Nonequilibrium Phases in Rapidly Solidified High-Carbon Fe-Cr-Mo Alloys

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The effect of cooling rate and carbon content on the formation of nonequilibrium phases has been investigated in rapidly solidified 10Cr-5Mo and 10Cr-10Mo iron alloys containing very high carbon contents of 2 to 5% in mass. The cooling rate was varied by changing the nozzle size in a single roller method to result in an approximate value of $6 \cdot 10^4$ to $4 \cdot 10^5$ K/s. Nonequilibrium solid solutions of crystalline γ , ϵ and ψ phases as well as an amorphous phase were formed depending on the cooling rate and chemical composition of alloys. The optimum condition for obtaining the ϵ phase in the 10Cr-5Mo alloy and the ψ phase in the 10Cr-10Mo alloy was determined by the combination of cooling rate and carbon content. The higher carbon content and the higher cooling rate tend to bring about the amorphous formation. The amounts of carbon in solution in the γ , ϵ and ψ phases increased with increasing cooling rate and carbon content.

(Received April 30, 1992)

Keywords: rapid solidification, cooling rate, iron alloy, transition metal, nonequilibrium phase, A13 type structure, carbon in solution

I. Introduction

Rapid solidification techniques are used to obtain fine structures and nonequilibrium phases. The fine structures are generally favourable to mechanical properties. Very fine structures are attained by the decomposition of nonequilibrium phases and controlled by the alloying elements and the amount of the solute elements in solution of the nonequilibrium phases. In order to utilize materials having nonequilibrium phases, therefore, controls of nonequilibrium phase formation and the amount of the solute elements in solution are very important.

It is known that nonequilibrium γ (A1 structure, FCC)⁽¹⁾⁽²⁾, ϵ (A3, HCP)⁽³⁾⁻⁽⁹⁾, χ (A12, α -Mn type)⁽⁶⁾⁽¹⁰⁾, and ψ (A13, β -Mn)⁽¹¹⁾⁽¹²⁾ phases as well as an amorphous phase⁽⁶⁾⁻⁽⁹⁾⁽¹³⁾⁻⁽¹⁶⁾ are obtained in rapidly solidified high-carbon iron alloys. The ϵ phase is of a crystalline solid solution and has a large amount of carbon in solution. The χ and ψ phases are also of crystalline solid solutions and the characteristics of the phases have not been investigated in detail. The ϵ and ψ phases are obtained in high-carbon iron alloys by means of splat quenching⁽³⁾⁽¹²⁾, thermal spraying⁽¹⁷⁾⁽¹⁸⁾ and single roller method⁽⁴⁾⁻⁽⁹⁾. It seems, however, that tendency of the nonequilibrium crystalline phases is different among the solidification methods even when alloys of the same composition are used. The authors reported that an addition of transition metals to high-carbon iron alloys is effective in the formation of the ϵ and ψ phases⁽⁷⁾⁽⁸⁾⁽¹⁸⁾. These suggest that the formation of the nonequilibrium ϵ and ψ phases depends upon not only the cooling rate but also chemical composition of the alloys. Up to now, it has not been established what type of nonequilibrium phase is formed by rapid

solidification under the different conditions of cooling rate and chemical composition. Furthermore, the effect of cooling rate on the amount of carbon in solution has not been clarified yet. The present work was carried out to investigate the effect of cooling rate and carbon content on the formation of nonequilibrium phases in very high-carbon iron alloys with two levels of transition metals.

II. Experimental Procedure

Starting materials were prepared by melting from electrolytic iron, ferro-silicon (75 mass%Si), ferro-chromium (60 mass%Cr), ferro-molybdenum (60 mass%Mo), and graphite electrode. The iron alloys were remelted in a silica capsule and solidified into ribbons by a single roller method. The chemical compositions of ribbons are shown in Table 1. All alloys contained a small amount of silicon which is useful to make ribbons without difficulty. The base composition of Alloys A1 through A4 was 10%Cr and 5%Mo and the carbon content was changed from 2.3 to 4.9%. On the other hand, Alloys B1 through B3 had a base composition of 10%Cr and 10%Mo, and carbon from 2.7 to 4.5%.

Table 1 Chemical compositions of the alloys (mass%).

