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Alloyed White Cast Iron with Precipitates of Spheroidal Vanadium Carbides VC

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Abstract

The paper presents the results of tests on the spheroidising treatment of vanadium carbides VC done with magnesium master alloy and mischmetal. It has been proved that the introduction of magnesium master alloy to an Fe-C-V system of eutectic composition made 34% of carbides crystallise in the form of spheroids. Adding mischmetal to the base alloy melt caused 28% of the vanadium carbides crystallise as dendrites. In base alloy without the microstructure-modifying additives, vanadium carbides crystallised in the form of a branched fibrous eutectic skeleton.

Testing of mechanical properties has proved that the spheroidising treatment of VC carbides in high-vanadium cast iron increases the tensile strength by about 60% and elongation 14 - 21 times, depending on the type of the spheroidising agent used.

Tribological studies have shown that high-vanadium cast iron with eutectic, dendritic and spheroidal carbides has the abrasive wear resistance more than twice as high as the abrasion-resistant cast steel.

Keywords: Abrasive wear resistance, High-vanadium cast iron, Eutectic alloy, Spherodisation, Vanadium carbide

1. Introduction

Cast iron is a material used in nearly every branch of the industry, mainly because of a wide spectrum of grades offering different mechanical and performance properties. Nevertheless, new grades of cast iron are searched all the time, for example, by adding to cast iron the alloying elements that change its matrix and the morphological features of graphite, or result in carbides crystallisation. The element which has very interesting properties as an alloying addition is vanadium. Studies [1,2] provide information on the microstructure of high-vanadium white cast iron, which has been observed to contain a fibrous $\gamma + VC_{1-x}$ eutectic with the volume fraction of vanadium carbides at a level of about 20%, while in [3] the properties of vanadium carbides of the VC type have been discussed.

The results of microstructural examinations of these alloys, containing carbon in the range of 1.38-4.16% and vanadium in the range of 6.7-15.5%, and also the mechanical and tribological properties are given in [4,5]. Hence it follows that both the mechanical properties and abrasive wear resistance of the high-vanadium cast iron mainly depend on the type of the metallic matrix and change within the range of the following values: tensile strength from 433 to 839 MPa, yield strength from 185 to 655 MPa, hardness from 174 to 474, and elongation from 0.2 to 7.2%. The abrasive wear behaviour of high-vanadium cast iron is in straight relationship with the type of the crystallised metallic matrix, where the lowest resistance show alloys with a ferritic matrix, medium values – alloys with a pearlitic matrix, and the highest values - alloys with a complex matrix composed of lamellar and spheroidal pearlite. It is possible to obtain the Fe-C-V alloys with an abrasive wear resistance higher than that of Hadfield cast steel.

Analysis of the literature confirms growing interest in the ordinary high-alloyed white cast iron [6, 7] and in white cast iron with carbide precipitates in the form of spheroids. Studies [8-11] give information on the spheroidising treatment with rare-earth metals carried out on the alloyed white cast iron with a high content of chromium, vanadium and nickel to improve the abrasive wear resistance.

So, to combine the good casting properties of cast iron with the high ductility of cast steel, a spheroidising treatment is carried out, which produces the cast iron with spheroidal graphite. The spheroidal form of graphite is the most compact one and has the smallest surface-to-volume ratio, owing to which the active section of the casting is impaired to a lesser extent, and the concentration of stresses around the sites where the graphite occurs is reduced compared with the graphite in the form of lamellae [12].

These features of the spheroidising treatment were used in an attempt to obtain vanadium carbides VC in a spheroidal form, described in [13]. The spheroidising treatment of VC carbides resulted in an increase of the mechanical properties combined with improved alloy ductility.

The aim of the present study was to perform the spheroidising treatment of VC carbides using mischmetal. Another aim was to compare the microstructure, mechanical properties and abrasive wear resistance of Fe-C-V alloys with a nearly-eutectic microstructure containing VC carbides of both fibrous and spheroidal shape, produced as a result of the spheroidising treatment using magnesium master alloy and mischmetal.

2. Methods of investigations

To comply with the established programme of studies, three melts of cast iron of the same nearly-eutectic composition were conducted in a Balzers vacuum furnace, in a protective atmosphere of argon. The Fe-V master alloy with vanadium content of 81.7%, armco iron, and technically pure graphite were used in the melting process. The first melt was the base melt (W), the second one was subjected to a spheroidising treatment using magnesium master alloy (SMg), while the third melt was spheroidised with mischmetal (SMM). Moulds made of molochite flour with CO₂ – hardened sodium silicate were preheated at 550°C, then poured with liquid cast iron at a temperature of 1700°C. After knocking out of castings, specimens were cut for metallographic examinations, mechanical testing and determination of tribological properties.

