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WEAR RESISTANCE AND DYNAMIC FRACTURE TOUGHNESS OF HYPOEUTECTIC HIGH-CHROMIUM WHITE CAST IRON ALLOYED WITH NIOBIUM AND VANADIUM

ODPORNOST PROTI OBRABI IN DINAMIČNA LOMNA ŽILAVOST PODEVTEKTIČNEGA BELEGA LITEGA ŽELEZA, LEGIRANEGA Z NIOBIJEM IN VANADIJEM

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The influence of mass fractions 1.5 % Nb and 1.5 % V, added singly and in combination, on the microstructural characteristics and properties relevant to the service performance of the hypoeutectic high-chromium white iron containing 18 % Cr and 2.9 % C, namely, the wear resistance and the fracture toughness, has been examined. The Fe-Cr-C-Nb-V alloy gives the best compromise between the wear resistance and the fracture toughness. The dynamic fracture toughness of this alloy is larger by about 42 % and the abrasion wear resistance is larger by about 33 % than the properties of the basic Fe-Cr-C alloy. The presence of NbC carbides in the structure, caused by adding niobium to the alloy, contributes to an improvement of the wear resistance and the dynamic fracture toughness. On the other hand, the higher fracture toughness was attributed to the strengthening during fracture, since very fine secondary carbide particles were present, mainly in the austenitic matrix (as a result of the vanadium addition). The secondary carbides that precipitate in the matrix regions also influence the abrasion behaviour. By increasing the matrix strength through a dispersion-hardening effect, the fine secondary carbides can increase the mechanical support of M_7C_3 eutectic carbides.

Keywords: Fe-Cr-C-Nb-V alloy, NbC carbides, secondary carbides, wear resistance, fracture toughness

Preučevan je bil vpliv dodatka masnega deleža Nb 1,5 % in V 1,5 %, posamezno in v kombinaciji, na značilnosti mikrostrukture in uporabne lastnosti podevtektičnega kromovega belega železa z 18 % Cr in 2,9 % C ter na obrabno odpornost in lomno žilavost. Zlitina Fe-Cr-C-Nb-V je najboljši kompromis med odpornostjo proti obrabi in lomno žilavostjo. V primerjavi z osnovno Fe-Cr-C-zlitino ima ta zlitina okrog 42 % večjo dinamično lomno žilavost in okrog 33 % večjo odpornost proti abraziji. Prisotnost NbC-karbidov zaradi dodatka niobija zlitini prispeva k izboljšanju odpornosti proti obrabi in povečanju dinamične lomne žilavosti. Po drugi plati se višjo lomno žilavost pripisuje utrjevanju med širjenjem preloma, ker so zelo drobni delci sekundarnih karbidov pretežno v avstenitni osnovi (kot posledica dodatka vanadija). Sekundarni karbidi, ki se izločajo v osnovi, tudi vplivajo na vedenje pri obrabi. S povečanjem trdnosti osnove zaradi učinka disperzijskega utrjevanja drobni sekundarni karbidi lahko povečajo mehansko podporo evtektičnih karbidov M_7C_3.

Ključne besede: zlitina Fe-Cr-C-Nb-V, NbC-karbidi, sekundarni karbidi, odpornost proti obrabi, lomna žilavost

1 INTRODUCTION

High-chromium white cast irons constitute an important class of wear-resistant materials currently used in a variety of applications where the stability in an aggressive environment is the principal requirement, including the mining and mineral processing, cement production, slurry pumping, and the pulp and paper manufacturing industries.

In the case of high-chromium white cast irons, important microstructural parameters for the wear resistance include the volume fraction, hardness, orientation and morphology of carbides[1–5] and the type of matrix.[1,2,6] These factors also influence the hardness and fracture toughness of the material.[1,2,7]

Extensive industrial applications of high-chromium white cast irons have attracted researchers to try different carbide-forming elements such as tungsten,[8,9] vanadium,[8–16] niobium,[8,10,17–22] titanium[10,19,23–26] and boron[27] to further improve this type of material. An addition of an alloying element which confines carbon in the form of a carbide, with a greater hardness and a more favorable morphology, and which reduces the carbon content of the matrix, allows a simultaneous improvement of both toughness and abrasion resistance.[1,9,13,24] By controlling the morphology of the carbide phase and the matrix structure in these materials, a significant improvement in the toughness and service life may be achieved.

