

Strategies for the Development of Wear-Resistant Coatings: A Review

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Abstract: *This review presents the possible strategies to increase the wear resistance of hardfacing alloys based on metallic matrix and second hard phase's coupled design. As the wear resistance is not an intrinsic property of material, the results of many wear tests are discussed in light of the interaction between mechanical properties and wear severity, which is dependent on the microstructure. These strategies are based on the hardness increase, considering the kind and size of the second hard phase, the fracture toughness, and the dilution level of hardfacing. The guidelines provided for designing better the hardfacing alloys for usual abrasion conditions depending on the volume fraction of the second hard phase.*

Key-words: *Abrasive wear; Hardfacing; Carbides.*

Estratégias para o Desenvolvimento de Revestimentos Resistentes ao Desgaste: Uma Revisão

Resumo: *Esta revisão apresenta possíveis estratégias para aumentar a resistência ao desgaste de revestimentos duros, baseado no projeto conjunto de matriz metálica e segunda fase dura. Como a resistência ao desgaste não é uma propriedade intrínseca do material, os resultados de vários ensaios de desgaste são discutidos à luz da interação entre propriedades mecânicas e severidade de desgaste, o que é dependente da microestrutura. Estas estratégias são baseadas no aumento de dureza, considerando o tipo e tamanho da segunda fase dura; a tenacidade à fratura e o nível de diluição do revestimento. As diretrizes fornecidas para o melhor projeto de ligas de revestimentos duros para condições usuais de abrasão dependem da fração volumétrica de segunda fase dura.*

Palavras-chave: *Desgaste abrasivo; Revestimento duro; Carbonetos.*

1. Introduction

Wear resistance is not an intrinsic property of materials. The concept of tribo-system is presented by Czichos [1]. It consists of four tribo-elements, body (where the wear is crucial), counter-body, interfacial medium, and environment. Any change in each tribo-element can correspond to a modification of the wear mechanism, meaning changes in the body's wear rates. Following this standard, abrasion is one of the four primary mechanisms of wear. It can be defined as "[...] wear due to hard particles or hard protuberances forced against and moving along a solid surface [...]" [2:1] (ASTM International, 2021, p. 1). The abrasive wear can be considered the most probable mechanism to be found in practical situations, estimated to be about 50% [3].

Typical situations of abrasion occurrence are associated with the earthmoving, such as mining, agricultural, and civil construction. For many components, the deposition of a hardfacing alloy reduces costs, allowing for a cheaper and more rigid substrate. Renewal of worn surfaces can be done with new depositions, as a critical level of wear is achieved, avoiding a complete substitution of the whole component.

This review presents possible strategies related to the hardfacing alloys' microstructure in this fashion, aiming to increase the abrasion resistance.

2. Design Controlled by Hardness

A surface to be harder than another one is the fundamental requirement to promote abrasive wear. On the opposite, it is reasonable to harden a material to resist the abrasive action. It is evident from the equation 1 postulated by Rabinowicz et al. [4] for abrasive wear (expressed by the volume loss variation, dV , for each slid distance, dl), which was based on the generalized Archard equation of wear [5]:

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$$\frac{dV}{dl} = \frac{\tan\theta}{\pi} \frac{W}{H} \quad (1)$$

where $\tan\theta$ is the average tangents of all roughness angles of the abrasive particles, H is the bearing surface's hardness, and W is the total load.

From this premise, the question is: how hard is the most common abrasive? Following Wedepohl [6], quartz is the most common mineral on Earth's crust, corresponding to 61.5% of it. This mineral is relatively hard, Broz et al. [7] determined its hardness as 12 GPa.

Thinking of steel as a suitable solution for structural components, the harder constituent, martensite, will not surpass quartz's hardness. Ohmura et al. [8] determined the nanohardness of martensite, for the maximum content possible of carbon, as about 10 GPa. Consequently, quartz can abrade hardened steel.

The solution is looking for another constituent harder than quartz. Looking at the summaries published by Sano et al. [9] and Scandella and Scandella [10], various carbides are harder than quartz, especially those with MC stoichiometry. Indeed, the nanoindentation experiments conducted by Pöhl et al. [11] confirmed a hardness of 30 and 27 GPa for VC and WC carbides, respectively. These values are a very probable guarantee to have a wear-resistant material.

