Investigation on Acid-Resistant High-Silicon Iron (III)

Effects of Cooling Rate and Annealing on Mechanical Properties and Corrosion Resistance

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Abstract

The effects of the cooling rate of castings and annealing on the mechanical properties and corrosion resistance of acid-resistant high-silicon iron were studied.

The variations in cooling rate bring about great changes in graphite structure and influence mechanical properties but hardly the corrosion resistance. It seems that the annealing of castings is important only with respect to the relief of internal casting stress.

I. Introduction

In the previous studies,¹⁾² the experiments were made maintaining the constancy of shape and size of the specimens and the melting and casting conditions to investigate the effects of various alloying elements on the mechanical properties, corrosion resistance, and shrinkage of the high-silicon iron of Fe-Si-C system. Since the matrix structure of this alloy consists of α -iron in all temperature and composition ranges, the α - γ transformation does not take place and, consequently, the cooling process is simpler than that of common gray cast iron. However, the graphite structure of this alloy is greatly affected by cooling rate and it is known that the silico-carbide phase is formed³ under an extremely rapid cooling. Although the improvement of the properties of this alloy by means of heat treatment is scarcely expected from the equilibrium diagran of Fe-Si-C system,⁴ the annealing has a significance in that it eliminates the casting stress which is caused by the large shrinkage of this alloy. Hence, some experiments were performed on these subjects.

The alloying materials with which the specimens were prepared were the same as those used in the previous study¹) and the melting procedure was also the same.

II. Effects of Cooling Rate

(A) Experiments on Effect of Cooling Rate

(1) Preparation of Specimen and Method of Experiment

The melt of high-silicon iron was heated to 1450° C and poured, in order, into a metal mould, shell mould, green sand mould, and dry sand mould heated at 150° C. The pouring started at 1320° C and ended at about 1300° C. The shell mould used in the present experiment was the same as in the previous experiment¹⁾ and the other three moulds were made into the same shape and size as the shell mould. The castings were numbered from 1 to 6 according to different heats and each number was appended with M, S, G, and D representing metal mould, shell mould, green sand mould, and dry sand mould, respectively. The test bars for the transverse bend tests were ground with a No. 80 carborundum wheel and were finished into rods of 14mm in diameter. The transverse bend tests, hardness tests, corrosion tests, and microstructure tests were carried out, in the same manner as in the previous study,¹⁾ in order to investigate the influence of the cooling rate.

As given in Table 1, the chemical compositions of the specimens were the same as those of ordinary high-silicon iron except No. 5 and 6 which had a little lower silicon content of about 14.5 pct.

(2) Experimental Results

The experimental results are given in Table 1 and graphically shown in Figs. 1, 2 and 3. According to Fig. 1, the transverse strength is very high in the specimens which were prepared by pouring into the metal mould and cooled very rapidly. It shows the medium values of $22-25 \text{ kg/mm}^2$ in the specimens which were cooled at medium rate in the shell mould and the green sand mould, and

Speci-	Composition (%)		Trans- verse	Deflec-	Hardness		Corrosion Loss in Weight (mg/cm ² /4hr.)		Type & Size of Graphite
Number	Si	С	Strength (kg/mm ²)	(mm)	(HrC)	(HMV)	1:10 H ₂ SO ₄	1:1 HCl	according to ASTM
			28.8	0.75	49.2	650			1
1.M	- 15.15		1 —		50.0	666			D-8
1-1/1		0.54	-		50.3	666			
			28.8	0.75	49.8	661			
			22.8	0.52	42.5	623			
10			22.5	0.50	43.7	613			D-8 90%
1-2					43.0	623		_	D or A-6
			22.7	0.51	43.1	620			10%
			22.4	0.57	42.7	593			
10			22.1	0.57	43.0	593			D-8 90%
1-0					41.1	584			A-5 10%
[]			22.3	0.57	42.3	590			, -
1-D					42.0	599			
			_		41.2	589			D-8 70%
			1 _		39.8	598	_		A-5 30%
			<u> </u>		41.0	595			

