad (1)$$

Applying this equation for the present alloy shows that T_R for A356.1 alloy is about 570.8°C.

TABLE 2

(a) Modifier additions and corresponding A356 alloy codes, graphite mold castings

Alloy	Mold type	Mold temp. (°C)	Alloy code	Modifier addition (wt.%)					
				Aimed	Actual				
				Sr	La	Ce	Sr	La	Ce
A356	Graphite	600	TB	0	0	0	0	0	0
			T10	0	0.2	0	0	0.165	0
			T1	0	0.5	0	0	0.356	0
			T2	0	1	0	0	0.685	0
			T3	0	1.5	0	0	1.025	0
			T11	0	0	0.2	0	0.002	0.082
			T4	0	0	0.5	0	0.006	0.185
			T5	0	0	1	0	0.006	0.317
			T6	0	0	1.5	0	0.009	1.088
			T7	0	0.5	0.5	0	0.442	0.282
			T8	0	1	1	0	0.781	0.377
			T9	0	1.5	1.5	0	1.073	0.531
			T10S	0.01	0.2	0	0.0079	0.165	0
			T1S	0.01	0.5	0	0.0109	0.356	0
			T2S	0.01	1	0	0.0077	0.685	0
			T3S	0.01	1.5	0	0.0077	1.025	0
			T11S	0.01	0	0.2	0.0073	0.002	0.182
			T4S	0.01	0	0.5	0.0078	0.006	0.358
			T5S	0.01	0	1	0.0081	0.006	0.817
			T6S	0.01	0	1.5	0.0081	0.009	1.288
			T7S	0.01	0.5	0.5	0.0083	0.442	0.382
			T8S	0.01	1	1	0.0083	0.781	0.877
			T9S	0.01	1.5	1.5	0.0089	1.073	1.231

(b) Actual Sr concentrations obtained for the step-like and variable angle mold castings of A356 alloy

Mold	Alloy code	Sr (ppm)*
Step-likemold	S12	83
	S22	95
	S32	84
	S42	105
	S52	108
	S14	79
	S24	73
	S34	77
	S44	88
	S54	89
Variable angle mold	DBLS	127
	D10LS	79
	D1LS	109
	D2LS	74
	D3LS	74
	D11LS	73
	D4LS	70
	D5LS	71
	D6LS	77
	D7LS	75
	D8LS	78
	D9LS	70

* Aimed amount was 100 ppm $\pm$ 20 ppm.

FIGURE 1

Figure 3(a) presents the solidification curve and its first derivative obtained from the base A356 alloy using the preheated graphite mold while Figure 3(b) shows the effect of 100 ppm Sr addition to the base alloy. It is inferred from Figure 3 that addition of Sr resulted in increasing the nucleation temperature of α -Al from about 614.4°C to 616.4°C, that is, 2°C, with a decrease in the eutectic temperature from 569.65°C to 562.23°C (approximately 7.4°C) with a total

increase in the freezing zone by about 9.5°C. Modification with Sr also resulted in the merging of peaks (3) and (4) observed in Figure 3(a). The studies carried out by Samuel et al. [18, 19] revealed that Sr addition causes fragmentation of the π -iron phase during the course of solidification which explains the disappearance of peak (2) seen in Figure 3(b). Due to the directional solidification nature of castings made using the variable angle mold (Figure 3(c)), it is difficult

FIGURE 2: Solidification parameters of 356 alloy [16].

(a) Temperature-time curve and first derivative of the A356 base alloy showing (1) precipitation of α -Al dendrite network, (2) Al-Si eutectic reaction, (3) transformation of β -Fe to π -Fe phase, (4) precipitation of Mg_2Si , and (5) end of solidification [31]

(b) Temperature-time curve and its first derivative obtained from the A356 alloy modified with about 100 ppm Sr

(c) Temperature-time curves obtained from the variable angle mold at different angles

FIGURE 3

TABLE 3: Average secondary dendrite arm spacing of the examined A356 alloy samples.