An introduction of niobium to these alloys resulted in a preferential formation of NbC which is appreciably harder than the other carbides present and which forms efficiently since niobium is fully partitioned to these phases.[17–19,21] Vanadium appears to be of special interest, due to its double effect on both the matrix structure and stereological characteristics of carbides.[12,14] Subsequently, niobium and vanadium improve the hardness and wear resistance.[10,11,13,20] However, there is little information[1] available concerning the influence of niobium and vanadium on the fracture toughness or explaining how much of these elements should be combined with high-chromium white iron to obtain the optimum fracture toughness and abrasive-wear resistance.

In this study the influence of the mass fractions 1.5 % Nb and 1.5 % V, added singly and in combination, on the microstructural characteristics and properties relevant to the service performance of the hypoeutectic high-chromium white iron containing 18 % Cr and 2.9 % C, namely, the wear resistance and the fracture toughness, was examined.

2 EXPERIMENTAL PROCEDURE

The chemical compositions of the tested alloys are listed in **Table 1**. An induction furnace was used for melting, and rods with a length of 200 mm and a diameter of 30 mm were cast in sand molds. Samples for the structural analysis, hardness, wear, and fracture-toughness tests were cut from the cast rods.

The microstructure was examined using conventional light microscopy (LM) and transmission electron microscopy (TEM). The samples for the light-microscope examinations were prepared using the standard metallographic technique (etched with a picric acid solution (1 g) in methanol (100 mL) with an addition of 5 mL of hydrochloric acid). The sizes and volume fractions of the phases present in the structure were determined using an image analyzer.

The Cr K_α radiation was used for measuring the amount of the retained austenite by means of X-rays, as it is considered to be more appropriate for the structures containing greater amounts of carbides (in order to increase the dispersion, if there are interference peaks, for example).[28] A continuously rotating/tilting specimen holder was used to eliminate the effect of the preferred orientation of the columnar structure, which was shown to affect the results (as described in detail in[29]). At a scanning rate of 1° min^{-1}, the integrated intensities under the peaks of (200)α, (220)α, (220)γ and (331)γ were measured with a diffractometer.

The hardness of nickel-chromium and high-chromium white cast-iron alloys was examined with the Vickers method at a load of 294 N. The abrasive wear resistance was evaluated according to the ASTM Standard Practice G-65, Procedure B (dry-sand/rubber wheel abrasion test). Rounded quartz-grain sand with a mesh of 50–70 was used as an abrasive particle. The volume loss, ΔV, was then calculated by dividing the mass loss by the alloy density. The reciprocal value of the volume loss, ΔV, due to the wear is called the wear resistance, ΔV^{-1}. The dynamic fracture toughness was measured at room temperature using an impact test machine equipped with an instrumented Charpy tub. The testing methodology selected was based on the three-point bending tests. The specimens with the dimentions of 10 mm × 10 mm × 55 mm were notched and precracked by fatigue following the ASTM E399 recommendations. The dynamic-stress-intensity factor, K_{Id}, was determined using the following equation:[30,31]

$$K_{Id} = \left(\frac{P_{max} S}{B W^{3/2}} \right) f\left(\frac{a}{W} \right) \tag{1}$$

where P_{max} is the maximum load, S is the span, B is the specimen thickness, W is the specimen width, a is the initial crack length and $f(a/W)$ is the geometry factor.

3 RESULTS

The as-cast microstructure of the tested hypoeutectic white cast irons with a high-chromium content consists primary of austenite dendrites and eutectic colonies,

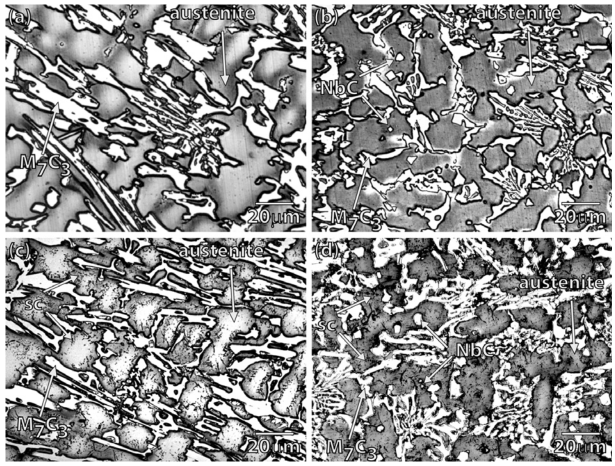

Figure 1: LM micrographs of the: a) basic Fe-Cr-C alloy, b) Fe-Cr--C-Nb alloy containing 1.58 % Nb, c) Fe-Cr-C-V alloy containing 1.55 % V and d) Fe-Cr-C-Nb-V alloy containing 1.53 % Nb and 1.47 % V

