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EFFECT OF SILICON ON THE SOLIDIFICATION PROCESS OF HIGH CHROMIUM CAST IRONS

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Abstract: This study investigates the effect of silicon on the microstructure of high-chromium white cast iron. The alloys were examined in the as-cast and heat-treated conditions. The influence of silicon additions on the size of eutectic carbides and on the matrix, structure was analyzed.

Keywords: austenite, wear resistance, impact toughness, brittleness, carbide

Introduction

High-chromium (Hi-Cr) white cast irons contain 11–30 wt.% chromium and 1.8–3.6 wt.% carbon [1]. Their microstructure typically consists of hard primary and/or eutectic carbides in an austenitic matrix. Owing to their high wear resistance, these alloys are widely used in mining, mineral processing, and the cement, pulp and paper, and steel industries. Both the eutectic carbides and the surrounding matrix contribute to their wear resistance and strength. In addition, heat treatment of the as-cast austenitic matrix produces a structure of martensite and retained austenite with fine secondary carbide precipitates.

For different abrasive wear applications, the microstructure of these cast irons can be tailored, with the carbide volume fraction varying from 10 to 45% [2]. As-cast austenitic high-chromium cast irons show adequate abrasive wear resistance, but the best properties are obtained after heat treatment that transforms the matrix into martensite. Refining the morphology of the eutectic carbides can increase both the toughness and the wear resistance of white cast irons under sliding wear. Rapid cooling or low melt superheat promotes carbide nucleation and restricts carbide growth, whereas slow cooling produces coarser eutectic structures.

The aim of this study is to investigate the effect of silicon additions on the microstructure of 17 wt.% Cr high-chromium cast iron cast in permanent molds. Published data on the effect of silicon on the microstructure of high-chromium cast irons are contradictory and remain insufficiently understood. Some studies report that increasing the silicon content refines the carbides and alters their morphology, whereas others suggest that silicon may inhibit carbide nucleation without affecting carbide growth [3]. Nevertheless, some researchers argue that silicon does influence the growth of eutectic M_7C_3 carbides, since a silicon content of 1.5 wt.% has been shown to reduce the tendency of the eutectic carbides to form an interconnected network.

Experimental study

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High-chromium cast irons were produced by remelting a base alloy with silicon additions and casting the melt into permanent molds, giving seven alloys of different chemical composition. Part of the castings was heat-treated at 1273 K for 45 min in a nitrogen atmosphere and then cooled to room temperature. The secondary dendrite arm spacing (SDAS) and the carbide volume fraction were measured by optical microscopy on deep-etched as-cast specimens. The austenite content of the as-cast alloys and the retained austenite content of the heat-treated specimens were determined by X-ray diffraction.

Segregation in the as-cast condition was studied by energy-dispersive X-ray spectroscopy (EDS) on a scanning electron microscope equipped with an Oxford Instruments eXL EDS system. Carbon could not be quantified reliably by EDS because of its low atomic number. Carbon was therefore excluded from the analysis, which introduced some error into the normalized elemental compositions. Transmission electron microscopy (TEM) was also performed, and the microhardness of the matrix was measured.

Fracture toughness was determined by three-point bend tests on a Hounsfield universal testing machine. The fracture surfaces were then examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Results

The chemical compositions of the cast iron specimens are given in Table 1. Apart from silicon, the alloys have similar compositions, and the sulfur and phosphorus contents are low. The differences in microstructure can therefore be attributed to the effect of silicon.

Table 1.

Chemical composition (wt%)

Elements	Content (%)	Accuracy
Cr	16.80	±0.2
C	2.56	±0.01
Mo	1.93	±0.2
Ni	1.77	±0.2
S	0.005	±0.001
P	0.005	-
Fe	balance	

The alloy under study is a hypoeutectic high-chromium cast iron. Its microstructure consists of primary austenite dendrites and an austenite–M_7C_3 eutectic, with a thin martensite layer at the

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carbide/matrix interfaces. The chromium- and carbon-rich carbides draw these elements from the adjacent austenite, forming a chromium- and carbon-depleted zone in the matrix next to the carbides. Because of its low alloying element content, this zone can transform to martensite on cooling. XRD analysis shows that increasing the silicon content destabilizes the as-cast austenitic matrix, and cementite appears at the highest silicon contents. This indicates that, on cooling to room temperature, the austenite partially transforms into ferrite, pearlite and martensite, with some austenite retained.