Mold	Mold temp. (°C)	Mold section	SDAS* (μm)	
			Average	SD
Graphite	600	Center	68.63	5.49
	200	Large	31.56	2.92
	200	Small	16.17	1.89
Step-like	400	Large	41.66	3.02
	400	Small	22.46	3.96
Variable angle	325	Large	53.62	5.7
	325	Small	25.04	3.0

*Secondary dendrite arm spacing obtained over 20 measurements per sample. SD: standard deviation.

FIGURE 4: Backscattered electron images of A356 alloy in the as-cast condition: (a) nonmodified and (b) modified with 100 ppm Sr, showing π -phase and β -phase particles.

FIGURE 5

FIGURE 6: Variation in the eutectic Si morphology as a function of melt treatment: (a) no addition, (b) addition of 3% RE (alloy #11 in Figure 4(a)), (c) modification with 100 ppm Sr, and (d) addition of 2% RE to Sr-modified alloy (alloy #10 in Figure 4(b)).

(a) Effect of La addition on the depression in the eutectic temperature in non-Sr-modified A356 alloys (b) Effect of La addition on the depression in the eutectic temperature in non-Sr-modified A356 alloys

FIGURE 7

FIGURE 8: Eutectic Si morphology revealed in deep etched samples of (a) base alloy without Sr and (b) base alloy + Sr.

to identify the sequence of reactions taking place during solidification. Thus, in this case, the values of SDAS are based on the polished samples. Figure 4 illustrates the effect of the Sr modification on the microstructure of the A356 alloy.

Figure 5(a) illustrates the changes in the characteristics of the temperature-time curves as a function of the added amount of La and Ce. In Figure 5(a), addition of 1% La resulted in increasing the freezing zone from 44.8°C (Figure 3(a)) to 56.8°C, with a further increase to 61°C and 623°C with the use of 1.5% La + 1.5% Ce (see Table 2(a) for actual concentrations). This behavior depends on the added element, that is, La or Ce. The reported increase in the freezing zone is brought about by the increase in the nucleation temperature of α -Al coupled with the depression in the eutectic temperature. The increase in the freezing zone is expected to result in poor feedability of the alloy and hence more porosity [20, 21]. It should be noted that La is more effective than Ce in increasing the freezing zone. It should be emphasized here that the addition of the RE elements changes the nucleation process of the molten alloy and, hence, the undercooling of the melt will be influenced. Modifying the alloys with about 100 ppm Sr resulted in neutralizing the effect of RE on the change in both α -Al and eutectic precipitation temperatures, as shown in Figure 5(b), which is very close to that presented in Figure 3(b). In this case, the solidification temperature range is about 53°C. Reis et al. [20] presented a model for prediction of shrinkage defects in long and short freezing range materials. Their results showed that internal and external shrinkage defects depend on the freezing range of the metal. A short freezing range results mainly in internal shrinkage whereas the long freezing range shows more external shrinkage. Figure 6 presents the microstructure of the eutectic Si when the alloy was subjected to different melt treatments. It is evident from Figure 6(b) that addition of 3% RE to the base alloy has no significant modification effect in spite of the observed decrease in the eutectic temperature. Thus, in this case, the observed depression in the eutectic temperature should not be used as an indicator of modification [11]. When the base alloy is treated with 100 ppm Sr (Figure 6(c)), the microstructure is

fully modified. Due to RE-Sr interaction, the Si particles tend to lose their fibrous morphology; that is, they are partially modified (Figure 6(d)). These observations will be discussed in more detail in the next section.

The depression of the eutectic temperature is the feature that is used most often in thermal analysis as an indicator of modification [22]. As eutectic temperature is easy to measure, it is generally employed to assess whether or not a melt is properly modified. However, if temperature alone is used as the criterion for proper modification, it is difficult to detect overmodified structures, because the greatest change of temperature occurs in the unmodified-to-modified transition [23]. Figure 7(a) exhibits the depression in the eutectic temperature with the addition of La in the absence of Sr. In this case, addition of 1.5% La resulted in decreasing the eutectic temperature by about 8°C. Modification of the same alloys with 100 ppm Sr neutralized this effect, as seen from Figure 7(b). Thus, the depression in the eutectic temperature is mainly due to Sr modification (6°C) with undercooling of about 2°C. It should be mentioned here that the addition of 0.2% RE has no noticeable effect on the eutectic temperature.

