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## MORPHOLOGY OF CARBIDES CRYSTALLIZING IN Fe-C-V AND Fe-C-V-Si ALLOYS

### MORFOLOGIA WĘGLIKÓW KRYSTALIZUJĄCYCH W STOPACH Fe-C-V ORAZ Fe-C-V-Si

Fe-C-V alloys with high vanadium content are included in the family of white cast irons, because all carbon present in this material is bound into vanadium carbides.

The study presents the results of microstructural examinations of the volume solidifying Fe-C-V and Fe-C-V-Si alloys containing carbon in the range of 1.38÷4.14%, vanadium in the range of 6.77÷16.34% and silicon in the range of 0÷3.10%. Attention was focused on near-eutectic alloys.

In Fe-C-V and Fe-C-V-Si alloys, depending on the chemical composition, can crystallize eutectic composed of ferrite and VC-type carbides highly differentiated morphology. In these alloys were observed following types of eutectic: fibrous eutectic, spiral, quasi-regular and globular.

Moreover, both these alloys are crystallized in the form of non-faceted dendrites primary carbides and faceted dendrites primary carbides. The paper presents examples of the different microstructures. Also in order to examine the shape of the primary carbides and eutectics in a closer detail the specimens were deep-etched with aqua regia and then examined in the SEM.

*Keywords:* white cast iron, microstructure, vanadium carbide, eutectic

Stopy Fe-C-V o wysokiej zawartości wanadu zaliczane są do grupy żeliwa białego, ponieważ cały węgiel związany jest w węgliki wanadu.

W pracy przedstawiono wyniki szczegółowej analizy mikrostruktury stopów Fe-C-V oraz Fe-C-V-Si, o zawartości węgla w zakresie 1,38÷4,14%, wanadu w zakresie 6,77÷16,34% i krzemu w zakresie 0÷3,10%, krystalizujących w sposób objętościowy. Szczególną uwagę zwrócono na stopy okołoeutektyczne.

W stopach Fe-C-V i Fe-C-V-Si, w zależności od składu chemicznego, może krystalizować eutektyka składająca się z ferrytu i węglików wanadu typu VC o bardzo zróżnicowanej morfologii. W stopach tych zaobserwowano występowanie następujących typów eutektyki: eutektyki włóknistej, spiralnej, quasi-regularnej oraz globularnej. Ponadto, w stopach tych krystalizują zarówno węgliki pierwotne w postaci dendrytów nieścianowych jak i ścianowych. Przykłady poszczególnych mikrostruktur zamieszczono w pracy.

Dodatkowo, w celu szczegółowego przedstawienia morfologii krystalizujących eutektyk oraz węglików pierwotnych, stopy poddano głębokiemu trawieniu wodą królewską, a następnie obserwacji przy użyciu mikroskopu skaningowego.

## 1. Introduction

Cast iron is a relatively inexpensive structural alloy with a good combination of thermal and wear properties which makes it unique for making cast components used in diverse industrial applications. Hence, there is significant interest in the development of new grades of cast irons for enhanced applications. Thus far, new grades of cast irons have been produced based on the physical and chemical properties of the liquid cast iron, implementing heat treatments to the solid cast iron and alloying with other elements. The first trend has led to the development of high-quality cast iron grades such as inoculated cast iron, nodular cast iron, as well as cast iron with vermicular graphite. The second trend has resulted in the development of cast iron with an ausferritic matrix. In the

third case, there has been an attempt to change the chemical composition of conventional cast iron through the introduction of alloying elements which can have a strong impact in modifying the matrix or the graphite morphology, as well as by influencing to some extent the crystallization of various carbide phases [1,2].

In cast iron one of the alloying elements with a high potential for microstructural modification is V and the combination of V and Si. In the literature, there are limited data regarding the phase equilibrium diagrams [2-6], nucleation of vanadium carbides [7] and the microstructure of alloys Fe-C-V [8-10]. Effect of vanadium on the microstructure is much more complex. Hence the objective of the research, including the execution of alloys Fe-C-V and Fe-C-V-Si with different chemical composition and analysis of their microstructure.