Alloy	C	Si	Cr	Mo	Remarks
A1	2.34	1.06	10.37	5.31	10Cr-5Mo
A2	3.27	1.01	10.03	5.16	
A3	4.06	0.85	9.47	4.94	
A4	4.94	1.06	9.71	5.29	
B1	2.72	0.90	9.77	10.02	10Cr-10Mo
B2	3.72	1.03	9.99	10.00	
B3	4.45	1.15	9.75	9.90	

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Table 2 shows the solidification condition of the ribbons in a single roller method. The peripheral speed of the roller was 34 m/s. In order to change the cooling rate, silica nozzles with four types of holes were used and, as a result, the ribbon thickness changed from 10 to 90 μm . Cooling rate was estimated experimentally from a dendrite arm spacing measurement of an alloy containing

3.3% carbon and 1.0% silicon and also theoretically from a cooling curve calculation. Secondary dendrite arm spacings in ribbons solidified using the four types of nozzles were measured and the cooling rates were estimated from the relationship given by Ibaragi *et al.*⁽¹⁹⁾ The cooling rates of theoretical calculation were obtained from the calculated cooling curves using a one-dimensional heat conduction equation. The cooling rates of ribbons were estimated at 1273 K. The cooling rates obtained experimentally and theoretically are listed in Table 2. These values are relatively in close agreement and varies from $6 \cdot 10^4$ to $4 \cdot 10^5$ K/s. The cooling rates obtained by use of the four types of nozzle were termed V1 through V4 as shown in Table 2.

Structures of nonequilibrium phases were determined by use of an X-ray apparatus (Fe radiation), a scanning electron microscope (SEM), and a transmission electron microscope (TEM) with an acceleration voltage of 300 kV. The peak positions in X-ray diffraction angle were corrected with a pure silicon (99.999%Si) and the regression method was applied in order to estimate accurate lattice parameters of the nonequilibrium phases.

Table 2 Solidification condition.

Hole shape of nozzle	Ribbon thickness (μm)	Cooling rate (K/s)*		Remarks
		Experimental	Calculated
80 ± 10	$6 \cdot 10^4$	$4 \cdot 10^4$	V1
50 ± 10	$9 \cdot 10^4$	$8 \cdot 10^4$	V2
35 ± 5	$2 \cdot 10^5$	$4 \cdot 10^5$	V3
15 ± 5	$4 \cdot 10^5$	$7 \cdot 10^5$	V4

* Obtained from Fe-3.3 mass% C-1.0 mass% Si alloy.

Fig. 1 SEM micrographs showing (a): γ in Alloy A1 (V4), (b): ϵ in Alloy A3 (V3), (c): ψ in Alloy B1 (V4), and (d): amorphous phase in Alloy B3 (V4). Top and bottom of each micrograph correspond to the free surface side and the roller side, respectively. Longitudinal section.

III. Results and Discussion

1. Microstructure of nonequilibrium phases

Figure 1 shows typical microstructures of non-equilibrium γ , ε , ψ and amorphous phases. The bottom surface of the ribbons in the photographs is roller side and the top is free surface side. χ phase was not obtained in all the alloys at any cooling rate in this study. The γ phase reveals a dendrite structure (Fig. 1(a)). The higher the cooling rate, the finer the γ dendrite structure was. It seems that the ε phase nucleated at the surface of the roller side and grew radially (Fig. 1(b)). Thus, the ε phase has a fan-like morphology of lath grains. The triangle region which has little contrast at the roller side in Fig. 1(b) is an amorphous phase. Figure 1(c) shows ψ phase which reveals equi-axed grains. This grain structure is consistent with the previous work⁽⁷⁾. Figure 1(d) shows an amorphous phase of little contrast throughout the ribbon. Thus, the γ , ψ and amorphous phases were obtained as an almost single phase in the ribbons but the ε phase was accompanied by a small amount of other phases.

2. X-ray diffraction

(1) 10Cr-5Mo alloy

Figure 2 shows X-ray diffraction patterns of Alloy A1 (2.3C) which is rapidly solidified into ribbons at the cooling rates of V1 through V4. Diffraction peak height became low with increasing cooling rate because the X-

Fig. 2 X-ray diffraction patterns of Alloy A1.

ray radiation area of a specimen becomes smaller with the decrease of the ribbon size. It is seen that Alloy A1 composed mainly of the γ phase at any cooling rate accompanying a small amount of the ferrite (α) phase and that diffraction peaks of the γ phase shift to a lower angle with increasing cooling rate. The X-ray diffraction patterns of Alloy A2 (3.3C) were similar to those of Alloy A1.