3.2. Eutectic Si Particle Characteristics

3.2.1. Variable Angle Mold. Figure 8(a) shows the morphology of the eutectic Si in deep etched samples of A356 alloy. In the case of the nonmodified alloy sample, the Si appears in the form of platelets with sharp edges (arrow). Addition of 80 ppm Sr (Figure 8(b)) resulted in changing the Si morphology into an interconnected “branched tree” type, with the particles exhibiting necking (arrow). Table 4 lists the eutectic Si particle characteristics measured from the variable angle mold at two tilting angles, that is, 0 and 15 degrees. At zero tilting angle (SDAS $\sim 25 \mu\text{m}$), the Si particles were refined due to the high solidification rate, as documented in Table 4(a). It is evident that the addition of RE up to 3% has no significant refining effect. Also, the standard deviation is noticeably large, indicating a marked variation in the Si particle size. Increasing the mold tilting angle to 15 degrees, thereby reducing the solidification rate (SDAS $\sim 52 \mu\text{m}$), the

FIGURE 9: Examples of the eutectic Si particle size and distribution after different melt treatments/additions in A356 alloy samples obtained from the variable angle mold (large) castings.

TABLE 4

(a) Eutectic Si particle characteristics observed in variable angle mold (small*) samples of A356 alloys containing La and Ce additions

Alloy code	RE content		Silicon particle characteristics					
	Actual		Area (μm^2)		Length (μm)		Aspect ratio	Density (number/mm ²)
	La (wt.%)	Ce (wt.%)	Average	SD	Average	SD		
DBS	0	0	5.990	7.032	5.957	7.421	2.671	8240
D10S	0.165	0	8.805	10.020	8.536	10.30	2.468	6037
D1S	0.356	0	6.492	6.958	6.459	11.70	2.282	8174
D2S	0.685	0	7.08	8.56	5.409	6.78	2.288	4201
D3S	1.025	0	3.211	5.164	3.101	5.82	2.221	10149
D11S	0.032	0.082	7.154	7.915	6.870	9.75	2.553	6307
D4S	0.136	0.185	6.413	7.472	6.307	8.53	2.533	7330
D5S	0.046	0.317	5.683	6.376	4.967	6.37	2.451	7902
D6S	0.089	1.088	8.105	9.673	6.094	9.01	2.367	6795
D7S	0.44	0.282	5.058	5.868	6.820	10.80	2.219	8331
D8S	0.781	0.877	5.917	6.754	7.555	9.96	2.355	6253
D9S	1.073	0.831	4.426	4.914	5.254	7.60	2.124	16277

Note. Mold temperature: 325°C; *small: angle of variable angle mold is 0°.

(b) Eutectic Si particle characteristics observed in variable angle mold (large*) samples of A356 alloys containing La and Ce additions

Alloy code	RE addition		Silicon particle characteristics					
	Actual		Area (μm^2)		Length (μm)		Aspect ratio	Density (number/mm ²)
	La (wt.%)	Ce (wt.%)	Average	SD	Average	SD		
DBL	0	0	21.45	29.53	9.467	9.397	2.586	35521
D10L	0.165	0	28.48	36.16	19.38	10.230	2.275	2349
D1L	0.356	0	18.24	28.87	11.42	9.498	2.237	5521
D2L	0.685	0	24.43	37.46	15.3	10.95	2.287	3754
D3L	1.025	0	19.59	13.96	9.374	5.804	2.195	9446
D11L	0.032	0.082	16.37	23.23	12.42	8.741	2.600	7352
D4L	0.136	0.185	16.19	25.41	10.23	8.960	2.499	5924
D5L	0.046	0.317	16.09	28.03	8.752	9.570	2.367	5668
D6L	0.089	1.088	18.66	31.05	9.310	10.410	2.305	5236
D7L	0.44	0.282	11.93	18.95	12.01	7.605	2.343	7515
D8L	0.781	0.877	15.95	24.51	13.200	8.162	2.332	4122
D9L	1.073	0.831	8.20	12.82	5.880	5.416	2.185	12862

Note. Mold temperature: 325°C; *large: angle of variable angle mold is 15°.

