



# Grain refinement of 25 wt% high-chromium white cast iron by addition of vanadium

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## Synopsis

Mill liner wear is a major cost item in the mining industry and there is continuous research to prolong the life of the liners. Over the years it has become apparent that even though high-chromium white cast irons are highly efficient as abrasion-resistant materials, a combination of wear resistance and fracture strength remains difficult to achieve. Increasing the hardness of the high-chrome white cast iron (HCWCI), which improves the resistance to abrasion wear, is often accompanied by a deterioration in fracture strength. Operational conditions inside the mill require that the liner should be made of highly wear-resistant material with some fracture strength. Vanadium additions ranging from 0.2 to 3 wt% were made to HCWCI in an attempt to refine the microstructure. It was found that an increase in vanadium content promotes grain refinement. A content of 1.5-3 wt% gave the best results as measured by the maximum breaking strength.

## Keywords

HCWCI, mill liners, grain refinement, hardness.

## Introduction

Over the years it has become apparent that even though high-chromium white cast irons are highly efficient abrasion-resistant material, a combination of excellent wear resistance and fracture strength remains difficult to achieve. The exceptional wear resistance of high-chromium white cast iron (HCWCI) is attributed to hard chromium carbides embedded in an austenitic/martensitic/pearlitic matrix. When the chromium contents exceed 12 wt%, interconnected  $MC_3$ -type carbides of conventional cast irons are replaced by rod-shaped and isolated  $M_7C_3$  carbides (Powell, 1980), leading to an improvement in the impact toughness, ductility and fatigue resistance. However, the main  $M_7C_3$  carbides in HCWCI are hard and brittle and can provide an easy path for crack propagation. This limits the applications of HCWCI, particularly in severe impact conditions. Most operations involving HCWCI are in crushing and grinding and the life of a part/liner is limited by its wear resistance. However, improving the wear resistance of HCWCI comes at the cost of a significant reduction in fracture strength. Concerns about premature failure of HCWCI

mill liners in the mining industries prompted a study to improve the wear resistance and mechanical properties of HCWCI.

Addition of alloying elements to HCWCI can significantly change the microstructure, which may result in adequate combinations of wear resistance and fracture strength (Powell, 1980; Filipovic *et al.*, 2013). Most studies have shown that eutectic carbides influence the fracture strength of the white cast iron and by controlling the morphology of the carbides and the matrix structure, can lead to major improvements in the fracture strength (Filipovic *et al.*, 2013, 2014; Filipovic, 2013). Research and development is ongoing on the effect of microalloying, heat treatments and different casting techniques on the properties of HCWCI. This is aimed at widening the application of these alloys by extending their service life and minimizing the maintenance cost through addition of strong carbide formers such as vanadium, tungsten, niobium and titanium (Liu *et al.*, 2005; Radulovic *et al.*, 1994; Sawamoto, Ogi and Matsuda, 1986; Anijdan *et al.*, 2007; Chung *et al.*, 2009; Lu, Soda and Mclean, 2003). Strong carbide-forming elements like vanadium, tungsten, niobium and titanium may also be added to improve the mechanical properties (Filipovic, 2013; Liu *et al.*, 2005; Radulovic *et al.*, 1994).

Addition of vanadium to HCWCI can form vanadium carbides, which are much harder than  $M_7C_3$  carbides and may lead to strengthening of the austenitic matrix and improve the fracture strength of the HCWCI (Liu *et al.*, 2005). The hardness of vanadium carbides differs with composition; their round morphology reduces splitting to the matrix and

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improves the fracture strength due to formation of a fine-grained microstructure (Nelson, 2010; Liu *et al.*, 2005). Dupin and Schissler (1984), as quoted by Filipovic (2013), indicated that the addition of as little as 1% vanadium does not produce any vanadium carbides, but refines the eutectic carbides. This conclusion is supported by Bedolla-Jacuinde (2001), who indicated that even the addition of 2 wt.% vanadium did not form any vanadium carbides but increased the volume fraction of the  $M_7C_3$  carbides (Filipovic, Kamberovic and Korac, 2011).

Most of the work to date has been aimed at improving the tough of HCWCI, mostly on the hypereutectic alloys. The research was centred on modifying the shape of carbides but there has been no breakthrough. The work in this current study focuses on improving the fracture strength of hypoeutectic white cast iron by the addition of vanadium.