Slika 1: Mikrostruktura: a) osnovne Fe-Cr-C-zlitine, b) Fe-Cr-C-Nb--zlitine z 1,58 % Nb, c) Fe-Cr-C-V-zlitine z 1,55 % V in d) Fe-Cr--C-Nb-V-zlitine z 1,53 % Nb in 1,47 % V

Table 1: Chemical compositions of the tested alloys in mass fractions (*w*/%)

Tabela 1: Kemijska sestava preizkušanih zlitin v masnih deležih (*w*/%)

Alloy	C	Si	Mn	Cr	Ni	Mo	Cu	Nb	V
Fe-Cr-C	2.93	0.55	0.85	17.93	0.73	0.92	0.83	–	–
Fe-Cr-C-Nb	2.94	0.59	0.84	17.97	0.71	0.91	0.87	1.58	–
Fe-Cr-C-V	2.89	0.58	0.79	18.12	0.75	0.96	0.86	–	1.55
Fe-Cr-C-Nb-V	2.91	0.51	0.81	18.01	0.70	0.91	0.84	1.53	1.47

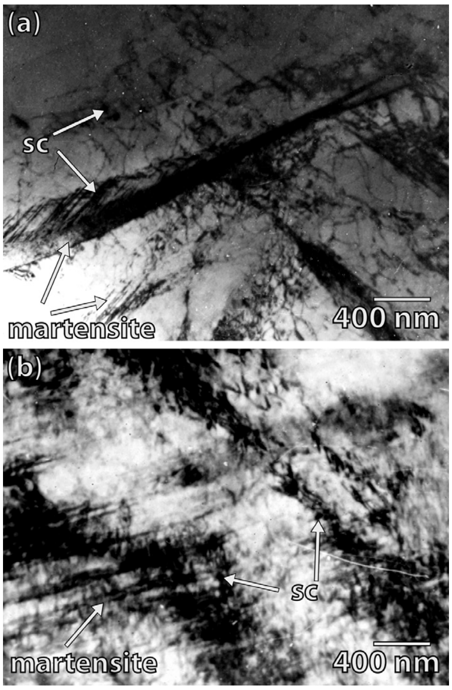

Figure 2: TEM micrographs of the: a) Fe-Cr-C-V alloy and b) Fe-Cr--C-Nb-V alloy showing secondary carbides and martensite
Slika 2: TEM-posnetka: a) Fe-Cr-C-V-zlitine in b) Fe-Cr-C-Nb-V--zlitine s sekundarnimi karbidi in martenzitom

composed of M_7C_3 carbide and austenite (**Figure 1**). Also, nodular- or hexagonal-disc NbC carbides were observed to form in the tested alloys containing niobium (**Figures 1b** and **1d**).

The primary austenite in the basic Fe-Cr-C and Fe-Cr-C-Nb white irons, is mainly stable when cooling down to room temperature (**Figures 1a** and **1b**). Very fine particles are observed in the primary austenite dendrites of Fe-Cr-C-V and Fe-Cr-C-Nb-V alloys (**Figures 1c** and **1d**). In a previous paper[12] these particles precipitating in the matrix were identified to be the carbides of the $M_{23}C_6$ type. Martensite is noticed around the carbide particles (**Figures 2a** and **2b**). The volume