Figure 3 shows the X-ray diffraction patterns of Alloy A3 (4.1C) which contains a higher amount of carbon than Alloys A1 and A2. Compared with Alloys A1 and A2, the diffraction peaks of M_3C carbide are seen at the low cooling rates of V1 and V2, in addition to the α and γ

Fig. 3 X-ray diffraction patterns of Alloy A3.

Fig. 4 SEM micrograph of Alloy A3 at a cooling rate of V1. Longitudinal section.

Fig. 5 X-ray diffraction patterns of Alloy A4.

Fig. 6 X-ray diffraction patterns of Alloy B1.

peaks. Figure 4 shows a SEM micrograph of Alloy A3 at the cooling rate of V1. A ledeburite structure ($\gamma + M_3C$) is observed, indicating that the diffraction peaks of M_3C carbide are attributed to a ledeburite structure. Thus the ledeburite ($\gamma + M_3C$) formed in this alloy upon a solidification at the low cooling rates. At the higher cooling rates of V3 and V4, the diffraction peaks of the ϵ phase and a broad peak of the halo pattern are observed. The diffraction peaks of the ϵ phase also shift to a lower angle with increasing cooling rate. The halo pattern is attributed to an amorphous phase.

Alloy A4 (4.9C) containing the highest amount of carbon reveals ϵ and amorphous phases at the cooling rates of V2 through V4, as shown in Fig. 5. It should be noted that an increase of the cooling rate and carbon content makes it easy to form ϵ and amorphous phases.

(2) 10Cr-10Mo alloy

Figure 6 shows X-ray diffraction patterns of Alloy B1 (2.7C) of the lowest carbon content. Alloy B1 consists mainly of γ and ψ phases at the cooling rates of V1 and V2. An increase of the cooling rate promotes the formation of the ψ phase and as a result the γ phase decreases. It is seen that the diffraction peaks of the ψ phase also shift to a lower angle with increasing cooling rate.

The formation behavior of nonequilibrium phases in Alloy B2 (3.7C) is similar to that of Alloy B1 (Fig. 7). It is to be noted, however, that amorphous phase becomes remarkable at the increased cooling rates of V3 and V4. Alloy B3 (4.5C) of the highest carbon content reveals

Fig. 7 X-ray diffraction patterns of Alloy B2.

Fig. 8 X-ray diffraction patterns of Alloy B3.

only halo patterns and no diffraction peak of crystals at any cooling rate (Fig. 8). This shows that amorphous phase forms as a single phase throughout the ribbons of Alloy B3.

It is apparent from Figs. 6 to 8 that the ψ phase and the amorphous phase are dominant in Alloy B1 and in Alloy B3, respectively, depending on the carbon content in the 10Cr–10Mo alloy.

3. Effect of cooling rate and carbon content on nonequilibrium phase formation

The tendency of nonequilibrium phase formation is schematically illustrated in regard to the approximate cooling rate and carbon content in Fig. 9. For the 10Cr–5Mo alloy (Fig. 9(a)), the γ phase is predominant at a carbon content less than 4%. On the other hand, a high carbon content more than 4% is effective in the formation of ledeburite ($\gamma + M_3C$), ε and amorphous phases, de-

Fig. 9 Schematic illustrations of nonequilibrium phase formation in (a): 10Cr–5Mo and (b): 10Cr–10Mo alloys with respect to the cooling rate and carbon content.

pending on the cooling rate. Ledeburite forms at a low cooling rate. The ε and amorphous phases appear at a higher cooling rate. An amorphous phase becomes dominant and the ε phase decreases with increasing cooling rate and carbon content. It is seen that the ε phase forms in a narrow range of the cooling rates and carbon contents and therefore it is difficult to get a ribbon composed only of the ε phase. For the 10Cr–10Mo alloy (Fig. 9(b)), the γ phase forms in the alloy of a carbon content less than 4% at low cooling rates. The ψ phase hardly forms at low cooling rates, but easily at an increased cooling rate, accompanying γ or amorphous phase. For obtaining a large amount of the ψ phase, a high cooling rate is needed at a low carbon content and, conversely, a lower cooling rate at a high carbon content.