For the reasons above-mentioned, here the described experiments are concentrated in those that use silica (or softer materials) as abrasive.

Then, what are the families of materials that contain carbides as constituents? Most of the hardfacing alloys are based on four families: tool steels [12], abrasion-resistant cast irons [13], cemented carbides [14], and metal matrix composites [15]. Different examples will be described here, considering the following aspects in the design of microstructure:

- i) carbide size;
- ii) kind of carbide (combination between its morphology and mechanical properties).

Regarding the carbide size, it is complicated to vary this parameter without change the volume fraction. In this sense, this effect should be separated depending on the typical volume fraction of the second hard phase of each hardfaced material. For didactical purposes, two classes can be presented: i) materials with volume fraction ranging from 15 to 40%, and ii) materials with volume fraction higher than 80%.

A laborious methodology could be applied by Desai et al. [16] for Co-base alloys. They verified in dry sand/rubber wheel abrasion test (DSRW) the carbide size effect, as summarized in Figure 1.

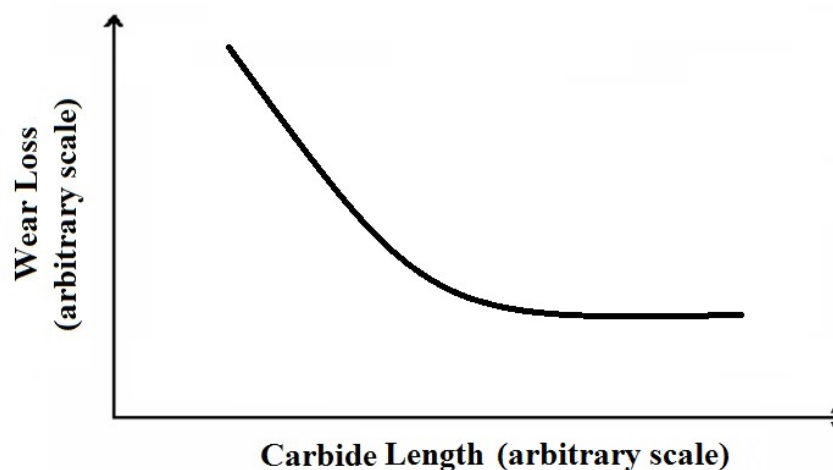


Figure 1 shows that the higher the carbide size, the higher the abrasion resistance. This behavior can be explained, keeping in mind that the abrasive particle's main action is to cut the surface. When the particle finds a harder phase, such as carbides, depends on its size, the hard phase can block the cutting action. Small carbide sizes tend to be removed together with the metallic matrix since the load applied per particle can cause a width on a worn track larger than its diameter. The effect of blocking the action of an abrasive particle was described by Pintaude et al. [17], who performed a manual scratch on a polished surface using a glass fragment, softer than the chromium carbide (Figure 2).

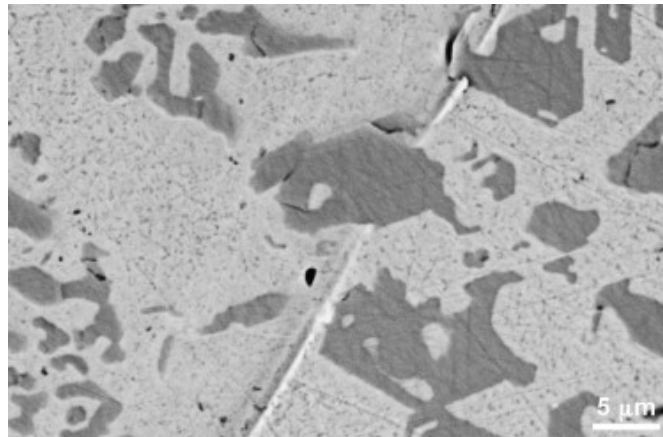


Figure 2. The blocking action promoted by a chromium carbide on a manual scratch did with a glass fragment [17].