(c) Characteristics of eutectic Si particles in variable angle mold (large*) samples of Sr-modified A356 alloys containing La and Ce additions

Alloy code	Addition			Silicon particle characteristics					
	Sr (ppm)	Actual		Area (μm^2)		Length (μm)		Aspect ratio	Density (number/mm ²)
		La (wt.%)	Ce (wt.%)	Average	SD	Average	SD		
DBLS	127	0	0	1.765	3.906	2.161	2.431	2.061	64199
D10LS	69	0.165	0	2.138	3.930	2.345	2.378	1.952	58454
D1LS	109	0.356	0	2.385	5.157	2.494	2.958	1.974	42526
D2LS	74	0.685	0	4.240	2.470	2.625	8.348	2.370	5374
D3LS	74	1.025	0	5.775	2.633	3.815	4.688	2.262	18163
D11LS	73	0.033	0.082	3.549	6.440	3.207	3.862	2.114	38504
D4LS	70	0.136	0.185	1.876	3.542	2.165	2.053	1.937	55283
D5LS	71	0.046	0.317	2.524	4.593	2.565	2.854	1.906	49097
D6LS	77	0.089	1.088	1.885	4.197	2.155	2.435	1.927	61875
D7LS	75	0.44	0.282	3.119	5.461	2.931	3.235	1.927	36082
D8LS	78	0.781	0.877	7.421	12.000	4.937	5.439	2.184	17488
D9LS	72	1.073	0.831	4.622	7.183	3.840	4.001	2.151	26061

Note. Mold temperature: 325°C; *large: angle of variable angle mold is 15°.

FIGURE 10: Distribution of Sr in the modified A356 alloy.

addition of RE exhibited a tendency for Si modification as may be seen from Table 4(b). As in the previous case (zero tilting angle), the standard deviation is also high in this case. It should be noted that Ce is relatively more effective than La as an alternate modification agent. Figures 9(a)–9(f) show examples of the eutectic Si morphology in A356 alloy samples treated with different amounts of RE, without (a, c, d) and with (b, e, f) Sr addition. It should be mentioned here that, according to the atomic radius ratio, r_{La}/r_{Si} is 1.604 and r_{Ce}/r_{Si} is 1.559, which theoretically confirms the abovementioned observation [23].

Based on the data presented in Tables 4(a) and 4(b), the observed depression in the eutectic temperature is not necessarily related to modification of the eutectic Si particles. In confirmation of this conclusion, Table 4(c) lists the variation in the eutectic Si particles when the alloys were treated with 100 ppm Sr. It is obvious that Sr is the most effective agent for modification compared to the other RE elements analyzed in the present study from both size and distribution

aspects, as represented by the standard deviation. Figure 10 shows the distribution of Sr within the eutectic Si particles in the DBLS alloy. Figures 11 and 12 reveal the distribution of La, Ce, and Sr in RE-rich platelets, which explains the partial modification of the surrounding Si particles as less Sr is available for modification of the eutectic Si. It may be noted from Figures 9 and 10 that the affinity of La to react with Sr is relatively higher than that of Ce.

3.2.2. Step-Like Mold. Since the modification effect of La is similar to that provided by Ce, only La will be considered in this section. Table 5(a) lists the characteristics of the eutectic Si particles as a function of solidification rate and the level of La addition. Apparently, the solidification rate is the main factor affecting modification compared to the added La content. With the increase in the SDAS from $16\text{ }\mu\text{m}$ to $41\text{ }\mu\text{m}$, the average Si particle area increases from $3.7\text{ }\mu\text{m}^2$ to $14\text{ }\mu\text{m}^2$ with an increase in the La concentration to about 0.7 wt.%. It should also be noted that the corresponding standard

TABLE 5

(a) Silicon particle characteristics of La-containing A356 alloy samples obtained from step-like mold castings