It is summarized, as a general rule, from Fig. 9 that the rapidly solidified phase changes as follows with an increase of the cooling rate and/or carbon content.

for the 10Cr–5Mo alloy, and

for the 10Cr–10Mo alloy.

4. Lattice parameters of nonequilibrium phases

Figure 10 shows lattice parameters of the γ phase in the 10Cr–5Mo alloy solidified at various cooling rates. Coordinates of V1 through V4 in cooling rate are inferred from Table 2. Alloy A2 (3.3C) has larger lattice parameters by 0.01 nm than Alloy A1 at a given cooling rate. The lattice parameters of both alloys increase with increasing cooling rate and change from 0.363 to 0.366 nm, depending on the cooling rate and carbon content.

Figure 11 shows the lattice parameters of the ε phase. The ε phase of the 4.9% carbon content (A4) has larger lattice parameters by 0.02 nm for the a -axis and by 0.04 nm for the c -axis than that of the 4.1% carbon content (A3). The lattice parameter of the a -axis of Alloy A4 increases from 0.265 to 0.267 nm with increasing cooling rate, while the c -axis increases markedly from 0.432 to 0.438 nm. Therefore, the ratios of c/a of the ε phase are nearly constant in a range of 1.634 to 1.638 which are consistent with the values of the ε phase obtained by splat

Fig. 10 Lattice parameters of γ phase in Alloys A1 and A2 with respect to the cooling rate.

Fig. 11 Lattice parameters of ϵ phase in Alloys A3 and A4 with respect to the cooling rate.

Fig. 12 Lattice parameters of ψ phase in Alloys B1 and B2 with respect to the cooling rate.

quenching⁽³⁾.

The lattice parameters of the ψ phase in the 10Cr-10Mo alloy are shown in Fig. 12. It is seen that there is a remarkable difference of 0.04 nm in lattice parameter between Alloy B2 (3.7C) and Alloy B1 (2.7C) and that the lattice parameters increase with increasing cooling rate.

It is found that the all lattice parameters of the γ , ϵ , and ψ phases increase with increasing cooling rate and the carbon content of the alloys. It should be noted, however, that the cooling rate dependence of the lattice parameters is appreciably different among the γ , ϵ and ψ phases.

5. Carbon content in solution in nonequilibrium phases

The amount of carbon in solution in the non-equilibrium γ and ϵ phases are reported by Ruhl and Cohen⁽³⁾ and the relationship of the carbon contents in

solution and the lattice parameter or the unit cell volume are given by:

$$a = 0.3572 + 0.0033 \cdot (\text{mass}\% \text{C}) \text{ nm} \quad (3)$$

$$u = 0.02259 + 0.000171 \cdot (\text{at. ratio}\% \text{C}) \text{ nm}^3 \quad (4)$$

where a and u mean the lattice parameter of the γ phase and the unit cell volume of the ϵ phase, respectively. Equations (3) and (4) are applicable to the Fe-C binary system. The lattice parameter or the unit cell volume is also influenced by substitutional solute elements. Ruhl and Cohen evaluated the effect of solute elements on the slopes of the above linear equations, considering the contribution of silicon, chromium and molybdenum to the slopes for ferrite, i.e., $-1.26 \cdot 10^{-4}/(\text{mass}\% \text{Si})$, $+0.97 \cdot 10^{-4}/(\text{mass}\% \text{Cr})$, and $+2.27 \cdot 10^{-4}/(\text{mass}\% \text{Mo})$ ⁽²⁰⁾⁽²¹⁾.