The effect of carbide size is corroborated by the findings published by Bourithis et al. [18]. They compared the abrasion resistance of different cold work tool steels but were treated for having the same hardness. For a wide range of loads in the DRSW test, the D2 tool steel always behaved better than the O1 steel. Logically, the M_7C_3 carbide in the D2 steel is higher in size than the Fe_3C constituent in O1 steel, justifying the wear resistance performances. This difference opens the discussion about carbide's mechanical properties, i.e., what kind of carbide can bring a better abrasion resistance.

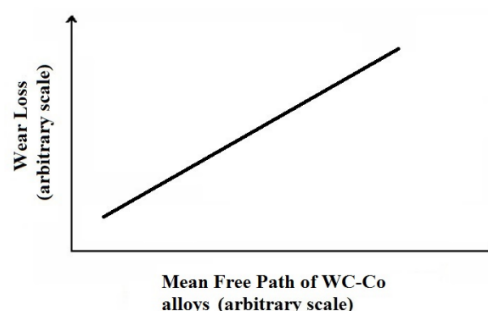
The comparison of different carbides in hardfacing alloys was well-described by Buchely et al. [19]. They deposited three hardfacing alloys onto ASTM A36 steel plates using the shielded metal arc welding (SMAW) method. They found an impressive result regarding W-rich carbides with M_6C stoichiometry and fishbone-like shape. During scratching, this carbide was able to deform, absorbing a significant level of plastic deformation. By opposite, a blocking action was provided by Cr-rich alloy, with the predominance of M_7C_3 carbide. However, the capacity of deformation of W-rich alloy provided a better wear resistance because, in this alloy, a significant amount of hard MC carbide constitutes the microstructure, giving proper support for effective action against abrasion.

It is clear from the results described by [19] that the shape of carbides can play a crucial role in protecting the metallic matrix, consequently affecting the abrasion resistance. However, the findings presented by Kusumoto et al. [20] showed that an alloy with a predominance of NbC carbide performed better against the abrasive wear than others, with more VC carbide. The reason for that is the larger diameter of NbC about the VC one. In this case, even one describing VC as harder than NbC [11], the blocking action due to the higher diameter was crucial to improve the abrasion resistance.

Coatings produced with high volume fractions of the second hard phase, based on hardmetals, differ on the carbide size approach to minimize the abrasive wear. The reason for that is to keep the same volume fraction, the increase in carbide size results in an increase of the mean free path, which exposed the metallic matrix, usually softer than the second phase.

Wang et al. [21] studied the WC grain size's effect on the wear resistance of HVOF-sprayed WC-20Cr3C2-7Ni coatings. Paying attention to the relevant abrasive used, when they tested three coatings against 180-mesh silica under three-body abrasive wear, the coating prepared with the coarse powder of WC size ($8\ \mu m$) worn approximately twice the one manufactured using fine WC ($0.8\ \mu m$).

Although these findings are in the opposite direction of those described in Figure 1, the reason is not so far from the mechanisms involved, which become the second hard phase able to protect the metallic matrix. This ability is intimately related to the mean free path determined for a specific microstructure. For WC-Co materials, Larsen-Basse and Koyanagi [22] determined the mean free path on the volume loss caused by silica under three-body abrasion (Figure 3).



The results provided by [22] showed that the increase in mean free path resulted in a higher volume loss under abrasion. The material removal can be described as a two-step process, as illustrated in Figure 4. This sequence is valid for both kinds of materials described here, with a relatively low volume fraction of the second hard phase and with high volume. The first step is the cutting action of abrasive on the metallic matrix. The sequential removal causes a loss on the bearing support for the carbides, which can either fracture or detach further contacts. This mechanism was described by Pintaude et al. [17], Wang et al. [21], and Larsen-Basse and Koyanagi [22], independent of the effect of the carbide size on wear.