Table 1. Effects of Cooling Rate

Speci-	Composition (%)		Trans- verse	Deflec-	Hardness		Corrosion Loss in Weight (mg/cm ² /4hr.)		Type & Size of Graphite	
Number	Si	С	(kg/mm ²)	(mm)	(HrC)	(HmV)	$\begin{array}{c} 1:10\\ \mathrm{H}_2\mathrm{SO}_4\end{array}$	1:1 HCl	ASTM	
2-M			29.7 29.7	0.73 0.73	52.2 52.2 51.0 51.8	708 650 708 689	1.94 2.12 2.03	3.27 3.15 3.21	D-8	
2- S	15.09	0.66	0.66	26.1 23.6 24.9	0.60 0.55 0.58	45.6 45.9 45.7 45.7	633 633 644 637	2.13 2.00 2.07	2.95 2.87 2.91	D-8 70% D or A-7,6 30%
2-G				24.5 24.0 24.3	0.60 0.61 	44.6 43.6 44.8 44.3	623 593 589 602	1.77 1.75 1.76	2.89 2.89 2.89 2.89	D-8 90% A-5 10%
2-D			19.9 17.4 	0.59 0.51 0.55	37.2 40.2 39.7 39.0	644 609 623 625	2.13 1.99 2.06	3.09 2.99 3.04	D-8 60% A-5 40%	
3-М	15.00	.00 0.70	39.2 	0.76	51.0 50.1 53.0 51.4	650 672 668 663	2.77	3.74 3.02 3.38	D-8	
3-S			25.0 24.7	0.52 0.52	48.5 46.8 47.5	633 623 628 628	3.36 3.49	2.78 2.63	D-8 80% D or A-7,6	
3-G			00 0.70	22.6 26.4 24.5	0.55 0.62 0.59	45.2 48.0 46.8 46.7	623 633 633 630	3.23 3.34 3.29	3.46 3.48 3.47	D-8 70% B-5 30%
3-D			22.9 19.9 21.4	0.59 0.50 0.55	42.7 42.1 41.2 42.0	644 624 603 624	3.18 2.86 3.02	2.59 2.67 2.63	D-8 70% A-5 30%	
4-M	15.12	12 0.81	38.9 	0.70 0.70	52.8 53.0 50.3 5 2.0	697 682 672 684	2.24 1.81 2.03	3.18 3.00 3.69	D-8	
4-S			22.9 25.0 24.0	0.55 0.60 0.58	42.5 44.0 44.0 43.5	613 603 633 616	2.36 2.68 2.52	3.04 2.94 2.99	D-8 70% D or A-7,6 30%	
4-G			23.6 — 23.6	0.60	39.0 38.8 38.0 38.6	633 623 613 623	1.52 1.67 1.60	3.12 3.02 	D-8 70% A-5 30%	
4-D			16.7 16.7 16.7 16.7	0.51 0.52 0.52	35.8 34.1 35.2 35.0	623 623 623 623 623	2.46 2.21 2.34	3.27 3.44 3.36	D-8 30% A-5 70%	
5-M	14.63	0.62	29.2 30.2 	0.56 0.57 0.57	51.3 48.6 49.3 4 9.7		2.39 2.39	3.59 3.59	D-8 60% Silico-carbide 40%	
6-M	14.50	0.77	36.0 42.8 39.4	0.66 0.75 0.71	50.0 52.8 50.6 51.1		2.35 2.35	3.46 	D-8	

The figures in Gothic type indicate the average values.

the low values of 17-21 kg/mm² in the specimens which were cooled slowly in the hot dry sand mould.

Among the specimens cast in the metal mould, specimens 3-M and 4-M show higher values of transverse strength than specimens 1-M and 2-M in the 15 pct silicon alloy series; and specimen 6-M shows a higher value than specimen 5-M in the 14.5 pct silicon alloys. The difference observed in transverse strength is perhaps due to the difference in the carbon content; i.e., the higher the carbon



Fig. 1 Effects of cooling rate on the mechanical properties of high-silicon irons.

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content, the greater the transverse strength.

The deflection, in general, seems to be high in the specimens which have a high transverse strength. The deflection vs. load curves are shown in Fig. 3. These curves are almost straight lines and the slopes of the lines represent ductility. It is seen that the slopes of the lines are steeper in the following order; the specimens cast in the dry sand mould, green sand mould, shell mould, and metal mould: i.e., the lower the cooling rate, the higher the ductility.

The Rockwell C hardness, as shown in Fig. 1, is affected in the same manner as the transverse strength by the rate of cooling. The micro-Vickers hardness of the α -phase is higher in the specimens which were rapidly cooled in the metal mould (M series) and the hardness numbers ranging from 650 to 700 are shown. The other specimens which belong to S, G, and D series have similar hardness numbers ranging from 590 to 630.

The results of corrosion tests are given in Table 1 and shown in Fig. 2. The corrosion of high-silicon irons is hardly affected by the cooling rate of the specimen for both sulphuric and hydrochloric acids.

