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Solidification behavior of Al-Si-Fe alloys and phase transformation of metastable intermetallic compound by heat treatment

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Solidification behavior of Al-20 wt % Si-8 wt % Fe and Al-30 wt % Si-5 wt % Fe alloys during cooling with a cooling rate of 10 K/min has been studied using optical microscopy, X-ray diffractometry, differential thermal analysis, scanning electron microscopy and energy dispersive X-ray spectroscopy. In Al-20Si-8Fe alloy, metastable δ-Al_4FeSi_2 phase with tetragonal structure formed first from melt, followed by primary Si precipitation and then remaining liquid solidified finally into ternary eutectic of α-Al, Si and δ phases. However, in Al-30Si-5Fe alloy, primary Si formed first, followed by the δ phase precipitation and then eutectic solidification. During isothermal heat treatment of as-solidified alloys, phase transformation from the δ phase to equilibrium β phase began at the interface between δ phase and α-Al matrix and progressed toward the inside of δ phase with co-precipitation of Si particles due to the difference in composition between δ-Al_4FeSi_2 and β-Al_5FeSi phases.

1. Introduction

Recently, high performance light metals are required to increase fuel efficiency of transport systems and to reduce environmental pollution which is being considered serious in modern society. Hypereutectic Al-Si alloys have been considered to be a potential substitute for cast iron, which has been used widely for wear resistant components in the automotive industry. The Al-Si alloys show good wear resistance, low thermal expansion coefficient and high elastic modulus. Most of these properties are attributed to uniform distribution of hard Si particles in a ductile α-Al matrix and are very dependent on the size distribution and volume fraction of Si particles. However, hypereutectic Al-Si alloy fabricated by conventional casting technology show low toughness and poor machinability due to the formation of coarse primary Si during slow cooling. Several different techniques have been applied to refine the primary Si such as addition of P [1, 2] or rapid solidification [3, 4]. In order to replace cast iron by hypereutectic Al-Si alloy, the Al-Si alloy should maintain its required mechanical properties at service temperature. Typical service temperature in automotive parts such as air-conditioning compressors is about 450 K. Although a copper and magnesium addition can improve the strength of Al alloys substantially by precipitation hardening, the precipitates are not stable at the elevated temperature resulting in rapid decrease in strength at high temperature [5]. Therefore, the addition of alloying elements forming a stable precipitate at high temperature is required. Thermally stable intermetallic compounds can be formed by the addition of transition elements like Fe, Ni to Al alloys. However, the amount of transition element addition is very limited in Al alloys due to their low solid solubility. Because large intermetallic compounds in Al matrix resulted in a deteriorating effect on ductility, rapid solidification has been applied to increase the amount of transition metal in Al alloys [6, 7].

We reported previously that metastable δ-Al_4FeSi_2 phase of tetragonal crystal structure formed in gas atomized Al-(20,30)Si-(3,5,8)Fe alloy powders and the δ phase transformed into the equilibrium β phase during hot consolidation [8, 9]. Mechanical properties and wear resistance of the alloys were improved substantially, compared with those of Al-Si binary alloys, due to the presence of intermetallic compound of β phase. However, the Al-Si-Fe phase diagram and solidification sequence of the alloys are not clear yet. Therefore it is important to understand solidification behavior of these alloys for controlling microstructure of hypereutectic Al-Si-Fe alloys. The δ phase formed in Al-Si-Fe alloy powders transformed into stable β-Al_5FeSi phase of monoclinic structure during degassing and hot extrusion. Although some observations on this phenomena exist [10, 11], there is no detailed study of the microstructural evolution with respect to the phase transformation.

In this study, the solidification behavior of Al-20Si-8Fe and Al-30Si-5Fe alloys has been studied by quenching experiments from predetermined temperatures during cooling with a cooling rate of 10 K/min.

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Heat treatment was performed to study solid state transformation from metastable δ-Al_4FeSi_2 to stable β-Al_5FeSi phase. Microstructure was characterized by optical microscopy, X-ray diffractometry (XRD) and energy dispersive X-ray spectroscopy (EDX).