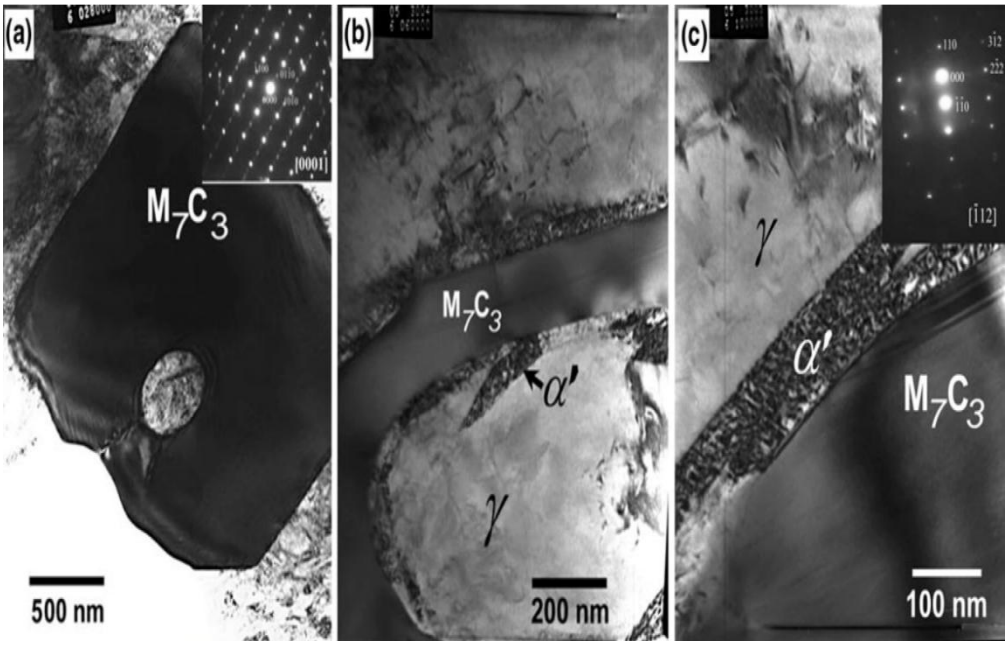


Fig. 1 - Bright-field TEM micrographs of the matrix: (a) cross-section of a hollow eutectic carbide and the corresponding selected area electron diffraction (SAED) pattern; (b) martensite laths at the carbide/austenite interface; (c) dark-field image of the martensite lath shown in (b).

Pearlite formation in high-chromium cast irons and the role of silicon. The results show that increasing the silicon content reduces the chromium concentration in the matrix, from 11 wt.% in the base alloy to 7 wt.% in the alloy containing 5 wt.% Si. EDS analysis also showed that silicon segregates to the matrix. The lower matrix chromium content can be explained by the effect of silicon on carbon solubility. Silicon dissolved in the melt reduces the solubility of carbon and thus promotes the formation of eutectic M_7C_3 carbides [5]. As a result, more chromium is bound in the carbides and less remains in the matrix. A small amount of pearlite was observed in the alloy containing 3 wt.% Si, but no M_3C carbide was detected by XRD. At 4 and 5 wt.% Si, the solidification structure changes markedly. The alloys become hypereutectic, with large primary hexagonal M_7C_3 carbides forming first during solidification [5].

The XRD patterns of the alloy containing 5 wt.% Si show M_3C carbide and distinct α-phase peaks. The matrix consists mainly of ferrite and/or martensite. In addition to the eutectic carbides, extensive carbide-free regions were observed, which are presumed to be ferrite.

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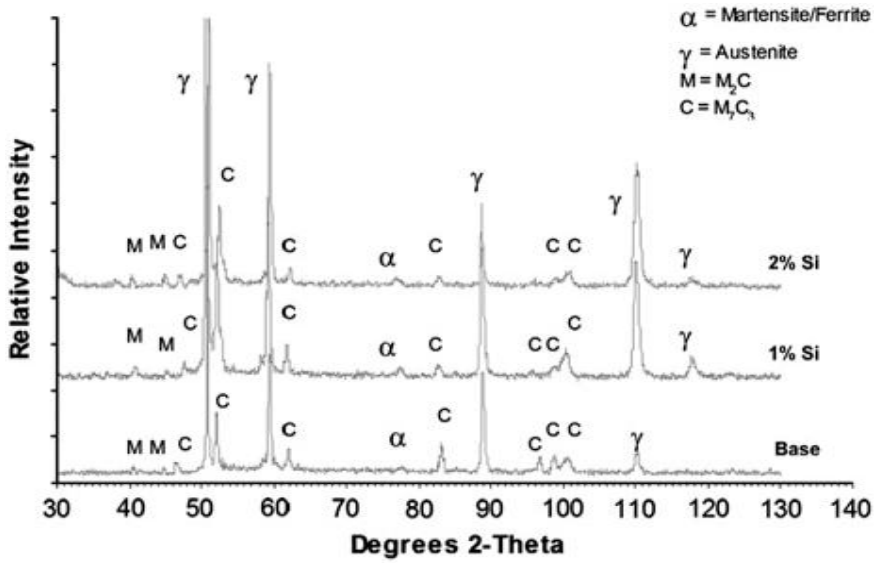


