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SOLIDIFICATION OF FE19CR2.9C2V ALLOY

M. Filipović*, Ž. Kamberović, M. Korać

Department of Metallurgical Engineering, Faculty of Technology and Metallurgy,
University of Belgrade, Belgrade, Serbia

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Abstract

The addition of 2% V affects the solidification process and changes the transformation characteristics of austenite in hypoeutectic white cast iron containing 19% Cr and 2.9% C. DTA analysis reveals that vanadium reduces the solidification temperature interval in tested alloy. The narrowing of the solidification temperature interval and the formation of vanadium carbides favours the appearance of a finer structure. Also, the phases volume fraction changes, i.e. the primary γ-phase fraction decreases and the amount of M7C3 carbide increases. Further, changes in conditions of solidification, influence the change in composition of austenite. Type and degree of transformation of austenite in the course of cooling after solidification in these alloys depend on chemical composition of austenite.

Keywords: *Fe-Cr-C-V alloy, solidification, vanadium carbide, liqudus temperature, eutectic temperature, microstructure*

1. Introduction

High chromium white cast irons have been widely used for applications where stability in severe environments is the main requirement, such as the mineral processing industry, cement and paper production, and the steel manufacturing industry.

The typical as-cast microstructure of these alloys consists of primary and/or eutectic M_7C_3 carbides in a metastable austenitic matrix.

The wear resistance of high chromium white cast irons depends upon the type, volume fraction, hardness, morphology, orientation and distribution of hard carbides [1-4] and properties of the matrix [1, 2, 5-7]. The hard carbides are crucial to the wear resistance, although the matrix makes a large contribution to the overall toughness [1, 6].

The effects of additional alloying elements in high chromium irons have been extensively studied [1,8-18]. Normally, alloying additions such as nickel, manganese, molybdenum and copper are used to increase hardenability and to prevent pearlite formation [1]. High chromium irons alloyed with carbide-forming elements such as tungsten [8,9], vanadium [8, 10-13], niobium [8, 10, 14, 15], titanium [11, 16, 17] and boron [18] have been developed for special applications such as hot working mill rolls in the steel industry. The addition of an alloying element which confines carbon in the form of a carbide, with a greater hardness and more favorable morphology, and which reduces the carbon content of the matrix, allows the simultaneous improvement of both toughness and abrasion resistance [12, 14]. Vanadium appeared to be of special interest, due to its double effects, on both the matrix structure and stereological characteristics of carbides.

In this work, the influence of the addition of 2% V on the solidification process of hypoeutectic white cast iron containing 2.9% C and 19% Cr has been examined.

2. Experimental Procedure

The chemical composition of tested alloys is listed in Table 1.

***Table 1**. Chemical composition of tested alloys.*

	Chemical composition (wt.%)							
Alloy	C	Si	Mn	Mo	Cu	Ni	Cr	V
1	2.89	0.85	0.71	0.48	0.99	0.1	19.03	0.0012
2	2.87	0.87	0.73	0.44	1.01	0.099	18.92	2.02

The phase transformations during solidification of the tested alloys were controlled by differential thermal analysis (DTA) method. For this examination a Du Pont 1090B analyzer was used with a high temperature cell, 1600DTA. The temperature difference of the examined and reference sample was recorded during cooling at a rate of 5 ºC min^{-1}, within temperature interval 1000-1480 ºC, in a helium

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[*] *Corresponding author: mirjanaf@tmf.bg.ac.rs*

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protective atmosphere. In order to determine whether the transformation of austenite (particularly pearlite transformation) occurs in the tested alloys at temperatures below 1000 ºC during slower cooling[1], the samples were cooled at the same rate (5 ºC min^{-1}) to room temperature.[2]

The observation and identification of solidification structure were done using conventional optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Samples for optical microscope examinations were prepared using standard metallographic technique (etched with picric acid solution (1g) in methanol (100 ml) by adding 5 ml of hydrochloric acid or etched with Murakami). Discs for TEM examinations were prepared by using a twin-jet electropolisher. These samples were examined at 200 kV in a JEOL-2000FX transmission electron microscope.