Unetched specimens were examined under a LEICA M MEF4 optical microscope and under a JEOL 5500LV SEM, using secondary electrons. This enabled distinguishing between vanadium carbides and other phases, which is not always possible when optical microscopy is the only tool applied in the studies. For more detailed examinations of the geometry of various phases, the specimens were deep-etched with aqua regia and examined by scanning electron microscopy. The percent content of structural constituents was determined with a LEICA QWin automatic image analyser.

Studies of abrasive wear resistance were carried out on a Miller machine, whose schematic diagram is shown in Figure 1a. Specimens of standard dimensions, i.e. 25.4 x 12, 7x5 ± 9 mm (Fig. 1b), were charged with the weights and subjected to an abrasive wear test, rubbing in a reciprocating motion against the bottom of a gutter containing an aqueous abrasive mixture (SiC + distilled water).

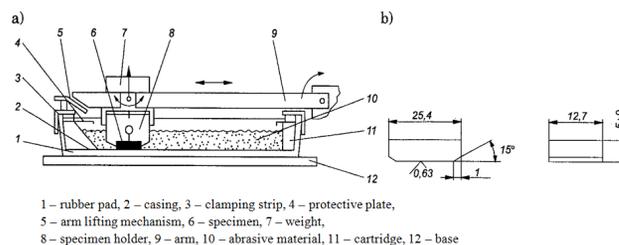


Fig. 1. Device for testing the abrasive wear resistance (a), dimensions of the specimen (b)

The study consisted of three tests performed in 16-hour series of four four-hour shifts each. This enabled plotting of the wear curves. After each run, the specimens were washed, dried and weighed to the nearest 0.01 g. Using the results of the measurements, individual weight losses and the cumulative weight loss were determined after each test in a given series; then the results were plotted as a time – weight curve. The cumulative (summarised) weight loss, calculated as a total of the weight losses observed since the start of the constant load effect, was recorded after 4, 8, 12 and 16 hours of the test cycle. The obtained results were approximated with an exponential curve described by relationship (1) [14]:

$$W(t) = A \cdot t^B \quad (1)$$

where:

W – the weight loss, [g],

t – the time, [hours],

A, B – the constants determined by the least square method.

Regardless of the number of tests in a series and the time of one test, a mass wear rate V_w determined by the slope of a tangent to the wear curve in the second hour of testing was adopted:

$$V_w = A \cdot B \cdot 2^{(B-1)} \quad (2)$$

where:

A, B – the constants from relationship (1).

3. Results and discussion

Table 1 describes the chemical composition of the examined specimens, the content of microstructural constituents and the degree of eutectic saturation determined from relationship (3).

Table 1.

Chemical composition and content of microstructural constituents in the examined alloys

Melt No.	Chemical composition			Content of microstructural constituents			$f_{w,e}$ [%]	$f_{w,s}$ [%]	$f_{w,d}$ [%]	C/V	S_c
	C [%]	V [%]	Si [%]	f_f [%]	$f_{p.z.}$ [%]	$f_{p.p.}$ [%]					
W	1.44	15.60	0.32	100	-	-	16.59	-	-	0.09	1.03
SMg	1.38	16.25	0.54	100	-	-	10.64	5.45	-	0.09	0.99
SMM	1.39	15.62	0.26	100	-	-	10.46	-	4.06	0.09	1.00

f_f – content of ferrite in cast iron
 $f_{p.z.}$ – content of granular pearlite in cast iron
 $f_{p.p.}$ – content of lamellar pearlite in cast iron
 $f_{w,e}$ – content of eutectic carbides in cast iron
 $f_{w,s}$ – content of spheroidal carbides in cast iron
 $f_{w,d}$ – content of dendritic carbides in cast iron

$$S_c = \frac{C}{C_e} = \frac{C}{7.618 \cdot V_e^{-0.617}} \quad (3)$$

where:

C_e and V_e – the carbon and vanadium content in a eutectic, respectively, [%],

C – the carbon content in cast iron, [%].