2. Experimental

Master alloys of Al-20 wt % Si-8 wt % Fe and Al-30 wt % Si-5 wt % Fe were manufactured by induction melting of commercially pure metals in graphite crucibles and then pouring the melt into graphite molds of outer diameter 15 mm, inner diameter 10 mm and height 100 mm. The master alloys were remelted in the graphite molds with a resistance furnace, cooled to predetermined temperatures with a cooling rate of about 10 K/min in the furnace and then quenched into water at ambient temperature. The quenching temperatures, selected after differential thermal analysis experiments, were 963, 873 and 833 K for Al-20Si-8Fe alloy and were 1033, 933 and 833 K for Al-30Si-5Fe alloy. Also Al-20Si-8Fe alloy was prepared by slow cooling to 298 K in a resistance furnace. The alloy was cut into 1.6 mm thick slices and then heat treated for 24 to 384 h at 773 K in a tube furnace to study the solid state transformation of the intermetallic compound. The microstructure of the quenched specimens and annealed specimens were observed by either optical or scanning electron microscopy after polishing and etching in 2M NaOH solution or 75HCl-25HNO_3-5HF-25H_2O solution. Local concentration profiles were determined by energy dispersive X-ray spectroscopy in a scanning electron microscope. The solidification behavior of Al-20Si-8Fe and Al-30Si-5Fe alloys was investigated by differential thermal analysis of rapidly solidified powder samples. Al-20Si-8Fe and Al-30Si-5Fe powders of about 20 mg were heated to 1273 and 1373 K with a heating rate of 20 K/min, respectively, and then cooled to 673 K with a cooling rate of 10 K/min. The crystal structures of cast and heat treated specimens were analyzed by XRD. XRD patterns were obtained with monochromatic CuK_α radiation over a 2θ range of 10–90°.

3. Results and discussion

3.1. Solidification behavior of Al-Si-Fe alloys

The solidification behavior of Al-20Si-8Fe and Al-30Si-5Fe alloy powders was investigated by using differential thermal analysis during cooling with a cooling rate of 10 K/min after heating powder samples to 1273 and 1373 K, respectively. Fig. 1a and b show typical DTA traces obtained during cooling Al-20Si-8Fe and Al-30Si-5Fe alloy powders respectively. Three exothermic peaks appeared during cooling in both specimens, indicating the presence of three different solidification events. The DTA trace of Al-20Si-8Fe alloy powder showed two small exotherms with onset temperatures of 1035 and 935 K, and a sharp exotherm with an onset temperature of 844 K. The DTA trace of Al-30Si-5Fe alloy powder showed again two small exotherms with onset temperatures of 1118 and 1018 K and a sharp exotherm with an onset temperature of

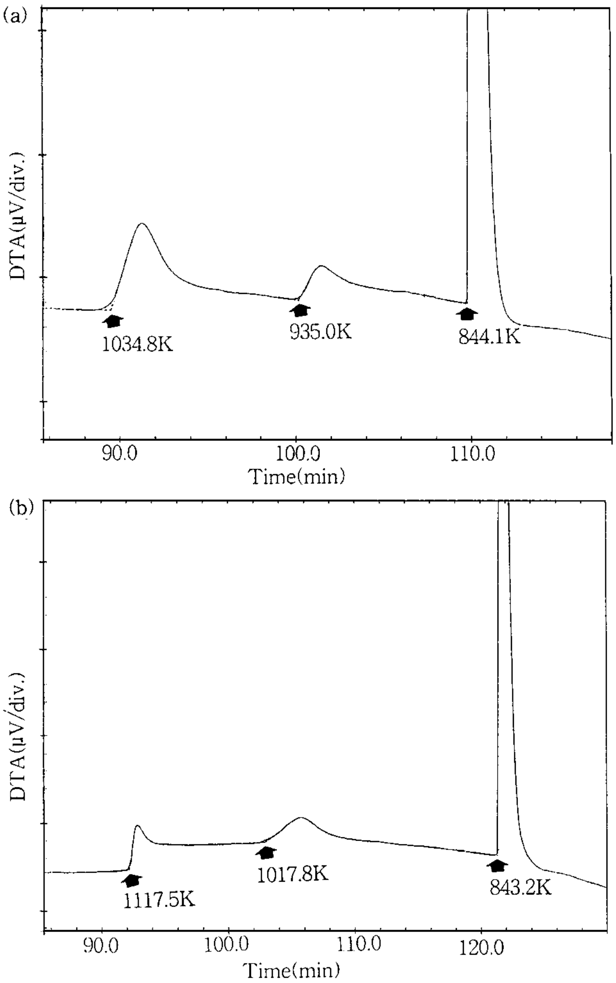

Figure 1 Typical DTA traces obtained during cooling (a) Al-20Si-8Fe and (b) Al-30Si-5Fe alloy powders with a cooling rate of 10 K/min.