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## 2. Experimental

A series of melts was made in a BALZERS (VSG 02) induction furnace under an argon atmosphere. The melting charge was ferro-vanadium with 81.7 wt.% V, Armco iron, spectrally pure graphite and technically pure silicon. The liquid alloys were overheated to 1700°C and then poured in rectangular shaped foundry molds fed from a large feeder. The molds were made from loose quick-setting sands with sodium silicate. The test samples were cut out from the lower part of the test blocks and they were free from any casting defects. Then the cast samples were prepared for metallographic characterization.

The metallographic specimens were examined in a JEOL 5500LV scanning electron microscope (SEM) using secondary electrons. By this means it was possible to distinguish the vanadium carbides from any other phases. The dendrite fraction and the fraction of vanadium carbides (primary + eutectic) were recorded from optical micrographs taken at 100× from non-etched specimens using a LEICA QWin automatic image analyzer. Also in order to examine the shape of the individual phases in a closer detail the specimens were deep-etched with aqua regia and then examined in the SEM. A LEICA QWin automatic image analyzer was used for volume fraction determinations of granular pearlite-like, lamellar pearlite, ferrite and cementite eutectic using Vilella's reagent etched specimens and with magnifications of 100 and 250×.

## 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 (1).

$$S_c = \frac{C}{7.618 \cdot V^{-0.617} - 0.2 \cdot Si} \quad (1)$$

where: C, V and Si are carbon, vanadium and silicon content in cast iron [11, 12].

The metallographic specimens were examined in a JEOL 5500LV scanning electron microscope (SEM) using secondary electrons. Thus, it was possible to distinguish the vanadium carbides from other phases (Fig. 1) the alloys were classified into three groups: hyper- (Fig. 1c, 1f, 1i), hypo- (Fig. 1a, 1d, 1h), and near-eutectic alloys (Fig. 1b, 1e).

Figure 2 shows the microstructure of the examined specimens etched with Vilella's reagent to reveal the matrix and vanadium carbides. This figure shows typical solidification microstructures for these alloy groups. As can be easily noted, except vanadium carbides of different shapes, the matrix is composed of granular pearlite-like  $f_{p,z}$  (eg. Fig. 2d), lamellar pearlite  $f_{p,p}$  (eg. Fig. 2a, 2e), alloyed ferrite  $f_f$  (eg. Fig. 2b, 2g) and cementite eutectic  $f_c$  (Fig. 2i). The performed metallographic studies have shown that addition the magnesium master alloy to an Fe-C-V system of eutectic composition (alloy No. 2 – Fig. 1b, 2b) causes the crystallisation of spheroidal carbides (alloy No. 7 – Fig. 1g, 2g). The content of these carbides is about 5.5% and representing 34% of all the crystallised vanadium carbides.

Figs. 2d, 2e, 2f shows the constituents of matrix in the Fe-C-V-Si alloys. The investigated Fe-C-V-Si alloys can also be classified as hyper- (Fig. 1f), hypo- (Fig. 1d) and near-eutectic (Fig. 1e) alloys. In addition SEM observations were used to confirm that in hypereutectic Fe-C-V-Si alloys the primary vanadium carbides crystallize as non-faceted/faceted dendrites (see Fig. 1f).

Deep etching with aqua regia followed by observations under the scanning microscope have proved that the primary vanadium carbides are crystallizing as non-faceted dendrites (Fig. 3b). Eutectic grains (Fig. 3a) have got inside a continuous, ramified skeleton of vanadium carbides. Figures 3d, 3e, 3f, 3g shows the effect of silicon addition on changes in

TABLE 1

Alloy's chemical composition and fraction component of structure

No. of Alloy	Chemical composition			Type of microstructure	C/V	$S_c$ (Eq. 1)
	C%	V%	Si%			
1	1.39	6.77	–	R; $f_{p,z}$	0.21	0.59▲
2	1.45	15.08	–	R; $f_f$	0.10	1.02●
3	2.57	16.34	–	R; $VC_{NF}$ ; $f_{p,z}$	0.16	1.89■
4	1.39	7.35	1.05	R+C; $f_{p,z}+f_{p,p}$	0.19	0.69▲
5	1.72	7.48	2.65	C; $f_{p,p}$	0.23	1.03●
6	1.76	7.77	3.10	C; $VC_F$ ; $f_{p,p}$	0.23	1.15■
7	1.38	16.25	–	$VC_s$ ; $f_f$	0.08	1.01●
8	1.53	10.81	–	R+C; $f_f+f_{p,z}$	0.14	0.87▲
9	4.14	12.59	–	R; $VC_{NF}$ ; $f_c+f_{p,p}$	0.33	2.59■