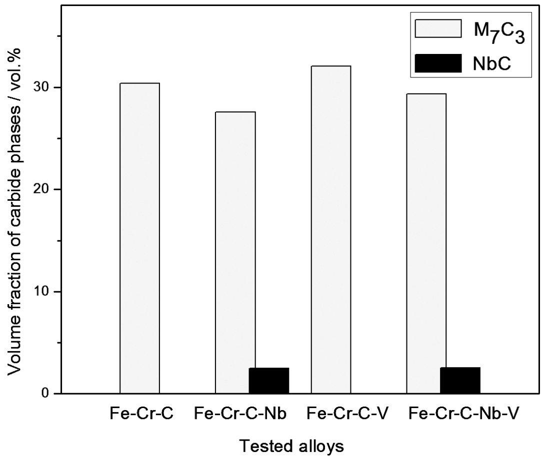

Figure 4: Volume fractions of carbide phases in the tested alloys
Slika 4: Volumenski deleži karbidnih faz v preizkusnih zlitinah

fraction of the retained austenite in the tested Fe-Cr-C-Nb alloy is approximately the same as in the basic Fe-Cr-C alloy (**Figure 3**). On the other hand, the amount of the retained austenite is found to decrease in the tested high-chromium white irons, alloyed with vanadium (Fe-Cr-C-V and Fe-Cr-C-Nb-V alloys, **Figure 3**).

The influence of niobium and vanadium on the volume fractions of the carbide phases in the tested alloys is shown in **Figure 4**. The volume fraction of M_7C_3 eutectic carbides decreases with a niobium addition, whereas it increases with a vanadium addition in the tested Fe-Cr-C white iron. The Fe-Cr-C-Nb-V type alloy has approximately the same volume fraction of M_7C_3 carbides as the basic Fe-Cr-C alloy.

Niobium and vanadium influenced the refinement of the structure of high-chromium white cast iron (**Figure 5**). The matrix microhardness of the Fe-Cr-C and Fe-Cr-C-Nb alloys is lower compared to the Fe-Cr-C-V and Fe-Cr-C-Nb-V alloys (**Figure 6**).

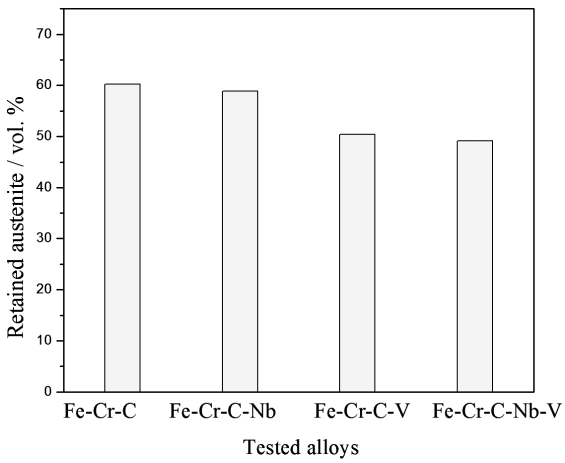

Figure 3: Volume fraction of the retained austenite in the tested alloys
Slika 3: Volumenski delež zaostalega avstenita v preizkusnih zlitinah

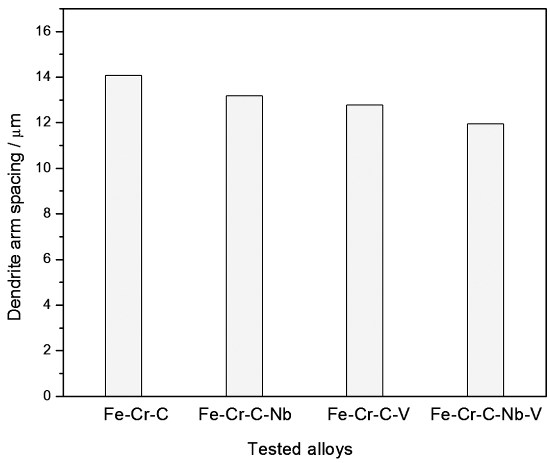

Figure 5: Dendrite arm spacing in the tested alloys
Slika 5: Razdalja med dendritnimi vejami v preizkusnih zlitinah

An addition of 1.5 % Nb and 1.5 % V, singly or in combination, to the Fe-Cr-C alloy with a high chromium amount results in an increase in the hardness, wear resistance and dynamic fracture toughness (**Figures 7**, **8** and **9**, respectively). Niobium makes a greater contribution to the improvement of the wear resistance, whereas vanadium makes a greater contribution to the improvement of the hardness and toughness of the tested alloys in the as-cast condition.

4 DISCUSSION

For the present study, all the alloys were solidified at the same rate and the differences observed are attributed to the effect of the alloying elements.