843 K. The two small exotherms could correspond to crystallization of two primary phases and the sharp exotherm corresponds to ternary eutectic solidification. The onset temperature of the third sharp exothermic temperature was lower than the onset temperature of melting measured during heating by about 5–6 K. The ternary eutectic temperature measured during heating was about 849 K, which is in good agreement with the reported value [12].

Fig. 2a–c show typical optical micrographs of Al-20Si-8Fe alloy, cooled to 963, 873 and 833 K, respectively and then water quenched. The quenching temperatures were selected after DTA experiments to find solidification behavior from each exotherm. Fig. 2a shows a microstructure of the alloy quenched from a temperature between the first and second exotherms in Fig. 1a. The microstructure consists of coarse faceted intermetallic compound of white color formed during slow cooling to 963 K and fine scale microstructure, which consists of fine intermetallic compound and Si particles embedded in a ternary eutectic, formed during subsequent quenching of the remaining liquid. Fig. 2b shows a microstructure of the alloy quenched from a temperature between the second and third exotherms in Fig. 1a. The microstructure consists of coarse faceted intermetallic compound of white color, two different sizes of Si particles of gray color and fine scale ternary eutectic microstructure. The intermetallic compound

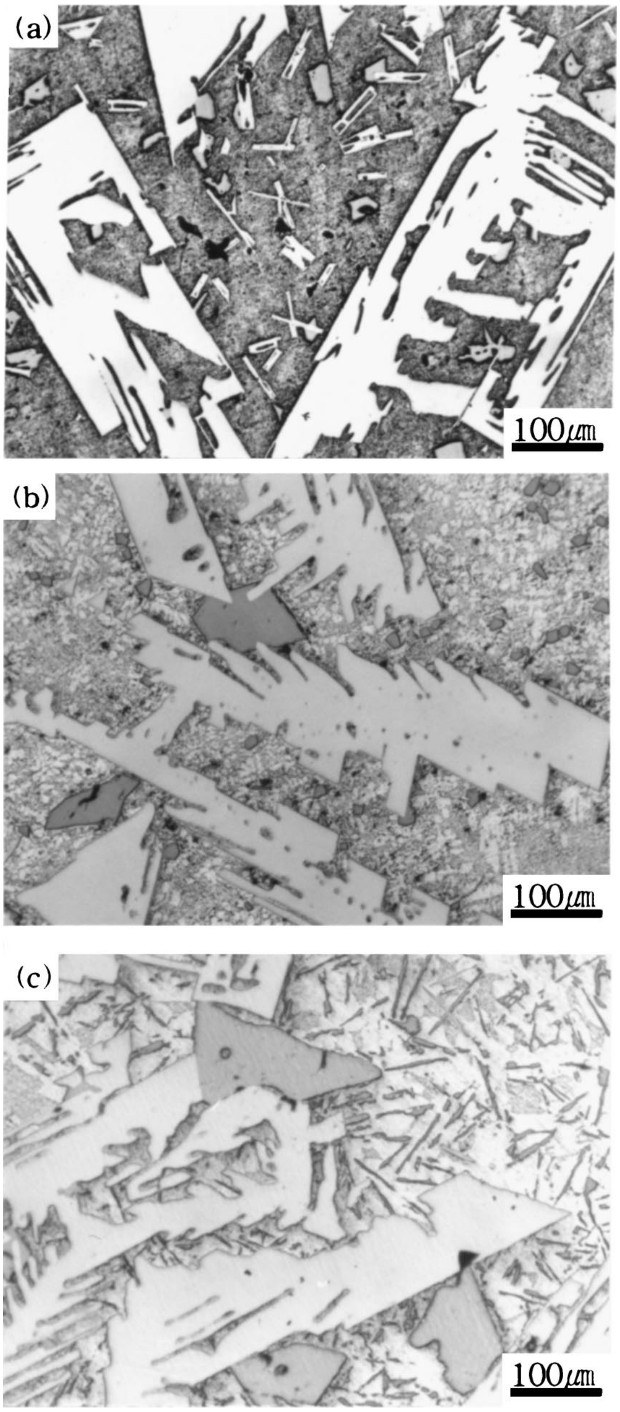

Figure 2 Typical optical micrographs of Al-20Si-8Fe alloy, water quenched from different temperatures: (a) 963, (b) 873, and (c) 833 K after cooling with a cooling rate of about 10 K/min.