## Experimental procedure

### Melting and casting

Melting of the HCWCI alloy was accomplished in a medium frequency induction furnace with a capacity of about 150 kg. The molten metal was poured into a sand mould and allowed to cool to room temperature. The chemical compositions of the alloys produced are given in Table I. The test materials produced for this project consisted of HCWCI in the form of  $50 \times 100 \times 500$  mm flat rectangular test bars (*i.e.* thickness  $\times$  width  $\times$  length) as shown in Figure 1a.

The alloys were examined for surface defects before proceeding with testing and there was no indication of defects (Figure 1b). The specimens were then polished and etched with 3% Nital. The microstructural analysis was carried out using an Olympus PGM optical microscope equipped with Analysis Image software and a scanning electron microscope

Brinell hardness measurements were performed through the cross-sections of the as-cast test samples, using a load of 750 kg. The measurements were taken from the surface to the centre of the rectangular test sample to ascertain if there were any hardness gradient changes within the test sample. It was found that the difference was minimal. Bending tests are intended for brittle materials when the scope of test is to determine the strength of material. To determine the bending strength  $Q_{max}$ , the beam must be so proportioned that it will not fail in shear or by lateral deflection before reaching its ultimate flexural strength. Hence, for a rectangular part in a three-point bending test, bending strength is the highest stress at the moment of rupture. Usually, long specimens with higher length to depth ratio ( $L/h > 10$ ) are recommended.

Table I  
Alloy compositions

Alloy ID	Composition
Reference	ASTM A 532 Class III
Alloy 1	ASTM A 532 Class III + 0.2-0.8V
Alloy 2	ASTM A 532 Class III+ 0.8-1.5V
Alloy 3	ASTM A 532 Class III+1.5-3.0V

## Results and discussion

### Effect of vanadium on the microstructural evolution

The microstructure of the as-cast reference alloy is shown in Figure 2a. The microstructure consists of primary austenite dendrites surrounded by a eutectic mixture of carbide particles and austenite. In hypoeutectic cast iron, solidification proceeds with austenite, eutectic vanadium carbides (VC) and finally  $M_7C_3$  carbides. It can be seen from Figure 2a that the  $M_7C_3$  carbides are of a rod and needle type of morphology and that the stress concentration factor will play a larger role when the material is exposed to an impact. Addition of vanadium to HCWCI has changed the needle-shaped  $M_7C_3$  to an isotropic morphology. This change in the carbide morphology may play a critical role in determining the fracture strength of the HCWCI.

The scanning electron microscope analysis of the alloy in the as-cast condition and corresponding EDS composition maps are shown in Figures 3 to 5. One can see that the element distributions are consistent with the identified phases in the microstructure. The microanalysis of the phases shown in Table II reveals that V substituted Cr and Fe in  $M_7C_3$  up to about 2.5 wt% V. V was also dissolved into the austenitic matrix, reaching a maximum of about 0.3 wt%. The presence of vanadium carbide particles in  $M_7C_3$ , which would result in significant refinement of the  $M_7C_3$  carbides by acting as the heterogeneous substrates of  $M_7C_3$  carbides, was

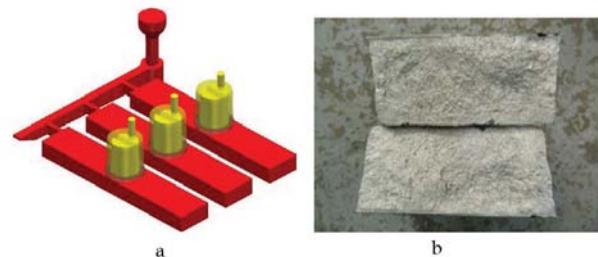


Figure 1—Pattern design that was used to produce test bars: (a) simulated pattern, (b) actual casting with no defects