Up to now, evaluation of the effect of the carbon in solution on the lattice parameter of ψ phase has not been performed. Assuming that the ψ phase is composed only of iron atoms, the lattice parameter of the phase (A13 structure) results in $a = \sqrt{6}D = 0.60806 \text{ nm}$ from a diameter of an iron atom, $D = 0.24824 \text{ nm}$ ⁽²²⁾. In this study, the lattice parameter of the ψ phase formed at the highest cooling rate of V4 in Alloy B1 (2.7C) was determined to be $a = 0.63050 \text{ nm}$. As the alloy consists only of the ψ phase as a single phase (see Fig. 6), it is regarded that all carbon in the alloy is in solution and the carbon content is 2.72%. The contribution of the substitutional solute elements (Si, Cr and Mo) to the lattice parameter of the ψ phase in the alloy (Fe-2.72%C-0.90%Si-9.77%Cr-10.02%Mo) is evaluated as $+9.76 \cdot 10^{-3}$ by the same calculation as that of Ruhl and Cohen. After compensating the contribution of the substitutional solute elements, a relationship between the lattice parameter

Fig. 13 The amounts of carbon in solution of γ , ϵ , and ψ phases with respect to the cooling rate.

and the carbon content in solution is given by:

$$a = 0.60806 + 0.00467 \cdot (\text{mass}\% \text{C}) \text{ nm}. \quad (5)$$

Equation (5) is also for the Fe-C binary alloy.

Figure 13 shows the amount of carbon in solution in the γ , ε and ψ phases. The carbon contents have been obtained from the corrected lattice parameters by considering the effect of the substitutional solute elements. The variation of the carbon content in solution is similar to that of the lattice parameters of the all phases with respect to the effect of carbon contents of the alloys and cooling rates (see Figs. 10 through 12). It is noticed that the amount of carbon in solution in the nonequilibrium phases is less than the carbon content of the alloys. It seems that the mass balance of the carbon content is not satisfied in these cases. For example, the γ phase of Alloy A1 (2.3C) at the lowest cooling rate (V1) contains 1.1% carbon in solution which is less than the carbon content of the alloy. As shown in Fig. 14, however, M_3C carbide is observed in the γ phase of Alloy A1 solidified at the cooling rate of V1. This indicates that the γ phase is inevitably accompanied by some amount of carbide depending on the cooling rate, though carbide peaks are not detected in the X-ray diffraction patterns probably because of hyper-fine dispersion of carbide particles. Figure 15 shows a TEM micrograph of Alloy A3 solidified at the cooling rate of V3. Laths of the ε phase and plate-like phase embedded between the ε phase laths are observed. This plate-like phase was identified as M_3C carbide as shown in the diffraction pattern in Fig. 15. Thus, the ε phase is also accompanied by a small amount

Fig. 14 TEM micrograph of Alloy A1 at a cooling rate of V1. (a): bright field image, (b): selected area diffraction pattern obtained from the region indicated by a circle in (a), and (c): indexed result.

Fig. 15 TEM micrograph of Alloy A3 at a cooling rate of V3. (a): bright field image, (b): selected area diffraction pattern obtained from the region indicated by a circle in (a), and (c): indexed result.

Fig. 16 TEM micrograph of Alloy B1 at a cooling rate of V1. (a): bright field image, (b): selected area diffraction pattern, and (c): indexed result.

of carbide which is not detected in the X-ray diffraction patterns. This suggests that the balance of the carbon in solution in the ε phase is used up in the formation of M_3C carbide. Figure 16 shows the ψ phase in Alloy B1 solidified at the cooling rate of V1. The ψ phase possesses spheroidal and irregular particles of the second phase. Although the structure of the second phase is not determined, the particles can be regarded as a carbon-enriched phase by comparing the amount of carbon in solution

and the carbon content of the alloy.

IV. Summary

High-carbon iron alloys with two levels of transition metals and different carbon contents were rapidly solidified by a single roller method at different cooling rates. The results obtained are summarized as follows:

(1) Nonequilibrium γ , ϵ and ψ phases as well as an amorphous phase were formed by changing the cooling rate and carbon content.

(2) The formation of ϵ phase or ψ phase as a single phase is limited in a small range of the cooling rate and carbon content. An amorphous phase formed in the alloys of higher carbon content at higher cooling rates.

(3) The amount of carbon in solution in the non-equilibrium γ , ϵ and ψ phases increased with increasing cooling rate and carbon content in the alloy melts.

(4) A relationship between the lattice parameter, a (nm), of a ψ phase and the amount of carbon in solution, mass%C, for the Fe-C binary alloy is given as follows:

$$a = 0.60806 + 0.00467 \cdot (\text{mass}\% \text{C}).$$

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