and coarse Si particles precipitated during slow cooling and fine Si seems to be formed during subsequent quenching before eutectic solidification starts. Due to rapid cooling during quenching, α-Al dendrites were formed before ternary eutectic solidification occurred, which is often observed in rapidly solidified eutectic Al-Si alloys. Most coarse Si particles were observed at boundaries of intermetallic compounds, indicating that the intermetallic compound surface may act as a nucleation site for these Si crystals. Fig. 2c, microstructure of the alloy quenched from a temperature below the third exotherm in Fig. 1a, consists of coarse faceted intermetallic compound of white color and Si particles of grey color and ternary eutectic structure.

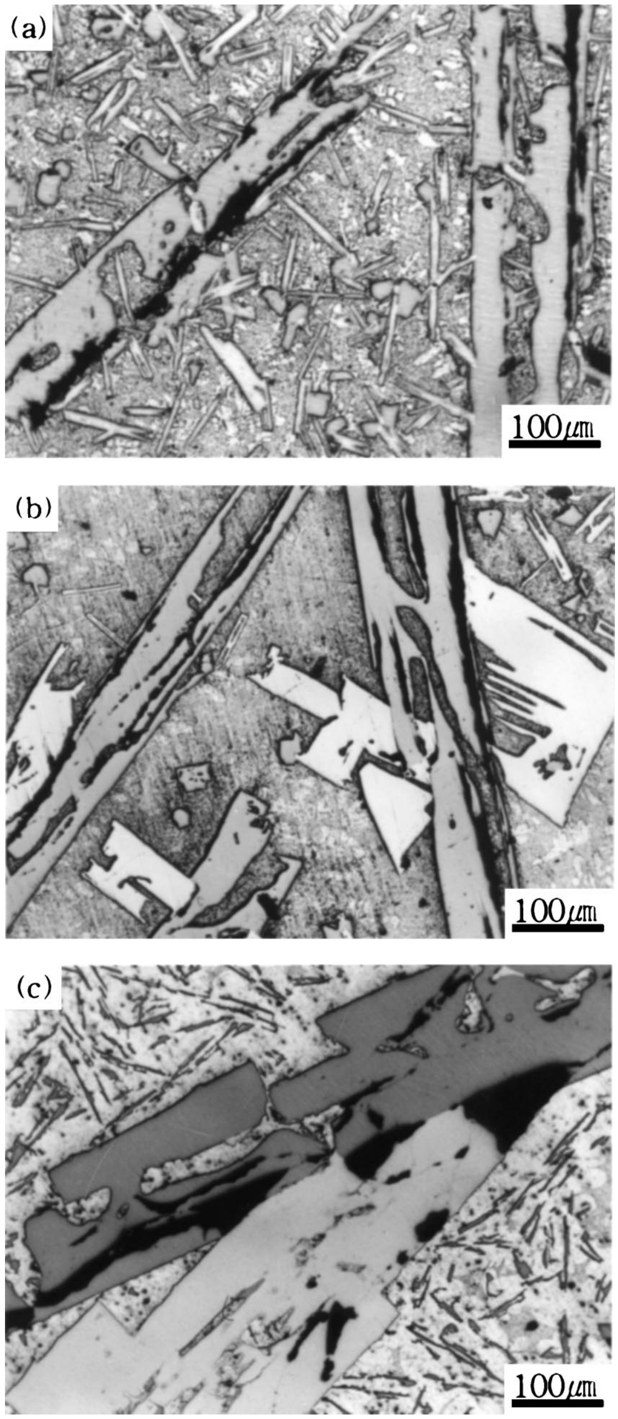

Figure 3 Typical optical micrographs of Al-30Si-5Fe alloy, water quenched from different temperatures: (a) 1033, (b) 933, and (c) 833 K after cooling with a cooling rate of about 10 K/min.