Alloy code	Mold temp. (°C)	Mold section	RE addition		Silicon particle characteristics				
			Actual	Area (μm^2)		Length (μm)		Aspect ratio	Density (number/mm ²)
			La (wt.%)	Average	SD	Average	SD		
12S	200	Small (SDAS: 16 μm)	0	3.663	5.680	3.444	3.567	2.272	13495
22S			0.165	1.685	3.740	2.132	2.376	2.044	27050
32S			0.356	1.364	3.825	1.898	2.229	2.029	38893
42S			0.685	1.464	3.665	1.952	2.119	2.022	33243
52S			1.025	1.506	4.175	1.879	2.306	1.978	35101
12L	200	Large (SDAS: 31 μm)	0	7.876	12.290	5.591	5.970	2.548	6471
22L			0.165	6.763	11.410	4.743	5.394	2.230	7416
32L			0.356	5.334	7.426	4.475	3.772	2.107	11179
42L			0.685	5.194	10.910	4.318	4.639	2.162	6644
52L			1.025	2.727	6.007	2.678	2.962	2.129	11145
14S	400	Small (SDAS: 22 μm)	0	5.245	7.768	4.360	4.452	2.393	9361
24S			0.165	3.371	4.856	3.148	2.908	2.147	13055
34S			0.356	5.152	8.234	4.119	4.040	2.129	10819
44S			0.685	4.517	7.080	3.671	3.844	2.092	13439
54S			1.025	2.680	5.351	2.648	3.153	2.034	25475
14L	400	Large (SDAS: 41 μm)	0	15.800	24.850	8.113	9.591	2.565	3457
24L			0.165	13.830	21.330	7.083	8.016	2.463	4007
34L			0.356	15.160	24.430	7.668	9.044	2.385	3555
44L			0.685	14.240	23.500	7.072	8.191	2.411	3788
54L			1.025	9.514	16.030	5.746	6.027	2.363	5904

Note. Small: sample sectioned from step of 5 mm height. Large: sample sectioned from step of 20 mm height. SD: standard deviation.

(b) Silicon particle characteristics of La-containing Sr-modified A356 alloy samples obtained from step-like mold castings

Alloy code	Mold temp. (°C)	Mold section	Composition		Silicon particle characteristics				
			Actual	Area (μm^2)		Length (μm)		Aspect ratio	Density (number/mm ²)
			Sr (ppm) La (wt.%)	Average	SD	Average	SD		
S12S	200	Small	83.3 0	0.875	3.592	1.268	1.212	1.84	85236
S22S			95.0 0.165	0.860	4.796	1.235	1.964	1.92	57253
S32S			84.1 0.356	0.669	3.963	1.108	1.330	1.81	90306
S42S			105.8 0.685	0.689	3.756	1.205	1.473	1.84	79410
S52S			108.3 1.025	0.853	4.438	1.246	1.685	1.85	74495
S12L	200	Large	83.3 0	1.653	3.738	1.948	1.661	1.89	48426
S22L			95.0 0.165	1.606	4.175	1.897	1.976	1.96	33046
S32L			84.1 0.356	1.401	3.898	1.763	1.820	1.95	39323
S42L			105.8 0.685	1.364	4.134	1.766	2.043	1.95	46551
S52L			108.3 1.025	1.406	4.180	1.853	2.229	2.02	37318
S14S	400	Small	79.1 0	0.996	3.526	1.548	1.465	1.83	74841
S24S			73.1 0.165	1.020	3.681	1.389	1.431	1.81	65911
S34S			77.0 0.356	0.899	3.619	1.409	1.485	1.88	75695
S44S			88.0 0.685	0.768	3.504	1.288	1.282	1.90	58987
S54S			89.5 1.025	1.042	5.243	1.539	2.948	1.91	65816
S14L	400	Large	79.1 0	2.532	5.228	2.640	2.254	1.90	32512
S24L			73.1 0.165	2.262	5.044	2.245	2.223	1.91	34871
S34L			77.0 0.356	1.679	3.691	2.003	1.896	1.96	43197
S44L			88.0 0.685	2.121	5.302	2.287	2.652	1.99	35591
S54L			89.5 1.025	2.471	3.718	2.600	1.748	2.06	30309

Note. Small: sample sectioned from step of 5 mm height. Large: sample sectioned from step of 20 mm height. SD: standard deviation.