3. Results

The results obtained by DTA analysis are presented in Fig. 1. The addition of 2.02% V in hypoeutectic Fe-Cr-C white iron containing 19% Cr and 2.9% C, liquidus temperature is decreasing, while eutectic temperature is increasing, i.e. the solidification temperature interval reduces.

The microstructure of tested alloys contain primary austenite dendrites and eutectic colonies composed of M_7C_3 carbides and austenite (Fig. 1).

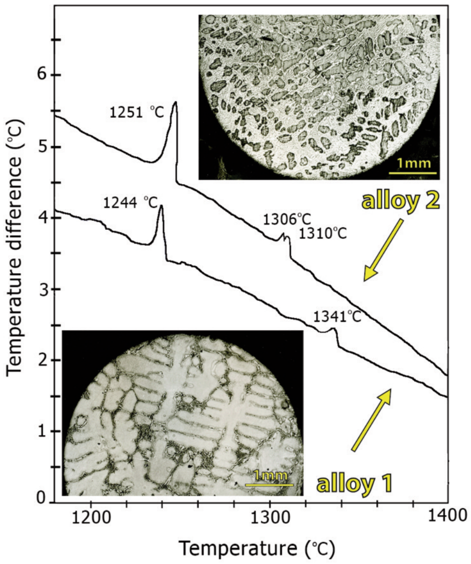

Figure 1. *DTA curves for tested alloys and their microstructure obtained at a cooling rate of 5ºC min^{-1}.*

Also, vanadium rich carbides are present in Fe-Cr-C-V alloy containing 2.02% V (Figs. 2, 3 and 4a). When the reagent for selective etching of carbides was used (whereby the M_7C_3 carbides become dark brown and vanadium carbides white), fine, white particles were noticed in the structure of this alloy (Fig. 2).

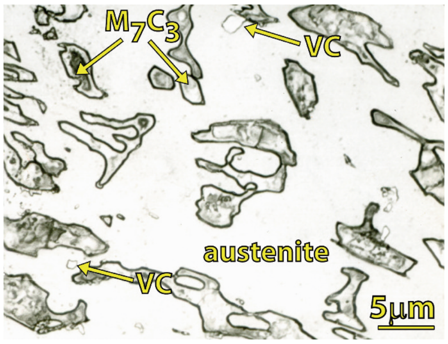

Figure 2. *OM micrograph of Fe-Cr-C-V alloy containing 2.02% V (etched with Murakami).*

Figure 3b shows not only that the vanadium is distributed between eutectic M_7C_3 carbide and the matrix and that its content in carbide is considerably higher, but also the area of high vanadium concentration, corresponding to particle marked VC from Fig. 3a.

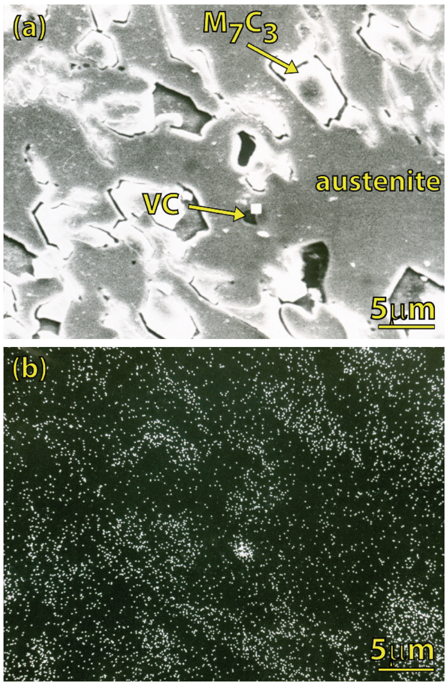

Figure 3. *SEM micrograph of Fe-Cr-C-V alloy containing 2.02% V (a) and corresponding vanadium distribution map (b).*

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[1] *Previous studies have shown [11] that at higher cooling rates (1 ºC s-1) austenite partially transformes to martensite in high chromium white iron alloyed with vanadium.*

[2] *For this temperature interval the DTA curve has not been recorded. Namely, according to literature [1], it is assumed that the solidification was completed at temperatures above 1000ºC.*

Vanadium influenced the refinement of the structure of tested alloy (Fig. 1). Further, the volume fraction of M_7C_3 carbides is increased, whereas the amount of retained austenite is decreased with vanadium addition in the alloy (Fig. 1).