Fig. 3a–c show typical optical micrographs of Al-30Si-5Fe alloy, quenched into a water during cooling at 1033, 933 and 833 K, respectively. Fig. 3a, the microstructure of the alloy quenched from a temperature between the first and second exotherms in Fig. 1b, consists of coarse faceted Si of grey color and finer scale intermetallic compound and Si particles embedded in a ternary eutectic. The irregular shaped coarse Si particles formed during slow cooling to 1033 K and finer scale microstructure formed during subsequent quenching from the remaining liquid. Fig. 3b, the microstructure of the alloy quenched from a temperature between the second and third exotherms in Fig. 1b, consists of coarse faceted Si of grey color and intermetallic

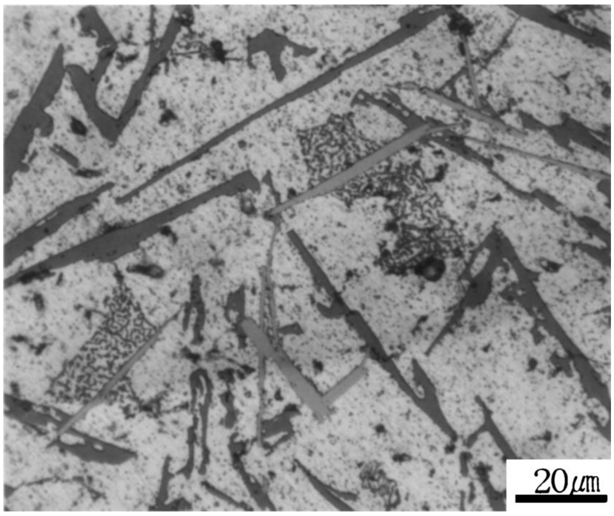

Figure 4 An enlarged view of the ternary eutectic structure in Fig. 3c.

compound of white color formed during slow cooling to 933 K and fine scale microstructure, consisting of fine intermetallic compound and Si particles embedded in a ternary eutectic. Fig. 3c, the microstructure of the alloy quenched from a temperature below the third exotherm in Fig. 1b, consists of coarse faceted Si particles of grey color and intermetallic compound of white color and ternary eutectic structure.

Fig. 4 shows a typical ternary eutectic structure from Fig. 3c, obtained from the quenched specimen just before solidification finishes. Two different scales of eutectic structure, namely, the coarse eutectic formed during slow cooling and a fine eutectic formed during quenching, are shown in Fig. 4. The ternary eutectic structure consisted of α-Al, Si (dark gray) and intermetallic compound (light gray) and shows an irregular eutectic structure.

Fig. 5a and b show XRD traces obtained from Al-20Si-8Fe and Al-30Si-5Fe alloys cooled slowly to 298 K in a furnace, respectively. Most diffraction peaks in both XRD traces could be analyzed into a mixture of fcc α-Al, diamond cubic Si and tetragonal δ-Al_4FeSi_2 phases. Even in the furnace cooled specimen, metastable δ phase with tetragonal structure was observed.

The results of thermal analysis, quenching and XRD experiments described previously can be summarized as follows. Al-20Si-8Fe alloy solidified with following sequence.: In the beginning of solidification, primary δ phase is crystallized and then primary Si nucleates on the δ phase and grows. Finally, the remaining liquid solidified into an irregular ternary eutectic of α-Al, Si and δ phase. This solidification procedure is in agreement with three steps in DTA analysis and is consistent with previous reports [13, 14]. However, in Al-30Si-5Fe alloy, primary Si forms first and then formation of δ primary phase follows, as can be seen in Fig. 3a and b. The formation of metastable δ phase instead of forming equilibrium β phase even in a furnace cooled specimen seems to be related to the difference in crystal structure. The β phase has monoclinic crystal structure with lattice constants of $a = 6.12$ Å, $b = 6.12$ Å, $c = 41.5$ Å and $\alpha = 91^\circ$, which is less symmetric and more complex than tetragonal