Specimens in unetched condition were observed by scanning electron microscopy coupled with BEI (Back Scattered Electron Image), which enabled distinguishing vanadium carbides from other phases, disturbing the metallographic analysis. Figure 2 shows the microstructure of the examined specimens etched with Vilella's reagent to reveal the matrix and vanadium carbides. As can be easily noted, except vanadium carbides of different shapes, the matrix is composed of alloyed ferrite. Deep etching with aqua regia, followed by examinations using scanning electron microscopy (SEM) enabled more detailed and accurate examination of the geometry of individual phases (Fig. 3).

The conducted metallographic studies have shown that introducing the magnesium master alloy to an Fe-C-V system of eutectic composition (SMg) causes the crystallisation of spheroidal carbides. The content of these carbides is about 5.5%, representing 34% of all the crystallised vanadium carbides. Slightly different was the behaviour of an alloy of the same composition after the introduction of mischmetal (SMM). An addition of this spheroidising agent made 4.06% of vanadium carbides (i.e. 28% of all vanadium carbides) crystallise in a dendritic form. In base alloy (W), without any additives modifying the alloy microstructure, vanadium carbides crystallised in the form of a branched skeleton.

The results of mechanical tests and hardness measurements are summarised in Table 2. A combination of these results clearly shows how strong is the influence of the shape of the crystallising vanadium carbides on the cast iron strength and ductility, better results being obtained in the case of spheroids. The base alloy W, in which a fibrous vanadium eutectic crystallised, showed a tensile strength of 316 MPa and an elongation of 0.6%. The SMg alloy, containing more than 5% of spheroidal carbides and nearly 11% of fibrous eutectic carbides, showed much higher values of the mechanical properties. Its tensile strength was 509 MPa, with elongation of 12.8%. The SMM alloy containing more than 4.06% of carbides of a dendritic shape and nearly 10.5% of fibrous eutectic carbides, showed a tensile strength similar to the SMg alloy (502 MPa), with slightly lower elongation (8.8%). Hence it

follows that the spheroidising treatment of VC carbides in high-vanadium cast iron increases the tensile strength by about 60% and multiplies the elongation 14 - 21 times, depending on the type of the spheroidising agent used.

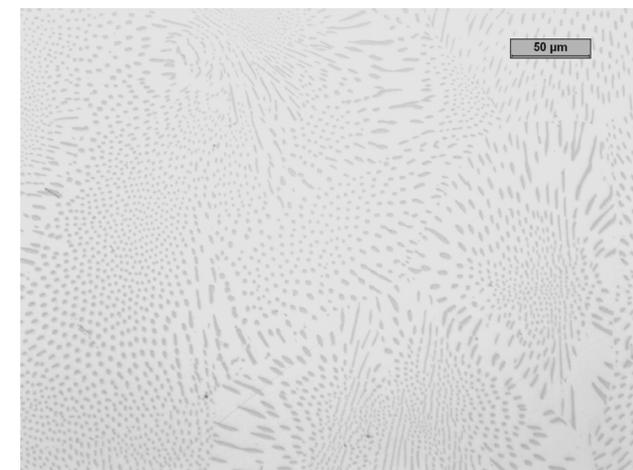
The spheroidising treatment did not affect the hardness of the tested alloys. In all cases, due mainly to the presence of hard VC carbides, high hardness values of about 200 HV30 were reported.

To compare fractures in the specimens taken from individual melts, they were examined by scanning electron microscopy. These studies have also confirmed the results discussed previously. The mechanical fracture of high-vanadium cast iron is brittle, but after spheroidising treatment (either with magnesium master alloy or with mischmetal) its nature changes to brittle-ductile.

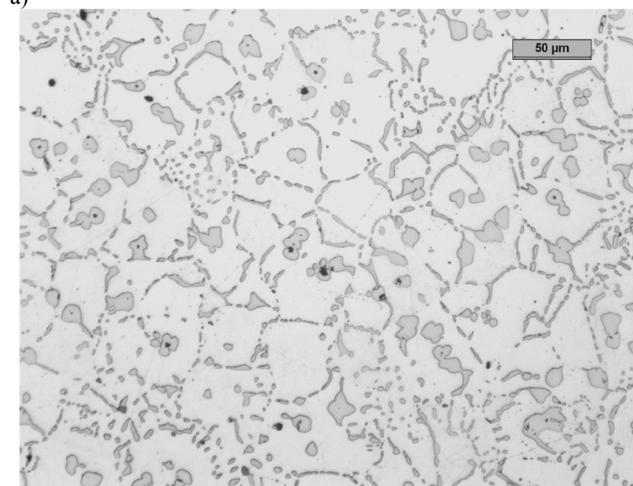
Tests of abrasive wear resistance conducted on a Miller machine enabled comparing the abrasive wear resistance of the three materials tested. In addition, as a reference, the fourth material was introduced, i.e. the quenched and tempered low-alloy structural cast steel, grade L70H2GNM, which is generally considered a material of high abrasion resistance.