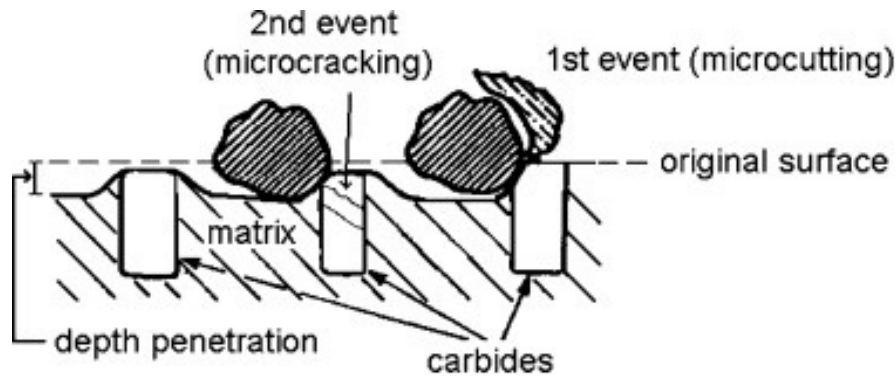


Figure 4. A two-step mechanism involved removing the second hard phase during abrasion [17,21-22].

The concept to protect the metallic matrix from achieving an adequate abrasion resistance was well described by Chang et al. [23]. It is better to reproduce their conclusion, which summarizes the guideline: “[...] wear resistance not only depends on surface fractions of carbides but also cladding hardness and the mean free path of carbides.” (Chang et al., 2010, p. 249). Hard carbides can be chosen to hard the alloy, but their sizes are a crucial variable to manufacture an adequate hardfacing.

3. Design Controlled by Fracture Toughness

After controlling the carbides’ aspects as the second hard phase, the abrasion resistance may have dictated by the fracture toughness. For brittle solids, Moore and King [24] described a model to abrasive wear (Equation 2), based on the removal of material by lateral cracking:

$$\frac{dV}{dl} = k \frac{d^{1/2}}{K_{IC}^{3/4}} \frac{p^{5/4}}{H^{1/2}} \quad (2)$$

where k is a constant, d is the average size of the abrasive particles, K_{IC} is the fracture toughness of the bearing surface, and p is the average pressure.

The severity of the system plays a crucial role in defining the abrasion resistance as a fracture toughness function. A summary of the behavior of abrasion-resistant materials was provided by Zum-Gahr and Doane [25], as shown in Figure 5.

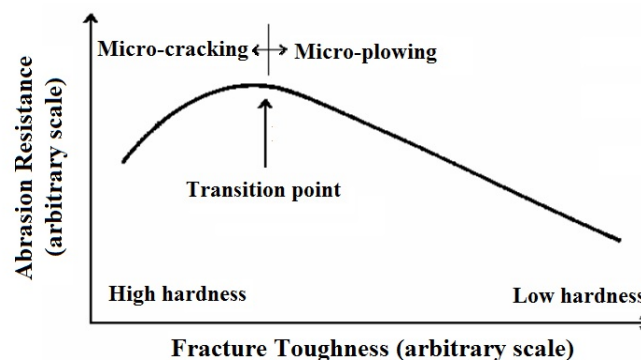


Figure 5 shows the existence of an optimum point in terms of fracture toughness for the abrasion resistance. This point can be shifted, depending on the severity of the tribological system.

Logically, the volume fraction of carbides will affect the fracture toughness of the alloy. Then, the volume fraction of carbides should be select taken into account the abrasive characteristics (hardness, size, and geometry).

An exciting investigation was performed by Sabet et al. [26]. They conducted DSRW tests on three compositions of Fe-Cr-C hardfacing alloys, keeping constant the Cr/C ratio. The resulting microstructures were hypoeutectic, eutectic, and hypereutectic, with 64, 77, and 85% volume fractions. The best performance of hypoeutectic alloy was a result of the wear mechanisms, which were related to the fracture toughness. Only for this alloy, the microcracking did not happen, leading to the lowest wear loss.

Nevertheless, would be the volume fraction of carbides the only microstructural variable to control to achieve a better fracture toughness? Another one plays a crucial role in this case: the metallic matrix.

For that purpose, the results obtained by Franco and Sinatora [27] are beneficial to understand the role of the metallic matrix on the fracture toughness of hard carbides. They measured this property using the Vickers hardness test, producing cracks during the indentation loading (Figure 6).