According to the microscopic examination, the microstructure of the specimens cast in the metal mould consists of very fine eutectic graphite as shown in Photo. 1 or 5, and that of the specimens cast in the shell and green sand mould consists of the mixture of eutecitc and flaky or rosette graphite of medium size as shown

in Photos. 2 and 3, same as in the standard specimens of ordinary high-silicon irons; and that of the specimens cast in the hot dry sand mould consists of large flaky graphite as shown in Photo. 4. A greater degree of cooling rate brings about a greater tendency for diminishing the size of graphite and for the formation of a dendritic pattern.

The changes in the transverse strength and Rockwell hardness with the varied rates of cooling can be explained by the change in the graphite structure illustrated in Photos. 1-4.

- (B) Experiments on Effect of Casting Temperature
 - (1) Preparation of Specimen and Method of Experiment

The effects of the casting temperature were examined upon the several specimens of ordinary



Fig. 4 Dimensions of the moulds used for the preparation of the metallographic specimens.

high-silicon iron which were cast at 1250 and 1350°C in the shell mould as usual. Further, in order to investigate the effects of the casting temperature and of the carbon content upon the microstructure of high-silicon iron, the two alloys containing about 0.2 pct and about 0.7 pct carbon were melted and heated to 1450° C, then poured into the metal mould and the shell mould shown in Fig. 4 at 1400, 1350, 1300, and 1250°C. Small amounts of the melt were also dropped directly into water at 1300 and 1250°C. The metal mould, used in this experiment, is made of steel and has a much greater mass compared with the specimen. Consequently, it has a greater cooling effect than the metal mould which was used in experiment (A). The chemical analysis of the alloys was as follows; 14.15 pct Si, 0.24 pct C and 14.53 pct Si, 0.72 pct C.

(2) Experimental Results

The effect of the casting temperature on the mechanical properties is given in Table 2 and shown in Figs. 5 and 6. The data show that the transverse strength

Specimen	Composition (%)		Casting Tempera- ture Transverse Strength		Deflection	Rockwell Hardness	Type & Size of Graphite according to	
Number Si		С	(°C)	(kg/mm^2)	(mm)	(HRC)	ASTM	
-	14.71	0.71	1350	19.8 	0.47	41.1 39.5 38.7 39.8	D-8 A-5	30% 70%
L			1250	23.5 23.7 23.6	0.52 0.53 0.53	43.5 42.2 41.9 42.5	D-8 A-5	50% 50%
	14.77	.77 0.59	1350	22.8 22.8	0.48 0.48	43.4 43.1 43.2 43.2	D-8 A-5	60% 40%
2	14.77		1250	25.7 25.7	0.51 — — 0.51	45.8 45.8 43.2 44.9	D-8 A-5	70% 30%
	14.77	0.52	1350	23.8 25.0 24.4	0.51 0.53 0.52	44.8 45.8 45.5 45.4	D-8 A-5	60% 40%
3	14.77		1250	26.1 25.0 25.6	0.57 0.56 0.57	45.2 44.8 44.5 44.8	D-8 A-5	70% 30%
	14 19	3 0.61	1350	22.0 23.1 22.6	0.50 0.54 0.52	42.0 41.4 42.0 41.8	D-8 A-5	40% 60%
4	14.18		1250	25.4 25.4	0.55 0.55	42.0 41.8 42.1 42.0	D-8 A-5	50% 50%

Table 2. Effects of Casting Temperature.

The figures in Gothic type indicate the average values.



Fig. 5 Effects of casting temperatureon the mechanical properties of high-silicon irons.



Fig. 6 Deflection-load curves of the specimens cast at different temperatures.

is somewhat higher in the specimens cast at the lower temperature and specimen No. 1, having the highest carbon content, is most sensitive to this change. This may be expected from the effect of the casting temperature on the microstructure mentioned below. The Rockwell hardness is hardly affected by the casting temperature in specimens No. 2, 3 and 4; but in specimen No. 1, a decrease in hardness caused by the growth of the graphite structure with higher casting temperature is seen as shown in the last column of Table 2. The deflection vs. load curves are shown in Fig. 6, in which the effect of casting temperature cannot be observed.