The primary austenite of a basic Fe-Cr-C alloy, with no vanadium addition, remains stable at cooling down to room temperature (Fig. 1). In Fe-Cr-C-V alloys containing 2.02% V, a remarkably higher degree of austenite transformation can be seen (Fig. 1). TEM analysis identified martensite and pearlite as products of this transformation (Figs. 4b-4d). Also, TEM observation revealed that the secondary carbides were present in the matrix in this alloy (Fig. 4b and 4d).

4. Discussion

Solidification starts with formation of γ-phase at 1341ºC in Fe-Cr-C alloy with no vanadium addition, at 1310ºC in Fe-Cr-C-V alloy containing 2.02% V (Fig.1). As solidification progresses, the composition of the remained liquid is changing due to limited solubility of carbon, chromium and vanadium in the austenite. These elements accumulate in front of the progressing solid-liquid interface. In tested high chromium white cast iron alloyed with 2.02 mass.% V, at 1306 ºC (Fig. 1) eutectic containing vanadium rich carbide and austenite was formed, in local areas enriched vanadium. Vanadium rich carbide particles disturb or entirely block further primary austenite dendrites growth.

As the temperature falls, the remaining liquid reaches the eutectic composition; then the monovariant eutectic reaction ($L \rightarrow \gamma + M_7C_3$) takes place and the coupled austenite/carbide eutectic is being developed at 1244ºC in Fe-Cr-C white iron with no vanadium addition, at 1251ºC in white iron containing 2.02% V (Fig. 1). The eutectic regions of carbide and austenite grow as colonies, indicating growth of a faceted-nonfaceted eutectic. A. Bedolla-Jacuinde et al. [19] found that M_7C_3 eutectic carbides in high chromium white irons nucleated on the surface of the primary and secondary dendrites arms. The eutectic γ-phase nucleated side-by-side with the hexagonal M_7C_3 carbides, and both eutectic constituents may then grow more or less at the same rate with bars surrounded by austenite, and coupled growth develops. During eutectic growth, the solute atoms (carbon, chromium and vanadium), which are rejected by one phase, are usually needed for the growth of the other.

Morphology of eutectic colonies depended mainly on the amount and shape of austenite dendrites.

When the solidification temperature interval is narrower (as the consequence, in this case, of alloying high chromium white iron with vanadium), around the primary dendrite of the γ-phase in the remaining portion of the melt, the temperature and concentration