Fig. 2. XRD patterns of the as-cast Hi-Cr cast irons: the base alloy and alloys containing up to 2 wt.% Si. No significant changes in phase composition were observed.

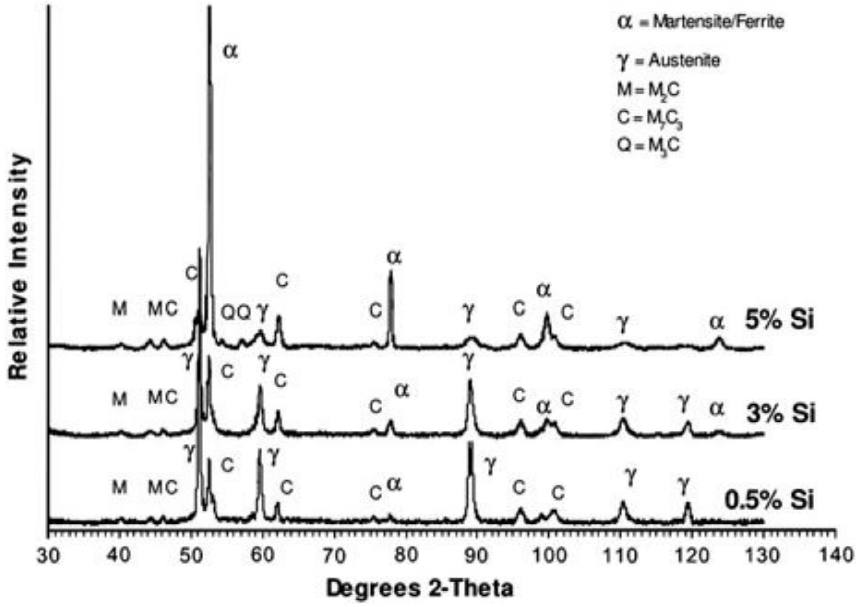


Fig. 3. XRD patterns of three as-cast Hi-Cr cast irons with different silicon contents. Note the increase in the intensity of the α peaks and the decrease in the γ peaks with increasing silicon content, as well as the presence of M_3C carbide in the cast iron containing 5 wt.% Si.

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Effect of Silicon on Phase Composition

The carbide volume fraction (CVF) of the Hi-Cr cast irons increases markedly with increasing silicon content. The CVF depends on several factors, including the carbon content, the content of carbide-forming elements and the type of carbides formed. For the base alloy, the empirical equation proposed by Maratray, CVF (%) = 12.33(%C) + 0.55(%Cr) − 15.2, gives a CVF of about 26 %. This agrees well with the measured value of 24 % for the silicon-free alloy. The CVF rises to 32 % in the alloy containing 5 wt.% Si (Fig. 4). The larger carbide fraction correspondingly reduces the fraction of austenite. This effect can be explained by silicon lowering the equilibrium solubility of carbon in austenite in Fe–C–Si alloys and increasing the activity of carbon in the melt during solidification. The matrix of the base alloy consists predominantly of austenite, whereas at higher silicon contents it also contains ferrite and regions of austenite and martensite. The decrease in austenite content with increasing silicon content is attributed to the ferrite-stabilizing effect of silicon.