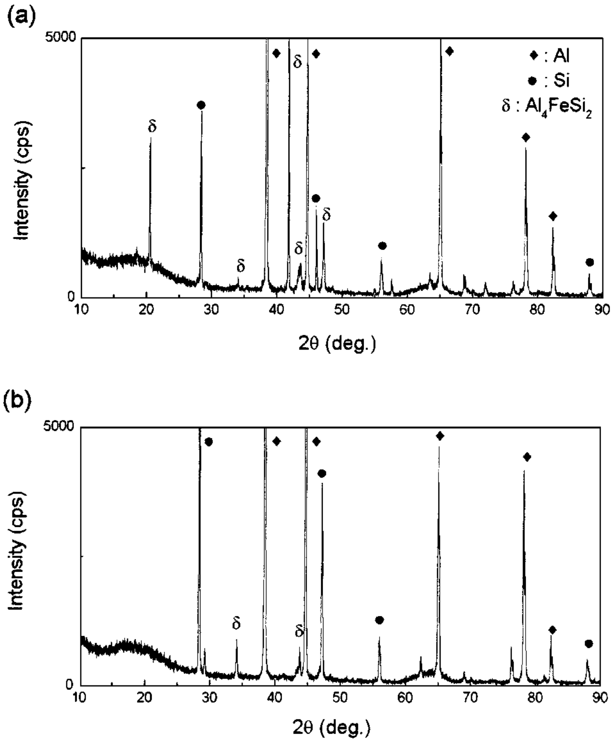

Figure 5 XRD traces obtained from (a) Al-20Si-8Fe and (b) Al-30Si-5Fe alloys cooled slowly to 298 K in a resistance furnace, respectively.

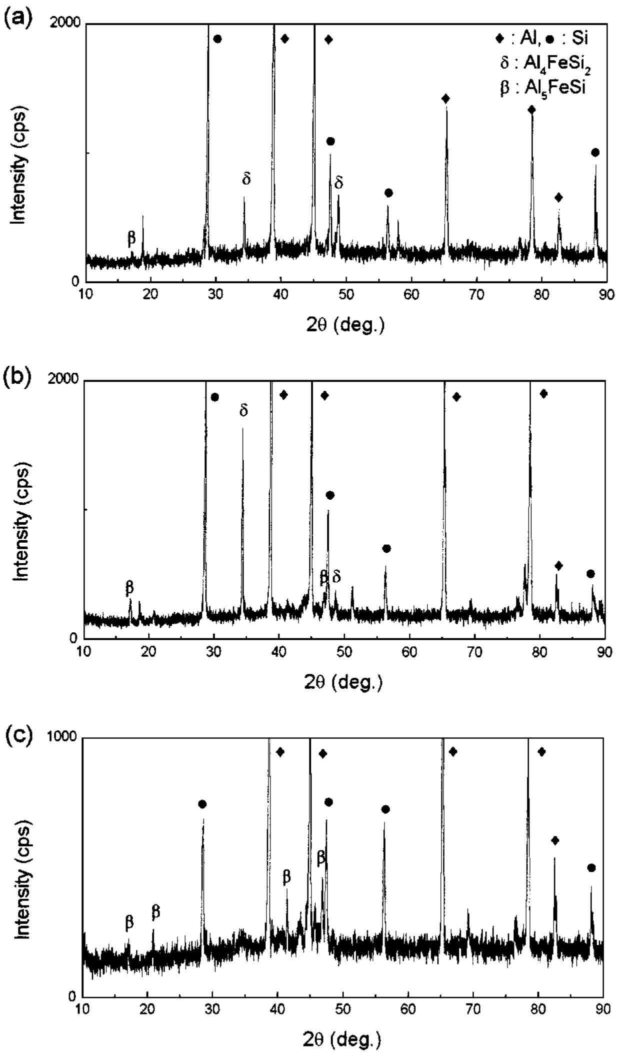

Figure 6 XRD traces obtained from Al-20Si-8Fe alloy heat-treated at 773 K for different times: (a) 24, (b) 96 and (c) 384 h.

δ phase with lattice constants of $a = 6.12$–6.16 Å and $c = 9.48$–9.49 Å [12]. In general, a crystal with simple structure can form more rapidly than a crystal with complex structure.

3.2. Phase transformation of the intermetallic compound by heat treatment

Fig. 6a–c show XRD traces with analysed results, obtained from Al-20Si-8Fe alloy heat treated at 773 K for 24, 96 and 384 h, respectively. Compared with Fig. 5a, metastable δ phase transformed gradually to stable β-Al_5FeSi phase with increasing time. The specimen heat-treated for 24 h consisted of strong diffraction peaks from δ phase and weak peaks from the monoclinic β-Al_5FeSi phase as well as peaks from Al and Si. As heat treatment time increased, the intensity of diffraction peaks from the δ phase decreased and the intensity of diffraction peaks from the β phase increased, as shown in Fig. 6b and c. The XRD trace taken from the specimen heat-treated for 384 h consisted of diffraction peaks corresponding to a mixture of Al, Si and β phase, indicating that most of the δ phase had transformed to β phase.