The results of microscopic examination are shown in Photos. 6-17. In the specimens cast in the metal mould, the effect of carbon content on the microstructure is clearly observed but the effect of casting temperature is hardly seen; i.e., in the specimen containing about 0.2 pct of carbon, carbon all exists as the silico-carbide phase at the α grain boundary as shown in Photos. 6 and 7 regardless of the casting temperature; while in the specimen containing about 0.7 pct of carbon, carbon exists partly as the silico-carbide phase and partly as very fine granular graphite as shown in Photos. 10 and 11 also regardless of the casting temperature. It seems that this fine granular graphite in dendritic dispersion is formed by breaking down of the silico-carbide during the cooling. Morrogh and Williams⁵) proved that the undercooled graphite occuring in the high-silicon iron containing 10 pct of silicon was formed as the result of decomposition of carbide after the eutectic solidification. In fact, the microstructure of the 0.7 pct C specimen, water quenched, shows the boundary silico-carbide phase to increase and graphite to decrease. In the 0.2 pct C specimen, water quenched, the entire carbon, of course, exists as the silico-carbide phase. From these results, it may be said that the high-silicon iron having a lower carbon content has a greater tendency for the formation of the silico-carbide phase under the same condition of melting and casting. Since the silico-carbide phase decreases the transverse strength and increases the hardness of high-silicon iron as seen in the specimens containing about 10 pct silicon,¹⁾ if the cooling rate is too high or the carbon content is too low for a rapid cooling condition and the fine granular graphite in dendritic dispersion, is not produced, the transverse strength will decrease.

In the specimens cast in the shell mould, the microstructure is affected by the carbon content and casting temperature. In the low corbon specimens, graphite exists in the form of fine granules or very short flakes arranged at the α grain boundary as shown in Photos. 8 and 9, and the size of the network of graphite becomes larger with increasing casting temperature. In the high carbon specimens, the effect of casting temperature is more remarkable than in the low carbon specimens; Photos. 12-15 shows that the graphite structure becomes coarser with increasing casting temperature. The increase of casting temperature naturally results in the decrease of cooling rate.

The silico-carbide phase mentioned above decomposed yielding graphite when it was annealed at 1000 °C for 5 hr. as shown in Photos. 16 and 17 although it was not affected by annealing at 800 °C for 4 hr.

III. Effects of Annealing

(1) Preparation of Specimen and Method of Experiment

The melt of ordinary high-silicon iron was poured at 1300°C into a shell mould

to produce the casting of the size shown in Fig. 7. The composition of the specimens is given in Table 3.

The annealing procedure was as follows; several test bars were put in the center of a porcelain tube of 50mm in inner diameter in an electric furnace and were heated to the annealing temperatures of 400, 600, and 800°C, respectively. After the specimens were kept at each annealing temperature for 4 hr., the electric current was cut off to allow them to cool slowly in the furnace.



Fig. 7 Dimensions of the specimen used in the experiment of annealieg.

The specimens were then ground with a No. 80 carborundum wheel and were finished into rods of 8.5mm in diameter and 110mm in length. They were tested at the span length of 90mm with a transverse testing machine of the maximum load of 200 kg and then submitted to hardness tests, corrosion tests and microstructure tests in the usual manner.

(2) Experimental Results

The results of the experiment are given in Table 3 and shown in Fig. 8. The transverse strength seems to increase with increasing annealing temperature but the Rockwell hardness is not affected by annealing. A higher value of the Rockwell hardness for specimen No. 3 in Table 3 may be caused by a higher silicon content and a lower carbon content.

The corrosion resistance to sulphuric acid is reduced more by annealing at higher temperature. It is shown clearly in specimen No. 3. The corrosion



Photo. 7×1000Photo. 8×180Photo. 9×400Same alloy as in Photo. 6,
cost in metal monld at
1250°C.Same alloy as in Photo. 6,
cast in shell mould at
sine graphite.Same as Photo. 8,
fine graphite.



About 0.7 C alloy, cast in

metal mould at 1350°C.

 $\times 1000$ Photo. 11

Same as Photo. 10.



Photo. 12 $\times 180$ Same alloy as in Pnoto. 10, cast in shell mould at 1250°C.



Photo. 13 Same alloy as in Photo. 12, cast in same monld at cast in same mould at 1300°C.

 $\times 180$ Photo. 14 Same alloy as in Photo. 12, 1350°C.

Photo. 15 $\times 180$ Same alloy as in Photo. 12, cast in same mould at 1400°C.



Photo. 16 Same as Photo. 6.

Photo. 17 $\times 400$ Same specimen as in Photo. 16, after annealing at $1000^{\circ}C$ for 5 hr.

The microsections appearing in Pnoto. 1-17 were all etched in the sodium picrate reagent at sbout 85°C.