The changes in the volume fractions (**Figure 4**) and sizes (**Figure 5**) of the phases in the structures of the tested alloys indicate that niobium and vanadium affect the crystallization process in hypoeutectic high-chromium white irons.

Niobium in the Fe-Cr-C-Nb and Fe-Cr-C-Nb-V alloys with high-chromium amounts forms niobium carbides of the MC type. The solubility of niobium in austenite and M_7C_3 carbide is very low, so the majority of the niobium present in the alloy is in the form of an MC carbide.[8,10,17] MC carbides are formed before M_7C_3,[17,21] causing a depletion of the carbon in the liquid. Since carbon is the primary element determining the amount of carbide in high-chromium iron, the amount of M_7C_3 carbide is lower in the Fe-Cr-C-Nb alloy when compared to the basic Fe-Cr-C alloy (**Figure 4**).

As a consequence of alloying high-chromium white iron with vanadium, the solidification-temperature interval is narrower. This effect was considered previously in detail.[14] The eutectic-colony growth rate increases significantly with the increasing eutectic temperature, i.e., with the decreasing solidification-temperature interval, thus stimulating the formation of a larger amount of finer M_7C_3 carbides (**Figure 4**).

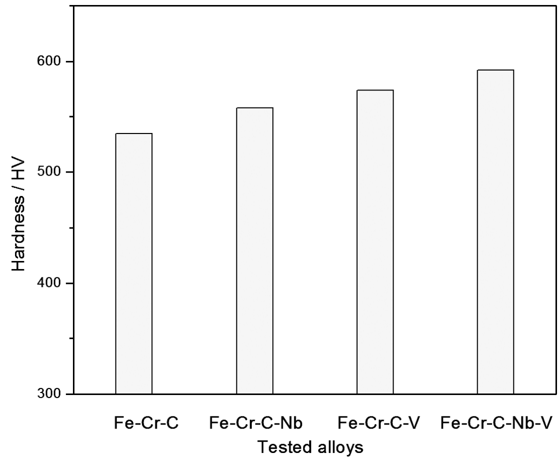

Figure 7: Hardness of the tested alloys
Slika 7: Trdota preizkusnih zlitin

The volume fraction of the M_7C_3 eutectic carbides in the tested Fe-Cr-C-Nb-V alloy is approximately the same as in the basic Fe-Cr-C alloy (**Figure 4**), since, on the one hand, a niobium addition causes a reduction, while vanadium, on the other hand, causes an increase in the amount of the M_7C_3 carbides in the structure.

Vanadium was found to affect the transformation of the austenite in the as-cast condition of the tested Fe-Cr--C-V and Fe-Cr-C-Nb-V alloys (**Figures 1c**, **1d** and **2**). At the temperatures below the solidus, in the course of further cooling after the solidification, $M_{23}C_6$ carbides precipitate in the austenite in the tested alloys containing vanadium (**Figures 1c**, **1d** and **2**). The transformation of the austenite into martensite in these alloys is closely related to the precipitation of secondary carbides. The precipitation of $M_{23}C_6$ carbides minimizes the carbon and chromium amounts in the matrix, and increases the Ms temperature.

Niobium and vanadium altered the microstructure characteristics of the high-chromium white iron and affected its properties.

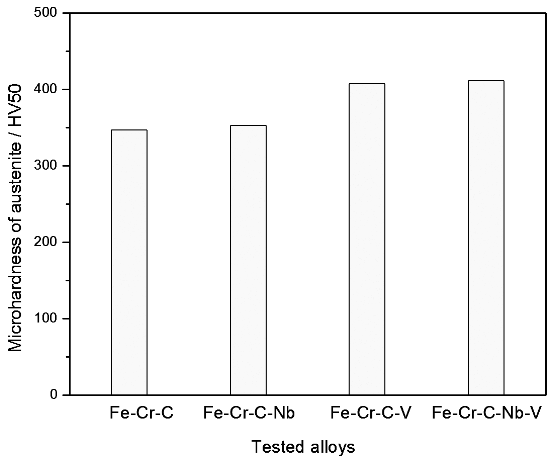

Figure 6: Microhardness of the tested alloys
Slika 6: Mikrotrdota preizkusnih zlitin