$f_f$  – alloyed ferrite;  $f_c$  – cementite eutectic;  $f_{p,p}$  – lamellar pearlite;  $f_{p,z}$  – granular pearlite;  $VC_s$  – spheroidal VC carbides;  $VC_{NF}$  – primary non-faceted VC carbides;  $VC_F$  – primary faceted VC carbides; ▲ – hypoeutectic structure; ● – eutectic structure; ■ – hypereutectic structure; R – regular fiber-like eutectic cells; C – complex regular morphology of eutectic cells.

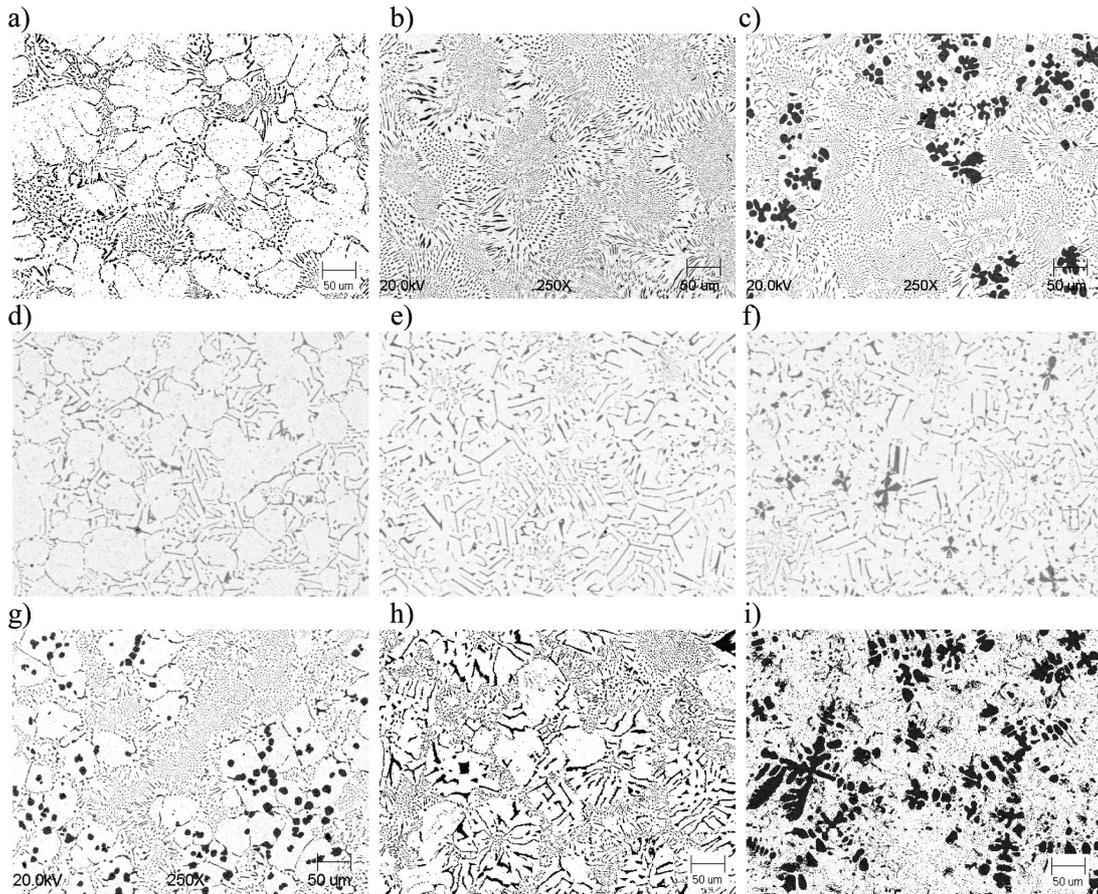


Fig. 1. Microstructures of studied alloys – a - i respectively alloy No. 1 - 9; unetched specimens, BEI