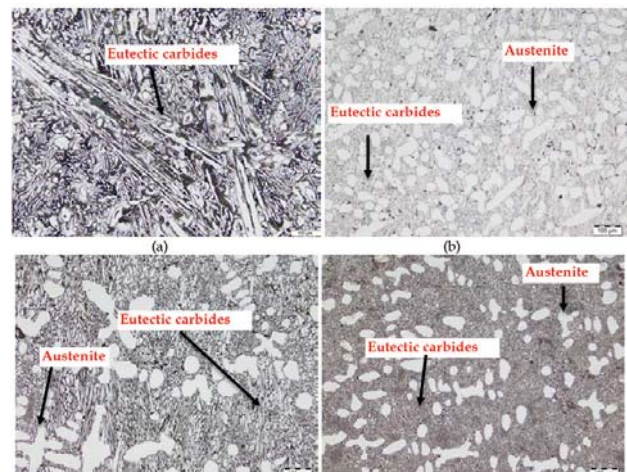


Figure 2—Micrograph of the (a) Reference alloy, (b) 0.2-0.8%V, (c) 0.8-1.5%V and (d) 1.5-3%V showing  $M_7C_3$  carbides in an austenite matrix

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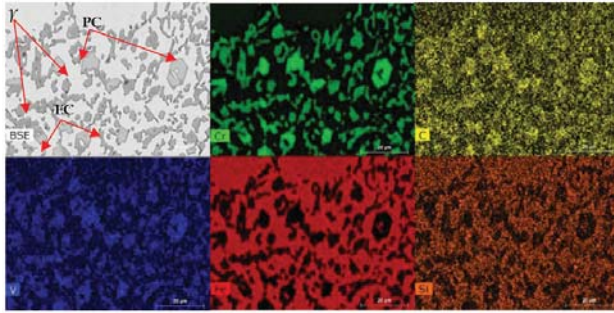


Figure 3—SEM-EDX mapping of the as-cast HCWCI with addition of 0.2-0.8%V. PC = primary carbides, EC, eutectic carbides and  $\gamma$  = austenite

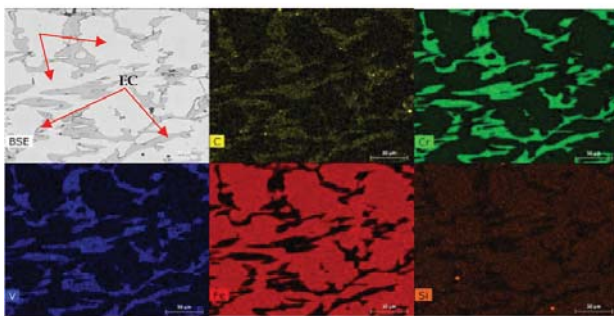


Figure 4—SEM-EDX mapping of the as-cast HCWCI with addition of 0.8-1.5%V. EC, eutectic carbides and  $\gamma$  = austenite

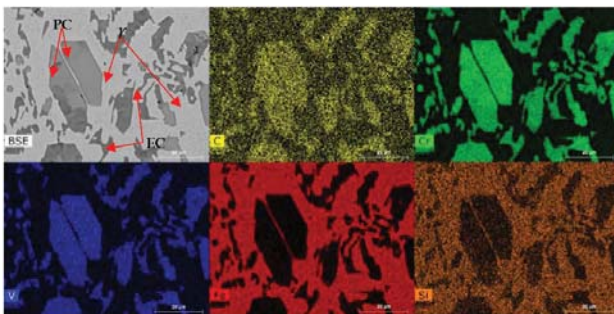


Figure 5—SEM-EDX mapping of the as-cast HCWCI with addition of 1.5-3.0%V. PC = primary carbides, EC, eutectic carbides and  $\gamma$  = austenite

Table II

**Composition (in wt%) of HCWCI-V phases determined by EDS**

Alloy	Phases	C	V	Cr	Fe
ASTM A 532 Class III + 0.2-0.8%V	M <sub>7</sub> C <sub>3</sub>	1.2	0.6	67.7	30.5
	Matrix	1.1	0.1	16.5	81.4
ASTM A 532 Class III+ 0.8-1.5%V	M <sub>7</sub> C <sub>3</sub>	1.5	0.3	68.4	29.6
	Matrix	0.2	0.25	19.4	79.2
ASTM A 532 Class III+1.5-3.0%V	M <sub>7</sub> C <sub>3</sub>	2.6	2.5	60.3	34.1
	Matrix	1.0	0.3	13.4	83.5

Trace elements: 0.5% V (Matrix 0.9), 1% V (Matrix 0.9) (M<sub>7</sub>C<sub>3</sub> 0.2) and 2% V (Matrix 1.8) (M<sub>7</sub>C<sub>3</sub> 0.5)

not observed. The results are in agreement with those of Dupin and Schissler (1984), who did not detect vanadium carbide formation in HCWCI with 1% V additions. This may be due to the lower vanadium content as reported by Sawamoto *et al.* and the literature has indicated that vanadium carbide can form when the V content exceeds 5% (Sawamoto, Ogi and Matsuda, 1986). This is in contradiction to the work by Filipovic (2013), which indicated that vanadium-rich carbides are found in Fe-Cr-C-V irons containing 1.19–4.73% V.