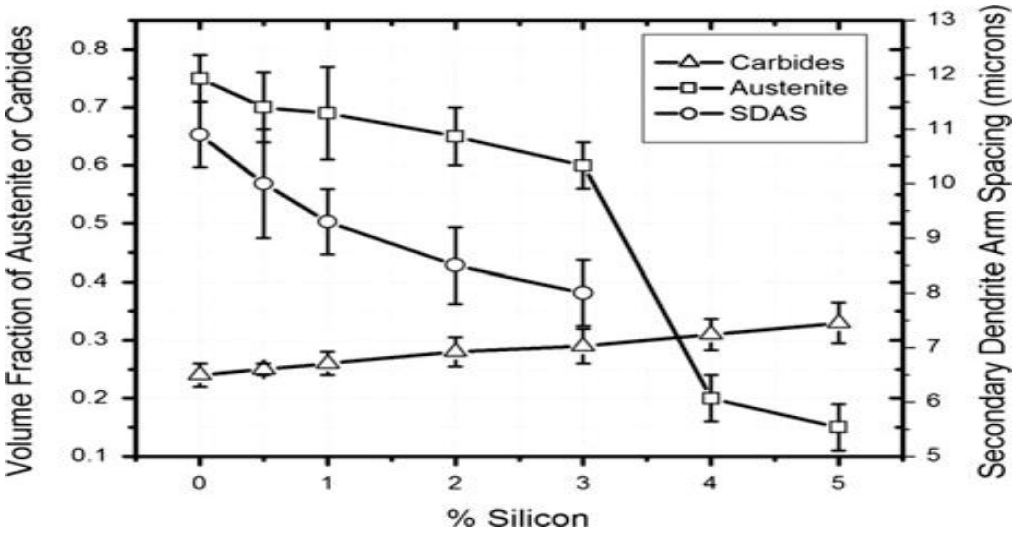


Fig. 4 - Carbide and austenite volume fractions and secondary dendrite arm spacing (SDAS) as a function of silicon content.

Silicon additions reduce the secondary dendrite arm spacing (SDAS) of the Hi-Cr cast irons from 11 to 8 µm, which indicates refinement of the solidification structure. At higher silicon contents, however, the alloys become hypereutectic, and the structure is no longer dendritic (Fig. 5). SDAS is known to depend on the solidification rate, chemical composition and solidification range [6]. Since all alloys were cast under the same conditions, the observed refinement can be attributed mainly to the effect of silicon on composition, possibly through a narrower solidification range.

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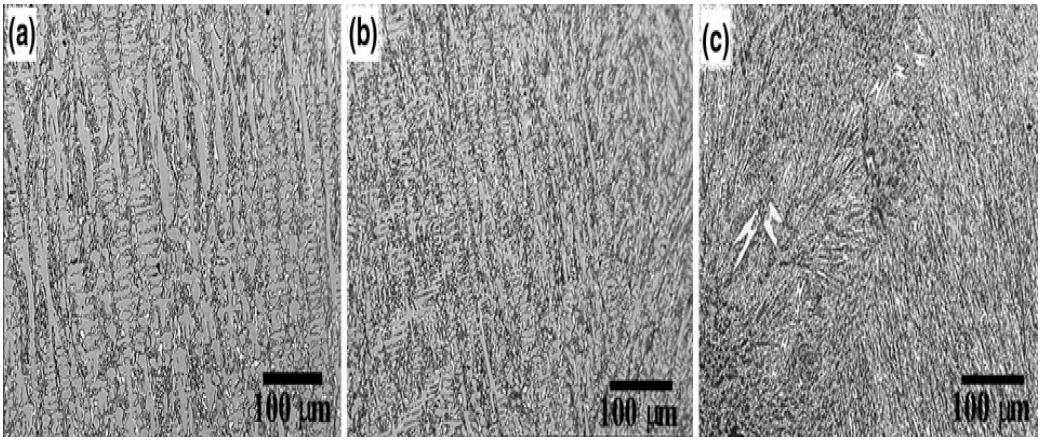
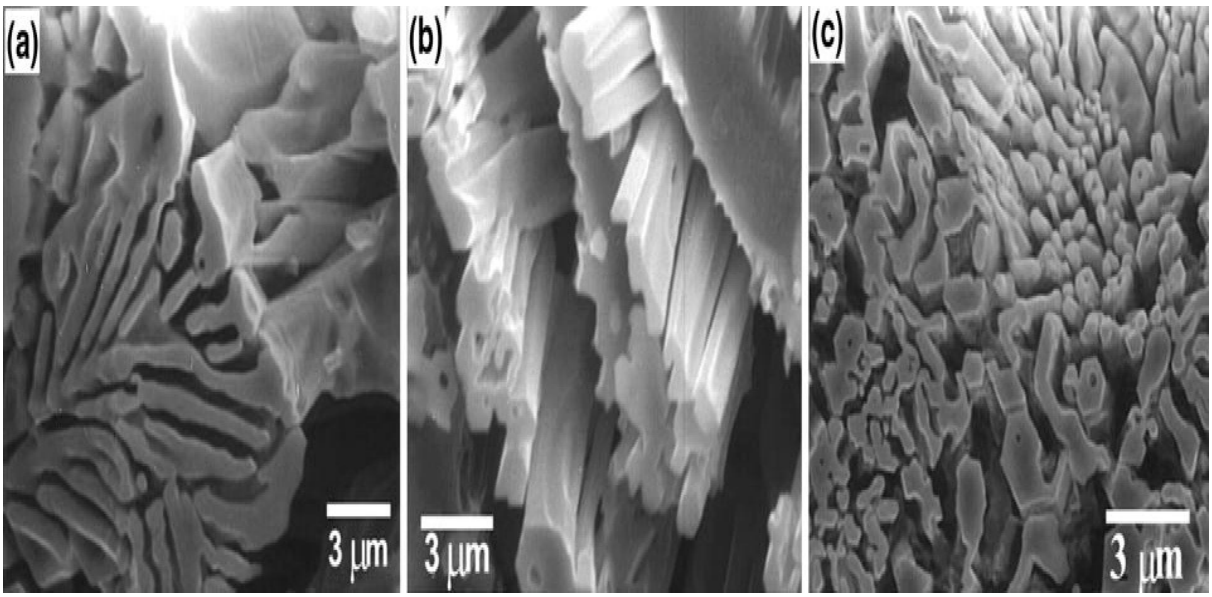