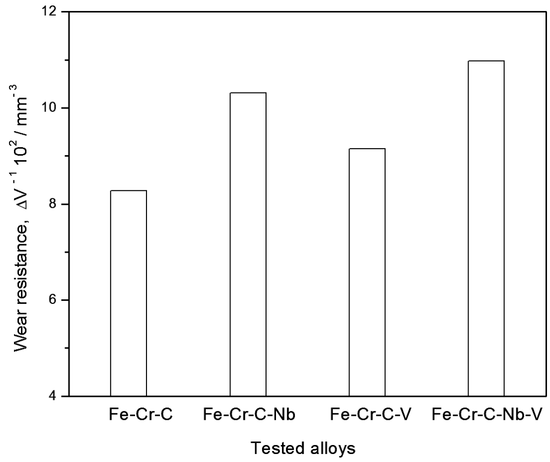

Figure 8: Wear resistance of the tested alloys
Slika 8: Obrabna odpornost preizkusnih zlitin

The improved hardness of the tested Fe-Cr-C-Nb alloy (**Figure 7**) is the result of a presence of hard NbC carbides in the structure (**Figures 1b** and **1d**).

The increased volume fraction of the eutectic M_7C_3 carbides (**Figure 4**), caused by adding vanadium to the Fe-Cr-C white iron, contributes to the improvement of the hardness (**Figure 7**). Moreover, the martensite present in the structure (**Figure 2**), improves the matrix microhardness (**Figure 6**) and, consequently, the alloy macrohardness (**Figure 7**).

The hard NbC carbide phase present in the microstructure (as the result of the niobium addition) and the martensite, together with a reduction in the volume fraction of the retained austenite (as the result of the vanadium addition) contribute to the improvement of the hardness of the tested Fe-Cr-C-Nb-V alloy.

The increase in the volume fraction of the M_7C_3 eutectic carbides in the tested Fe-Cr-C-V alloy and the NbC carbides present in Fe-Cr-C-Nb and Fe-Cr-C-Nb-V alloys (**Figure 4**) reduce the volume loss caused by the abrasive wear (**Figure 8**). The abrasion resistance of the carbide phase was more effective than the matrix in high-chromium white cast irons since, among other things, the hardness values of M_7C_3 carbides (1200–1800 HV)[1,10] and NbC carbides (2370 HV)[10] were greater than the hardness of the abrasive used (960 HV)[1]. Besides, NbC carbides, due to their characteristic morphology, show a higher wear resistance than M_7C_3 carbides. The wear under low-stress abrasion conditions, and in the case of a quartz abrasive, was apparently controlled by the rate of removing the carbide phase, while the protruding carbides protected the matrix from a direct attack of the abrasive particles.

In addition to the volume fraction of the carbides, the size of the phases present in the structure was another microstructure variable that affected the abrasive resistance of the Fe-Cr-C white iron alloyed with niobium and vanadium. The smaller size of the primary austenite dendrites, i.e., the average distance between the carbide particles, caused by adding niobium and vanadium to the alloy (**Figure 5**), protected the matrix better from a direct attack of the abrasive particles.

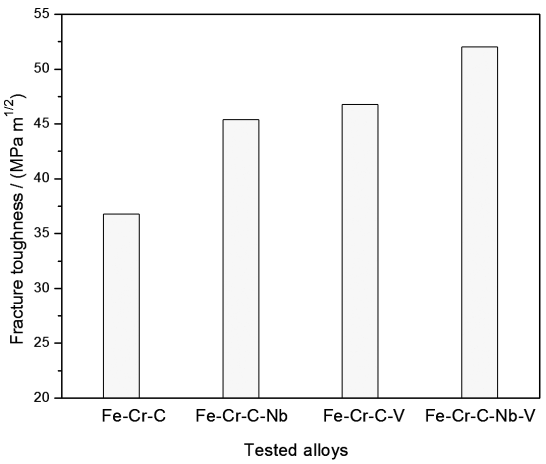

Figure 9: Dynamic fracture toughness of the tested alloys
Slika 9: Dinamična lomna žilavost preizkusnih zlitin

The wear resistance under low-stress abrasion conditions also depended on the matrix microstructure. In addition to the fact that the matrix helped control the penetration depth of the abrasive particles, it also played an important role in preventing a bodily removal of smaller carbides and cracking the massive ones.[3,5,6] Experimental results indicate that the secondary carbides that precipitate in the matrix regions of the tested high-chromium iron containing vanadium influence the abrasion behaviour. By increasing the matrix strength through a dispersion-hardening effect, the fine secondary carbides can increase the mechanical support of the carbides. These results agree with those of Liu et al.[32] and Wang et al.[33] who found that the precipitation of fine $M_{23}C_6$ carbides, as a result of the cryogenic treatment, is responsible for the improved wear resistance of high-chromium white irons.