Fig. 7a–d show typical optical micrographs of Al-20Si-8Fe alloys heat-treated at 773 K for various different times from 0 to 384 h, showing the process of transformation of δ phase to β phase. For this observation, the specimens were severely etched by using a solution of $75HCl$-$25HNO_3$-$5HF$-$25H_2O$. Fig. 7a shows a typical morphology of intermetallic compound (δ phase) in cast Al-20Si-8Fe. Fig. 7b shows the microstructure of the alloy heat-treated for 24 h. There was no significant change in morphology of the intermetallic compound during this heat treatment. However, a thin layer can be seen mainly at the interface between intermetallic compound and matrix as marked by arrows. As heat treatment time increases, this region becomes thicker by moving the boundary towards the inside of the intermetallic compound and finally covering the whole intermetallic compound, as shown in Fig. 7c and d. It can be also seen that precipitation and coarsening of Si particles at the interface between intermetallic compound and matrix occurred during heat treatment simultaneously. With the results of XRD experiments in Fig. 5, it can be conjectured that this microstructural evolution is related to phase transformation of metastable δ phase to equilibrium β phase. New β phase nucleated at the interface between δ phase and matrix and lateral growth occurred, resulting in formation of a uniform thickness of β phase. During the transformation, half of the Si in the δ phase should be replaced by Al. Therefore, during the transformation, precipitation of Si and structural coarsening accompanied.

Fig. 8 shows scanning electron micrograph of a specimen heat-treated for 192 h with an inset showing compositional profiles of Al and Si along the marked line in Fig. 8. Near the edge of the intermetallic compound, we can see a slight increase in Al and a decrease in Si