Specimen	Composition (%)		Annealing Tem-	Transverse Strength	Rockwell Hardness	Corrosion Loss in Weight (mg/cm ² /4hr.)		Type & Size of Graphite		
Number	Si	С	(°C)	(kg/mm^2)	(HrC)	$\begin{array}{c} 1:10\\ H_2SO_4 \end{array}$	1:1 HCl	ASTM		
			(as cast)	27.2, 26.5, 26.1, 26.1, 26.1 26.4	41.4 41.2 43.5 42.0	4.25 4.18 4.17 4.20	3.06 3.07 3.04 3.06	D-7 20% D-6 80%		
	14.54	0.55	400	26.9, 26.1, 26.1, 26.1, 25.7 26.2	42.1 42.2 41.5 41.9	4.07 4.47 4.04 4.19	3.11 3.20 3.02 3.11	D-7 20% D-6 80%		
T			600	28.4, 27.6, 27.2, 27.2, 26.9 27.5	42.0 41.9 43.5 42.5	4.14 4.22 4.58 4.31	4.18 3.74 3.90 3.94	D-7 20% D-6 80%		
			800	31.3, 29.5, 28.4, 28.0, 28.0 29.0	40.1 40.4 41.9 40.8	4.84 4.69 5.36 4.96	4.93 4.88 5.17 4.99	D-7 20% D-6 80%		
2	15.03	0.59	(as cast)	29.1, 27.6, 27.6, 26.9, 26.9 27.6	40.9 40.1 38.6 39.9	3.92 3.80 3.92 3.88	3.68 3.34 3.35 3.46	D-7 15% D-6 80% A-5 5%		
			400	29.5, 29.1, 28.7, 27.6, 26.9 28.4	39.9 40.0 39.2 39.7	4.07 3.68 3.45 3.73	3.27 3.51 3.09 3.29	D-7 15% D-6 80% A-5 5%		
			600	31.3, 31.0, 29.9, 29.5, 29.1 30.2	39.9 38.2 40.1 39.4	4.18 4.88 4.25 4.44	4.09 4.34 4.62 4.35	D-7 15% D-6 80% A-5 5%		
			800	32.8, 32.1, 31.3, 30.2, 29.5 31.2	40.3 38.4 39.8 39.5	4.11 4.03 4.56 4.23	5.71 5.23 5.52 5.49	D-7 15% D-6 80% A-5 5%		
3	15.23				(as cast)	32.5, 31.3, 29.5, 29.1, 29.1 30.3	49.0 49.3 49.0 49.1	1.75 1.98 1.57 1.77	2.86 2.81 2.87 2.85	D-8
		23 0.43	400	35.0, 34.3, 32.8, 32.8, 32.5 33.5	48.8 48.4 49.1 48.8	2.02 1.65 1.88 1.85	3.02 2.89 2.89 2.93	D-8		
			600	34.7, 33.2, 32.5, 31.3, 29.9 32.3	48.9 48.8 48.9 48.9	3.42 3.54 3.54 3.54 3.50	3.19 3.29 3.17 3.22	D-8		
				800	35.4, 32.1, 34.0, 30.2, 29.9 32.3	48.0 48.0 49.1 48.4	4.67 4.19 4.08 4.31	3.91 3.46 3.60 3.66	D-8	

Table 3. Effects of Annealing

The figures in Gothic type indicate the average values.



resistance of high-silicon irons.

resistance to hydrochloric acid shows a similar tendency and is reduced to a considerable extent by annealing at 600 and 800°C. The reason why the corrosion loss of specimen No. 3 is small is attributable to its comparatively higher silicon content.

No change in the microstructure was observed for the specimens annealed at a temperature below 800° C for 4 hr. The increase in transverse strength mentioned above is probably due to the relief of internal casting stress as in the case of common gray cast iron.⁶)

IV. Summary

In the present study the influences of the cooling rate and annealing on the properties of high-silicon irons were investigated and the results obtained are summarized as follows:

(1) The mechanical properties of high-silicon irons are influenced by the cooling rate of castings. A rapidly cooled casting, having a structure which consists of very fine eutectic graphite, has a very high transverse strength and a high Rockwell hardness but it has a low ductility. As the cooling rate of casting becomes smaller, the graphite structure grows and, consequently, the transverse strength and the Rockwell hardness become lower and the ductility becomes higher. The effect of the cooling rate on the corrosion resistance cannot be observed.

(2) Castings poured at higher temperatures have a lower cooling rate, which results in a coarser graphite structure and, consequently, influences the mechanical properties.

(3) The quenching effect on the graphite structure is greater in the lowcarbon alloy than in the high-carbon alloy; thus, the silico-carbide phase is more easily formed in the former than in the latter under the condition of very rapid cooling.

(4) The silico-carbide phase is broken down yielding fine graphite by annealing at a high temperature such as 1000°C.

(5) Annealing at 600-800°C relieves the internal casting stress of as-cast alloys which results in the increase of the transverse strength; however, the corrosion resistance is decreased.

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