Fig. 5. Fig. X. Optical micrographs showing the change in microstructure with silicon content: (a) base alloy; (b) 2 wt.% Si; (c) 5 wt.% Si.

Eutectic Carbides: Morphology and Size

In the alloys containing up to 3 wt.% Si, the eutectic carbides appear as rods, plates and more complex shapes, with rod-like carbides becoming more common as silicon is added. As the silicon content increases to 3 wt.%, the carbide size decreases and the aspect ratio increases from 0.31 to 0.66. In the alloys containing 4 and 5 wt.% Si, this morphology is no longer observed. Instead, long interconnected rods predominate, and the carbides become coarser and more irregular. Because of this irregular morphology, the carbide size in these alloys could not be measured accurately.



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Fig. 6. SEM micrographs of deep-etched specimens showing the morphology of eutectic carbides: (a) ledeburite-like carbides in the base alloy; (b) rod- and plate-shaped carbides in the base alloy; (c) rod-shaped carbides in the cast iron containing 2 wt.% Si.

The experimental Hi-Cr cast irons show the typical lamellar, petal-like and rod-like morphologies of eutectic carbides (Fig. 6), with rod-like carbides predominating in the silicon-containing alloys. Silicon additions modified the eutectic structure: up to 2 wt.% Si, the carbides became finer and more regular in shape. In the alloys containing 4 and 5 wt.% Si, long, highly interconnected carbide bands predominated. The modifying effect of alloying elements in Hi-Cr cast irons is related to their segregation behavior.

The partition coefficient of such elements during eutectic solidification is low, so they accumulate in the liquid ahead of the solid/liquid interface. At a microscopically planar interface, their concentration is not uniform, with the maximum located ahead of the center of each carbide plate. This solute enrichment lowers the local equilibrium (liquidus) temperature and thus restricts carbide growth. In addition, the Fe–Si bond is stronger than the Fe–C bond, so as the silicon content increases, more carbon is rejected from the primary austenite into the liquid. This reduces the undercooling required for carbide formation. Silicon also acts as a carbide growth inhibitor, producing thinner and shorter rod-like carbides as well as fine, isolated hexagonal carbides. At high cooling rates, coupled growth occurs, which reduces the carbide spacing and increases carbide interconnectivity.

Conclusion

Silicon additions modify the solidification structure of high-chromium cast iron. By raising the carbon equivalent, silicon shifts the alloy from hypoeutectic to hypereutectic. Silicon increases the volume fraction of eutectic carbides and changes the matrix: it promotes the transformation of austenite to martensite and increases the microhardness of austenite and the bulk hardness of the alloy. Silicon also reduces the chromium and carbon contents of the austenite, which decreases the volume of secondary carbide precipitates. The highest fracture toughness was obtained in the cast iron containing 2 wt.% Si, which is attributed to the refinement of the structure and the formation of finer, more rounded carbides.

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