However, the grain refinement effect of M<sub>7</sub>C<sub>3</sub> carbides with an increase in vanadium content can be explained by their influence on the eutectic solidification temperature. Filipovic, Kamberovic and Korac (2011) indicated that the addition of V decreased the liquidus temperature and increased the eutectic temperature, thus the eutectic solidification temperature interval was decreased. It has been previously reported that the carbides' spacing increases with the increase in the eutectic temperature range, so the decreasing eutectic temperature interval effectively reduced the carbides' spacing due to the addition of V (Ogi, Matsubara and Matsuda, 1982).

### Effect of vanadium on hardness

Effect of vanadium on the hardness of the HCWCI is shown in Table III. The hardness of the material is directly proportional to the wear resistance, *i.e.* an increase in hardness will lead to improved wear resistance. It can be seen from Table III that the bulk hardness increased and then decreased with increasing vanadium addition

The variation in hardness is attributed to two factors. Firstly, vanadium dissolves in the austenite and improves austenite hardness by solid solution strengthening. Secondly, from the microstructural analysis using SEM, vanadium existed in M<sub>7</sub>C<sub>3</sub> carbides and this may have increased the hardness of M<sub>7</sub>C<sub>3</sub> carbides as Ma *et al.* (2013) indicated. The results in Table III indicate that addition of vanadium led to improved wear resistance while retaining the fracture strength.

### Effect of vanadium on fracture strength

Table IV shows the experimental results of the fracture strength. Vanadium contributes to the improvement of fracture strength of Fe-Cr-C-V alloys in the as-cast condition as measured by the stress required to fracture the HCWCI. This increase in fracture strength indicates that the vanadium addition had a beneficial effect on the properties of HCWCI. Figures 3 to 5 show a clear dispersion of the vanadium in the matrix, and this might have led to matrix hardening/strengthening and hence improved the fracture strength.

Table III

**The effect of vanadium on the hardness of HCWCI**

Alloy	Brinell hardness (BHN)
ASTM A 532 Class III	432
ASTM A 532 Class III + 0.2-0.8%V	555
ASTM A 532 Class III+ 0.8-1.5%V	485
ASTM A 532 Class III+1.5-3.0%V	514

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Table IV

## The effect of vanadium on fracture strength of HCWCI

Alloy	Fracture load average (N)	Stress ( $Q_{max}$ ) (MPa)
ASTM A 532 Class III	184 400	332
ASTM A 532 Class III + 0.2-0.8%V	192 000	346
ASTM A 532 Class III+ 0.8-1.5%V	212 700	383
ASTM A 532 Class III+1.5-3%V	306 400	552

Morphology of the particles also plays a role. It can be seen from Figure 2 that in the reference HCWCI, the  $M_7C_3$  carbides are of the rod and needle type and therefore the stress concentration factor will play a bigger role when the material is exposed to an impact. The tip of the needle type carbides will act as a stress riser and thus lead to reduction in fracture strength. The increase in fracture strength brought about by increasing the vanadium content is also in agreement with the results of Liu *et al.* (2005), who attributed the increase in fracture strength to the finer primary austenite dendrites. Changing the morphology from rod to isotropic therefore leads to a significant increase in fracture strength.

### Conclusions

The main aim of this project is to improve the mechanical properties of high-chromium white cast iron (HCWCI) for mill liners with special emphasis on improving the fracture strength of these alloys. The influence of vanadium on the grain refinement of HCWCI was investigated. The addition of vanadium was found to change the morphology of eutectic carbides from plate- and rod-like shapes to isotropic shapes. Addition of vanadium led to an increase in fracture strength in the cast structure. This was due to the fine-grained microstructure and increased matrix strength through a dispersion-hardening effect of vanadium – the fine secondary carbides can increase the mechanical support offered by the eutectic carbides.

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