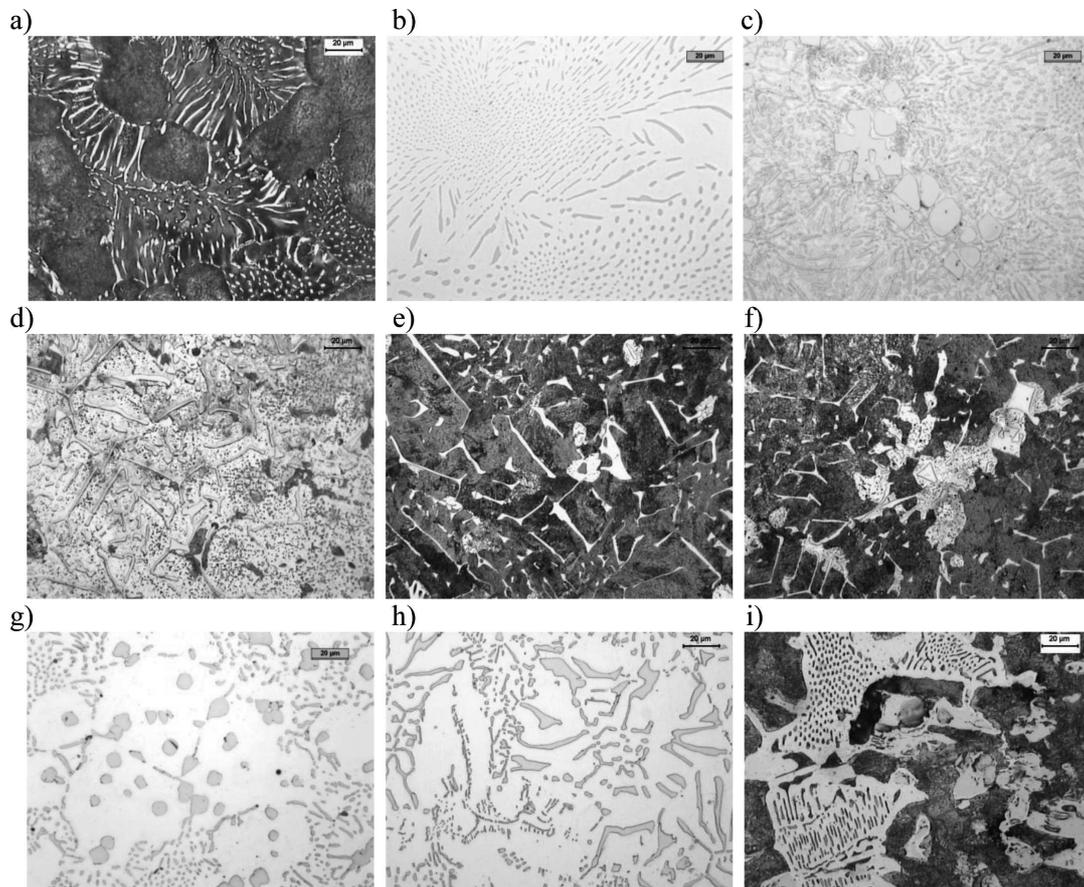


Fig. 2. Microstructures of studied alloys – a - i respectively alloy No. 1 - 9; specimens etched with Vilella's reagent