A brittle failure involved a crack initiation and propagation, the latter being controlled by the fracture toughness. Since the crack moved easily through eutectic carbides, decreasing the volume fraction of the brittle M_7C_3 carbide phase (**Figure 4**), caused by adding niobium to the Fe-Cr-C white iron, it increased the fracture toughness (**Figure 9**). In addition, NbC carbides, due to their characteristic morphology (**Figures 1b** and **1d**), have a higher toughness than M_7C_3 carbides and they, consequently, contribute to an improved fracture toughness of the tested Fe-Cr-C-Nb alloy.

In addition, the results of the fracture-toughness tests (**Figure 9**) show that the dynamic fracture toughness of the tested white irons is also determined by the properties of the matrix. The primary role of the matrix in the fracture process of the high-chromium white cast irons was to prevent the brittle cracks from propagating from one carbide particle to another. The matrix, therefore, had a crack-blunting effect, which subsequently increased the critical stress-intensity factor necessary to continue crack propagation.[1,2]

The vanadium addition to the tested high-chromium white iron increases the volume fraction of the M_7C_3 eutectic carbides and reduces the fracture toughness. Further, the amount of the retained austenite decreases (**Figure 3**), subsequently reducing the toughness. However, the tested alloy containing 1.55 % V showed a greater dynamic fracture toughness when compared to the basic Fe-C-Cr alloy (**Figure 9**). The fracture toughness was determined mainly with the energy that had to be consumed while the crack was extending through the ligaments of the matrix.[1,7] Since the austenite in these alloys contained very fine $M_{23}C_6$ carbide particles, the higher fracture toughness was attributed to the strengthening of the austenite during fracture. The improvement of the fracture toughness of the alloy containing 1.55 % V, due to the presence of fine $M_{23}C_6$ carbides within the austenite, was considerably higher than the reduction caused by an increase in the amount of M_7C_3 carbides and a reduction in the volume fraction of the retained austenite.

Due to the presence of NbC carbides in the structure (as a result of the niobium addition) and the presence of fine $M_{23}C_6$ carbides within the matrix (as a result of the vanadium addition), the tested Fe-Cr-C-Nb-V white iron showed a greater dynamic fracture toughness than the other experimental alloys (**Figure 9**).

It follows from the present results that the alloy containing 1.53 % Nb and 1.47 % V gives the best compromise between the wear resistance and fracture toughness (**Figures 8** and **9**). This alloy shows a dynamic fracture toughness that is greater by about 42 % and an abrasion wear resistance greater by about 33 % than the values for the basic Fe-Cr-C alloy. It may be used to produce dents and hammers for the fibrizer equipment recovering asbestos fibres, and in many other applications where good abrasion resistance and toughness are necessary.

5 CONCLUSIONS

Niobium and vanadium altered the microstructure characteristics of the hypoeutectic high-chromium white cast iron containing mass fractions 18 % Cr and 2.9 % C and affected its mechanical properties.

The alloy containing 1.53 % Nb and 1.47 % V gives the best compromise between the wear resistance and the fracture toughness. The dynamic fracture toughness of this alloy is larger by about 42 % and the abrasion wear resistance is larger by about 33 % than the properties of the basic alloy with no niobium and vanadium additions.

NbC carbides, due to their characteristic morphology, show a higher wear resistance and toughness than M_7C_3 carbides. The presence of this type of carbides in the structure, caused by an addition of niobium to the alloy, contributes to the improvement of the wear resistance and dynamic fracture toughness.

Besides, the higher fracture toughness is attributed to the strengthening during fracture, since very fine secondary carbide particles were present mainly in the austenitic matrix (as the consequence, in this case, of alloying high-chromium white iron with vanadium). The secondary carbides precipitating in the matrix regions also influence the abrasion behaviour. By increasing the matrix strength through a dispersion-hardening effect, the fine secondary carbides can increase the mechanical support of the eutectic carbides.

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