FIGURE 11: (a) Elemental distribution of Si, La, Sr, and P corresponding to a backscattered electron image showing La-rich platelet and surrounding Si particles in 100 ppm Sr-modified A356 alloy containing 1.025% wt.% La; (b) EDS spectrum of the La-rich platelet. Note the presence of P at the center of the Sr (circled areas).

deviation increased from ± 5.7 to ± 23.5 , indicating a wide range of Si particle sizes and distributions. At ~ 1 wt.% La level, a tendency for modification is observed, as demonstrated by Figures 13(a) and 13(c). The variations in the Si particle characteristics in the same series of alloys with the addition of ~ 100 ppm Sr are shown in Table 5(b). The average Si particle

area is about $1.5 \mu\text{m}^2 \pm 3.6$ regardless of the solidification rate and La concentration as displayed in Figures 13(b) and 13(d).

3.3. Porosity. Liao et al. [24] studied the effect of Sr addition on porosity formation in directionally solidified A356 alloy. Their results showed that the growth rate of pores decreases

FIGURE 12: (a) Backscattered electron image showing Ce-rich platelets in Sr-modified A356 alloy containing 1.025% wt.% Ce and elemental distribution of (b) Ce, (c) Sr, and (d) EDS spectrum corresponding to (a).

with the reduction in local liquid temperature, while it fluctuates violently during directional solidification. Addition of Sr weakens this fluctuation and decreases the average growth rate of pores. Addition of Sr has a considerable influence on the size distribution of pores.

The modification of Al-Si casting alloys was analyzed by Sigworth [25]. Modification may change the relative formation of porosity and shrinkage in a casting. The modifiers strontium and sodium are poisoned by phosphorus, antimony, and bismuth. Consequently, the levels of these impurities should be monitored carefully in secondary alloys.

The effect of Sr content on porosity formation in a directionally solidified Al-12.3 wt.% Si alloy was investigated by Hengcheng et al. [26] who suggested that Sr solute in liquid Al-Si alloys can diffuse into oxide inclusions to form loose oxide aggregations which are more active nucleation sites for

porosity. Stunov [27] concluded that, in Al-Si-Mg alloys, Sr has a negative effect on the level of gas porosity and on the distribution of shrinkage porosity.

The effect of the metallurgical parameters on porosity formation examined in the present study was limited to the variable angle mold and the step-like mold. Figure 14 shows the general distribution of porosity in Sr-free degassed A356 alloy castings obtained from the variable angle mold heated at 350°C, using different angles. As can be seen, the high solidification rate associated with the thin plates of the zero-degree angle castings may lead to the formation of hot spots within the casting as denoted by the black circled areas.

Figures 15(a) and 15(b) show two examples of the porosity observed in samples of Sr-modified A356 alloys containing La obtained from the 15° variable angle mold. These pores are associated with thick oxide films (white arrows), as inferred

FIGURE 13: Examples of the eutectic Si particles observed in A356 alloy following addition of Sr, La, or Sr + La in samples obtained from the small section (200°C) of the step-like mold casting.

FIGURE 14: Porosity distribution in degassed A356 alloy castings obtained from the variable angle mold heated at 350°C.

from the X-ray images of oxygen and strontium distribution corresponding to Figure 15(b), as shown in Figures 15(c) and 15(d). It should be kept in mind that these X-ray images were taken from deep pores. Thus, the distribution may have been affected by the pore morphology. Another important observation noted from Figure 15 is that the fragmentation of the La-rich platelets appears to occur in a similar manner to that reported for the fragmentation of β -Al₅FeSi platelets [28].

Porosity measurements were carried out on nonmodified and Sr-modified La-containing A356 alloys as a function of La content, using samples obtained from the step-like mold castings. The obtained data is documented in Figure 16. Since the molten metal was properly degassed (humidity in the vicinity of the melt was about 13%), the amount of dissolved hydrogen in the molten alloy would be at its threshold value. Thus, porosity in this case would be caused mainly by

FIGURE 15: (a, b) Backscattered electron images showing porosity in Sr-modified A356 alloy samples containing (a) 0.8% La and (b) 1.025% La; note the presence of thick oxide films (white arrows) (sample SDAS $\sim 42 \mu\text{m}$). (c, d) X-ray images showing the distribution of (c) oxygen and (d) strontium in (b).

shrinkage due to volumetric change during solidification. Liu et al. [29] reported that Sr oxide is one of the main sources of porosity due to the high affinity of Sr to react with oxygen. As was observed from Figure 5, the addition of RE resulted in an increase in the freezing range so that poor feedability of the molten metal would be expected.