Using the results of the weight measurements, individual weight losses and a cumulative weight loss were calculated after each test in a given series (Table 3). The results showing weight changes in individual specimens were approximated with an exponential curve described by relationship (1), and then the mass wear rate V_w was calculated according to equation (2), defined by the slope of a tangent to the wear curve in the second hour of testing. The results are shown in Table 3 and Figure 4.

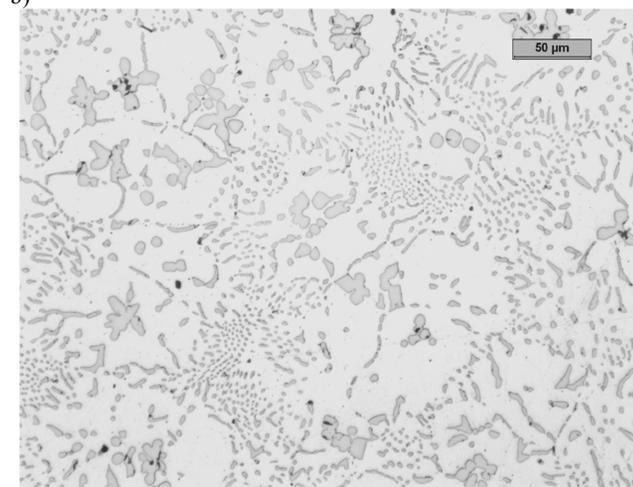
Analysing the results obtained it can be stated that the base high-vanadium cast iron (W), the cast iron after spheroidising treatment with magnesium master alloy, and the cast iron spheroidised with mischmetal (SMg and SMM, respectively) all show very good resistance to abrasive wear. The mass wear rate is very similar in the base cast iron and in the cast iron after the spheroidising treatment with magnesium master alloy, and is almost two times lower than that of the abrasion wear-resistant cast steel. The cast iron spheroidised with mischmetal showed slightly lower resistance to abrasive wear than the base cast iron, or cast iron spheroidised with magnesium master alloy, but still higher than the reference cast steel



a)

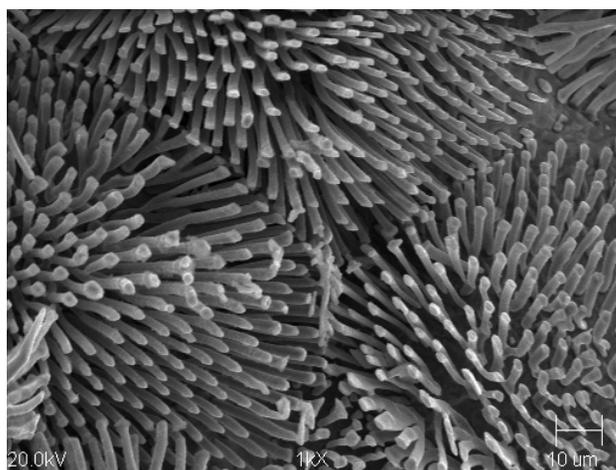


b)

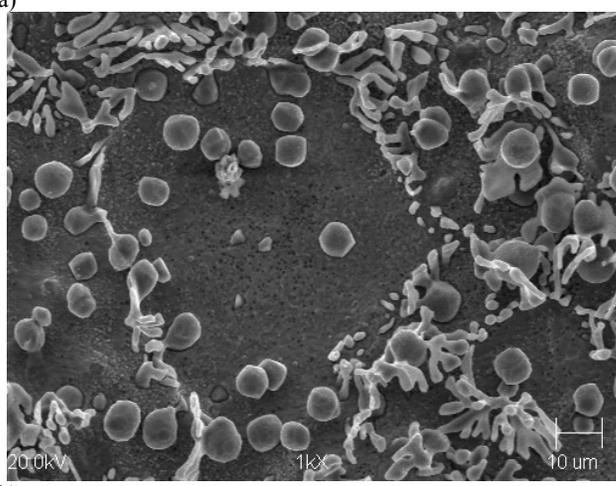


c)