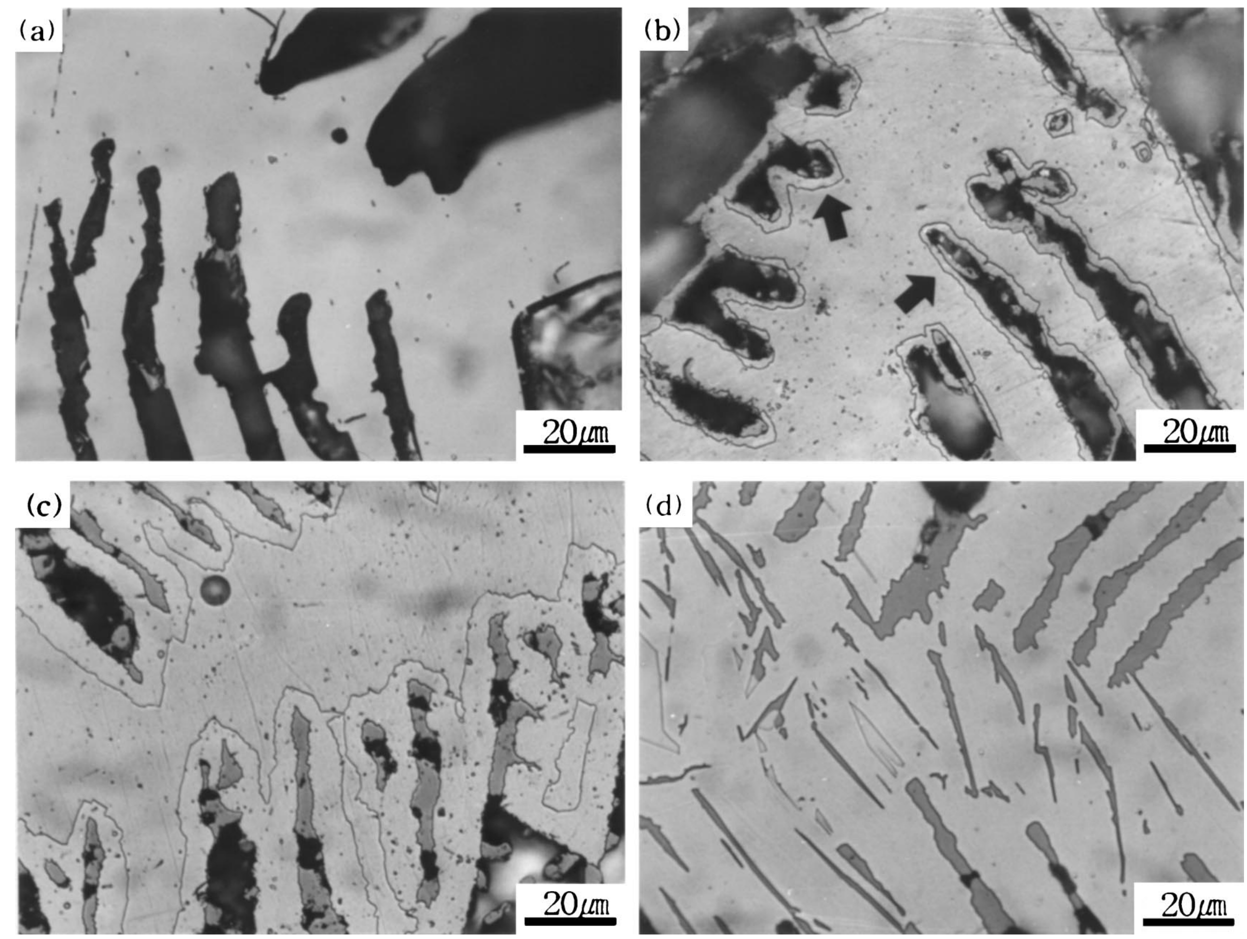

Figure 7 Optical micrographs of Al-20Si-8Fe alloys heat treated at 773 K for various different times: (a) 0, (b) 24, (c) 96 and (d) 384 h.

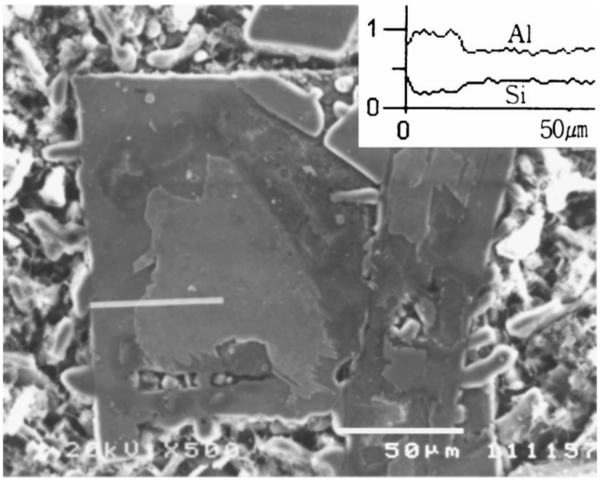

Figure 8 Scanning electron micrograph of Al-20Si-8Fe alloy heat-treated for 192 h with an inset showing compositional profiles of Al and Si along the marked line.

contents as shown in the compositional profile, which is in agreement with the formation of stable β phase at the interface between intermetallic compound and matrix as shown in Fig. 6.

These structural observations in quenched and heat-treated specimens may indicate that formation of the monoclinic β phase during solidification is difficult possibly due to its low crystallographic symmetry. Also the transformation of δ phase into β phase takes a very long time even at 773 K due to the coarse cast microstructure, compared with the reported phase transformation during degassing and extrusion of similar alloy powders involving about 3 h at 673 K [9].

4. Conclusions

(1) During solidification of Al-20Si-8Fe alloy, metastable δ phase formed first and then primary Si nucleated heterogeneously on the surface of δ and grew. Finally the remaining liquid solidified into ternary eutectic of α-Al, Si and δ.

(2) During solidification of Al-30Si-5Fe alloy, the primary Si formed first, followed by the heterogeneous nucleation of δ phase and finally the remaining liquid solidified into ternary eutectic of α-Al, Si and δ.

(3) The δ phase transformed to equilibrium β-Al_5FeSi phase during heat treatment at 773 K.

(4) The phase transformation of intermetallic compound began at the interface between intermetallic compound and matrix and progressed towards the inside of the δ phase. Si particles were precipitated and grown at the interface of the intermetallic compound and within the matrix during phase transformation, due to the difference in composition between δ-Al_4FeSi_2 phase and β-Al_5FeSi phase.

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