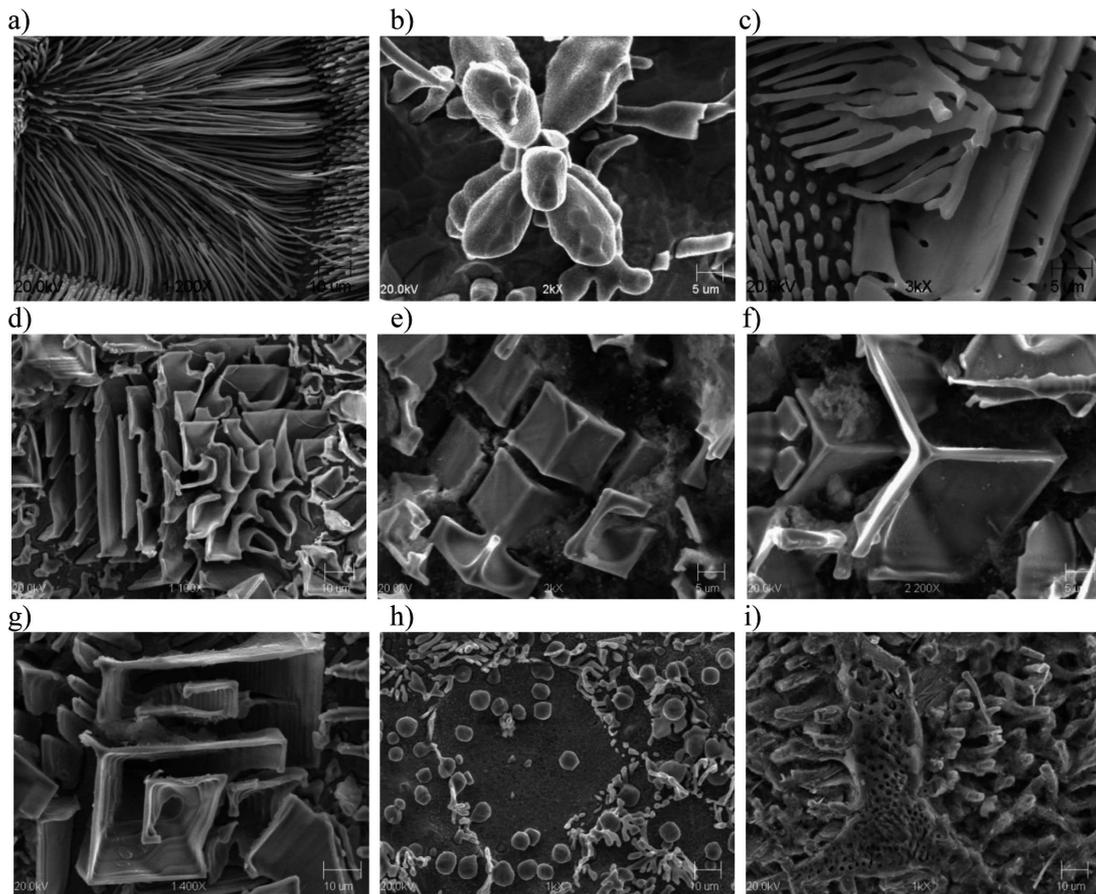


Fig. 3. Microstructures found in Fe-C-V and Fe-C-V-Si alloys: eutectic cell in near-eutectic Fe-C-V alloys (a), primary non-faceted VC dendrites in Fe-C-V alloys (b), continuous, ramified skeleton of vanadium carbides growing out from one common centre eutectic (c), cell in near-eutectic Fe-C-V-Si alloys (d), primary non-faceted/faceted VC dendrites in Fe-C-V-Si alloys (e), eutectic Fe-C-V-Si alloy showing overlapping of VC carbide spiral segments (f, g), spheroidal VC carbides (h), alloyed cementite (i); SEM micrographs of samples deep-etched with aqua regia

the microstructure of Fe-C-V alloys. Analysis of these results shows that silicon addition changes the morphology of the crystallising eutectic from fibrous (Fig. 3a) to complex regular (Fig. 3d). The shape of the primary carbides changes too. After the addition of silicon the non-faceted crystals (Fig. 3b) are transformed into the faceted ones (Fig. 3e).

#### 4. Conclusions

In high-vanadium cast iron (C = 0.85-4.14%, V = 6.77-16.34% and Si = 0-3.10%) the following phases have been identified: alloyed ferrite, alloyed cementite, VC carbides and the constituents in its matrix: alloyed ferrite, granular pearlite, and lamellar pearlite as well as a mixture of alloyed ferrite + granular pearlite, granular pearlite + lamellar pearlite. Addition 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.

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