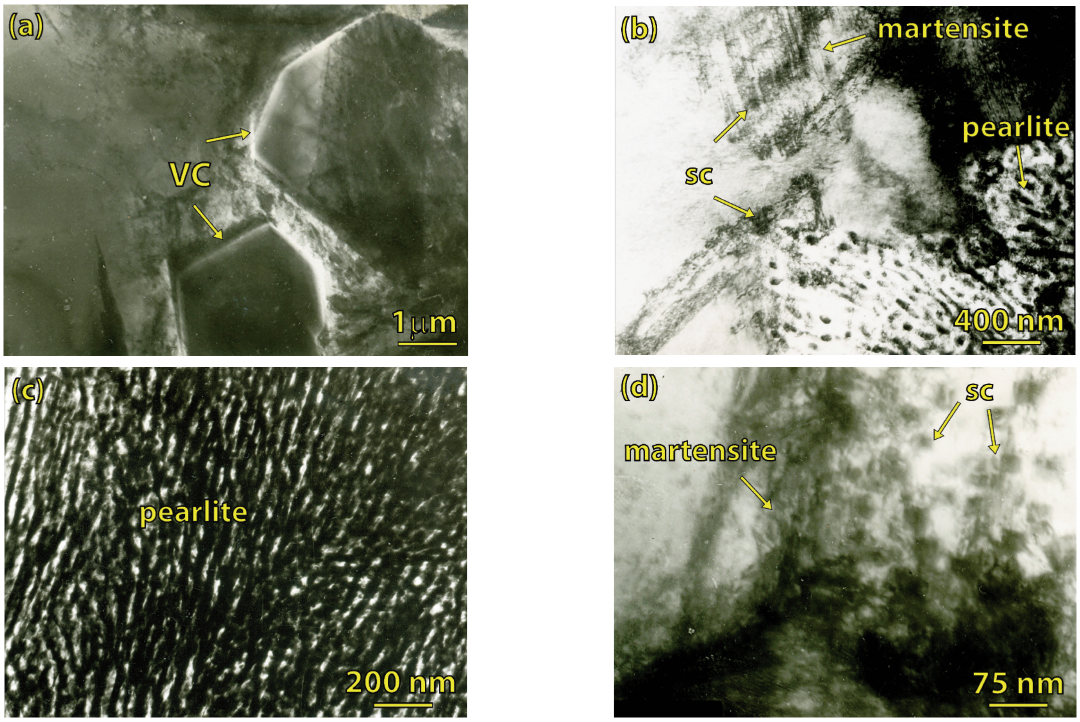

***Figure 4**. TEM micrographs of the Fe-C-Cr-V alloy containing 2.02%V showing VC carbides (a), pearlite (b) and (c), secondary carbides and martensite (b) and (d).*

conditions appear more readily, thus enabling the formation of eutectic colony nuclei and their growth which results in the interpretation of further γ-phase growth. The eutectic colonies growth rate well increase with increasing eutectic temperature, i.e. with a lowering of the solidification temperature interval, thus influencing the formation of a larger amount of finer M_7C_3 carbides (Fig. 1).

Type and degree of transformation of austenite in the course of cooling after solidification in high chromum white cast irons depend on chemical composition of austenite. Changes in conditions of solidification, as a result of adding vanadium to Fe-Cr-C white iron, influence the change in composition of austenite, which manifests itself in the form of different degrees of transformation of austenite (Fig. 1).

Austenite remains as a metastable phase at room temperature in Fe-Cr-C alloy with no vanadium addition (Fig. 1), due to the high amount of carbon and other alloying elements that lowers the martensite transformation start temperature M_s.

Adding vanadium into the tested Fe-Cr-C-V type alloy was followed by the presence of this element in the austenite as a normal consequence of its wide solubility range in the γ-solid solution. Besides, it can be assumed that carbon and chromium contents are lower in the matrix due to the larger amount of eutectic M_7C_3 carbides in this alloy.

With further cooling after solidification, at temperatures lower than solidus, secondary carbides precipitate in austenite, as presented in Figs. 4b and 4d. Precipitation of secondary carbides minimizes the carbon and chromium contents in the matrix, thus reducing its hardenability. As a result, for a given cooling rate, the concentration of molybdenum, manganese, copper and nickel in tested Fe-Cr-C-V cast iron will not be sufficient to prevent the pearlitic transformation. Consequently, larger or smaller part of the austenite will transform into pearlite (Fig. 4b and 4c). This effect was considered previously in detail [14].

The transformation of austenite to martensite in the Fe-Cr-C-V alloy, is closely connected with the secondary carbide deposition. In the process of cooling after solidification, this transformation is possible only after destabilization of the austenite by the secondary carbide particles precipitation. This effect was considered previously in detail [11].

5. Conclusions

Vanadium affects the solidification process in high chromium iron. The addition of 2.02% V in high chromium white cast iron causes a decrease of the solidification temperature interval, and thereby also changes the volume fraction, size and morphology of the present phases.

Vanadium change the transformation characteristics of austenite in the Fe-C-Cr-V type alloy. Type and degree of transformation of austenite during cooling, after solidification, depends on the chemical composition of austenite, i.e. on the content of carbon and other alloying elements.

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