Figure 16(a) presents the variation in percentage porosity as a function of solidification rate and the levels of La and Sr present in the alloy, where “Small” and “Large” correspond to samples obtained from the small and large steps of the step-like mold casting (see Figure 1(c)), and the suffixes 200 and 400 indicate the two temperatures of the mold during casting. In the absence of Sr, the total percentage porosity is less than 0.2% which decreases to 0.1% with the increase in the amount of La to 1.025 wt.%.

With 100 ppm Sr addition, a noticeable increase in the percentage porosity is observed, especially at low solidification rate (Figure 16(a)). It should be noted also that increasing the La content has no specific effect on percentage porosity. Figure 16(b) illustrates the increase in pore density (measured by number of pores/mm²) emphasizing the strong role of modification with Sr coupled with low solidification rate in the intensity of porosity in the final casting [30].

Figure 17 shows an example of the shape and size of the type of porosity observed in a 1.025 wt.% La-containing A356

alloy sample obtained from the large section of the step-like mold (mold heated at 400°C). The La-based intermetallic phase is seen to precipitate in the form of platelets, surrounded by partially modified eutectic Si. The EDS spectrum corresponding to the La-containing platelet is shown in Figure 17(b) indicating that it is composed of Al and La. The WDS analysis revealed that the composition of these platelets is Al₃La (77.4 at.% Al, 22.6 at.% La). Figure 18 shows the fragmentation of a La-rich platelet under the same casting conditions.

4. Conclusions

Based on an analysis of the results obtained in this study, the following conclusions may be drawn:

- (1) Addition of La and Ce rare earth (RE) metals leads to an increase in the α -Al precipitation temperature, lowering at the same time the Al-Si eutectic temperature, resulting in long freezing temperature ranges and hence poor feedability.
- (2) The changes in both α -Al and Si eutectic temperatures are independent of the undercooling.
- (3) Addition of Sr to RE-treated alloys eliminates their effect on the microstructure during solidification.

(a) Variation in surface area percentage porosity as a function of La content and casting/solidification condition of the A356 alloy samples (legend at the top center indicates the La level of the samples)

(b) Variation in pore density as a function of La content and casting/solidification condition of the A356 alloy samples (legend at the top center indicates the La level of the samples)

FIGURE 16

- (4) Rare earth metals have a minor effect on the refinement of the eutectic silicon particles whereas Sr is the dominating modifying agent.
- (5) According to the atomic radius ratio, $r_{\text{La}}/r_{\text{Si}}$ is 1.604 and $r_{\text{Ce}}/r_{\text{Si}}$ is 1.559, theoretically, which shows Ce to be a more effective modifier than La.
- (6) Strontium has a strong affinity for reacting with rare earth metals, which results in reducing its effectiveness as a eutectic Si modifier.
- (7) The presence of traces of P observed in the A356 alloy samples leads to a reaction between P and Sr in the Sr-modified alloys, forming a complex compound which acts as a nucleation site for the precipitation of RE-rich phases.
- (8) Porosity occurs mainly due to shrinkage and oxide films. In the absence of Sr, addition of rare earth metals, especially at high concentration, reduces the percentage of shrinkage porosity.

FIGURE 17: (a) Secondary electron image showing porosity in A356 alloy containing 1.025 wt.% La and no Sr (sample SDAS $\sim 42 \mu\text{m}$). (b) EDS spectrum corresponding to the La-rich phase platelet (black arrow) in (a).

FIGURE 18: Secondary electron image of La-rich platelet within a pore in Sr-modified, high (1.025%) La-containing A356 alloy (sample SDAS $\sim 42 \mu\text{m}$).

- (9) Addition of Sr causes fragmentation of the rare earth intermetallics similar to that observed for the β - Al_5FeSi iron intermetallic phase.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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