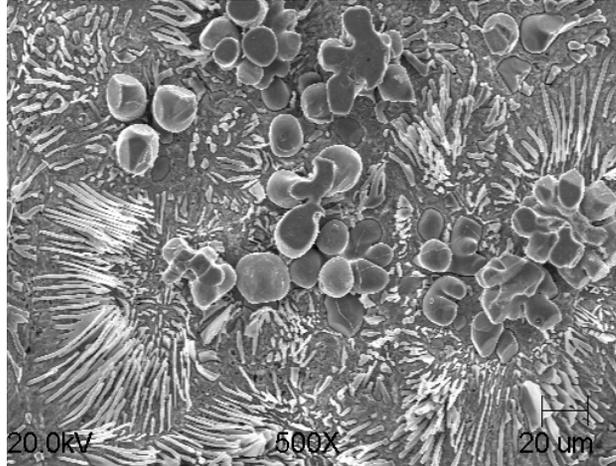
Fig. 2. Microstructure of base cast iron – W (a); cast iron after spheroidising with magnesium master alloy – SMg (b); cast iron after spheroidising with mischmetal – SMM (c); specimens etched with Vilella's reagent



a)



b)



c)

Fig. 3. Microstructure of base cast iron – W (a); cast iron after spheroidising with magnesium master alloy – SMg (b); cast iron after spheroidising with mischmetal – SMM (c); specimens deep etched with aqua regia, SEM

Table 2.

Mechanical properties and hardness of the examined alloys

Melt No.	Hardness		Mechanical properties		
	HV30	R _m [MPa]	R _{p0.2} [MPa]	R _{p0.05} [MPa]	A ₅ [%]
W	205	316	262	85	0.6
SMg	199	509	292	190	12.8
SMM	197	502	258	127	8.8

Table 3.

The results of abrasive wear resistance measurement

Melt No.	Weight loss [g]				A	B	V _w
	After 4 hours	After 8 hours	After 12 hours	After 16 hours			
W	0.18	0.32	0.44	0.56	0.058	0.816	0.042
SMg	0.22	0.35	0.42	0.50	0.096	0.595	0.043
SMM	0.25	0.41	0.54	0.66	0.095	0.700	0.054
Cast steel	0.35	0.59	0.80	0.99	0.124	0.750	0.078

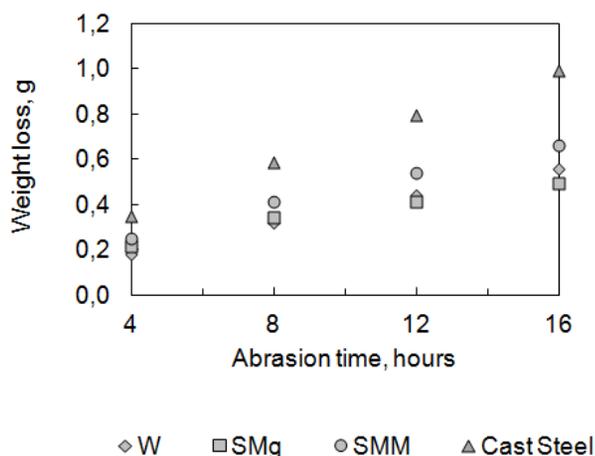


Fig. 4. The abrasive wear behaviour compared for high-vanadium cast iron and abrasion-resistant cast steel during 16 hour test cycle

4. Conclusions

The tests performed suggest the following conclusions:

1. Introducing magnesium master alloy to high-vanadium cast iron of nearly-eutectic composition results in crystallisation of some of the vanadium carbides in a spheroidal form, while after the addition of mischmetal – in a dendritic form.
2. The spheroidising treatment of high-vanadium cast iron increases the mechanical properties by 60%.
3. The spheroidising treatment of high-vanadium cast iron with magnesium master alloy increases the fracture toughness over twenty times, while the same treatment with mischmetal increases this property nearly fifteen times.

4. The tested alloys show high hardness related with the presence of hard VC carbides. The spheroidising treatment has never caused changes in hardness.
5. The high-vanadium cast iron in both base condition and after the spheroidising treatment with magnesium master alloy shows very good resistance to abrasive wear. The mass wear rate is in both cases very similar and nearly two times lower than in the case of the abrasion wear-resistant cast steel.
6. The cast iron subjected to spheroidising treatment with mischmetal shows slightly lower resistance to abrasive wear than the base cast iron or cast iron spheroidised with magnesium master alloy, but still higher than the abrasion wear-resistant cast steel.

Acknowledgements

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