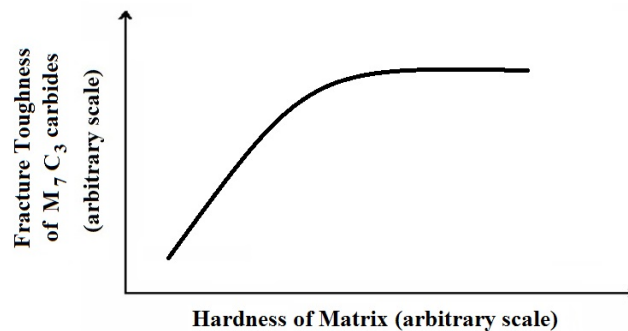
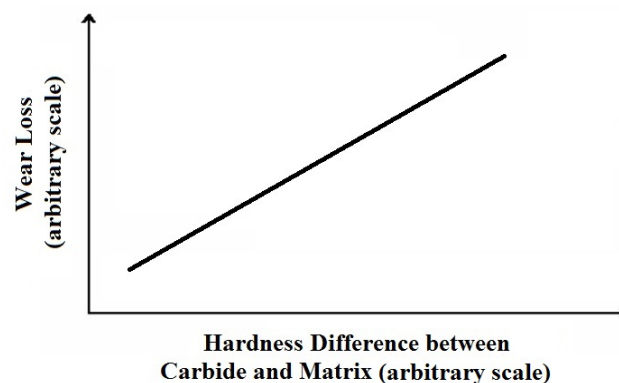


Figure 6 shows that the higher the matrix hardness, the higher the fracture toughness of carbide. The conclusion is that the metallic matrix's deformation should not be excessive to provide proper bearing support for the carbides. Consequently, carbides' fracture toughness is an apparent value, dependent on the matrix's mechanical properties that surround it.

This reasoning was confirmed by Kim et al. [28], who tested three white cast irons in DRSW equipment. Applying different heat-treatments, these researchers could verify the effect of the difference in hardness between the metallic matrix and carbides on the wear resistance, as shown in Figure 7.



An experimental result described by Pintaude et al. [17] is a suitable example to confirm the concept presented in Figure 7. The wear rate of multicomponent cast iron caused by glass particles was reduced in one order of magnitude when the metallic matrix was increased from 460 to 590 HV. This notorious increase was due to the matrix's support to MC carbides, which did

not experience cracking after this increase. Then, although the MC carbide could be an excellent candidate to design a wear-resistant alloy, it could not perform well against alumina abrasive due to the poor bearing support given by the metallic matrix, as shown in Figure 8.

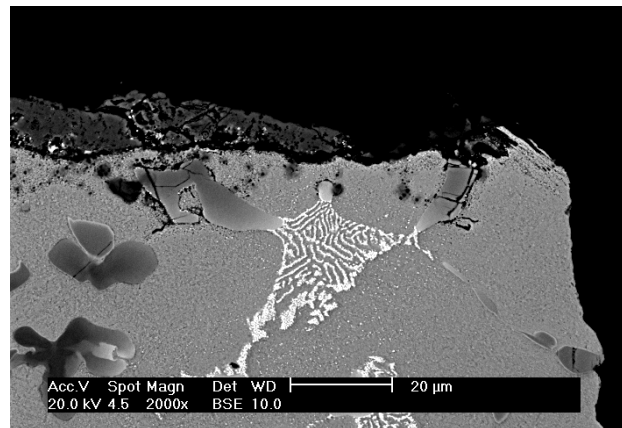


Figure 8. Microcracking of MC carbide observed in a softer multicomponent cast iron abraded by 0.2 mm alumina paper [17].

The fracture toughness design should be considered if the austenitic matrix was delivered to a hardfacing alloy. Amongst the challenges to produce a martensitic hardfacing, one is the high-cost of welding electrodes [29]. Therefore, it is useful to analyze the results related to the austenitic matrix, once the difference between its hardness and the carbide hardness would be a problem, following the premise of Figure 7.

In this sense, the investigation conducted by Correa et al. [30] is an excellent example of how the design of microstructure can be reconsidered in the case of a softer matrix. They used two hardfacing electrodes on mild steel, resulting in a conventional high-chromium alloy (austenitic matrix + M_7C_3 carbides) and another one with the addition of MC and M_3C carbides. They performed two wear tests to verify the differences caused by the microstructure, ASTM G65 and pin-on-disc coated with SiC abrasive. As expected, microcracks were identified after all tests, but the pin-on-disc could not differentiate the performance of tested alloys. On the contrary, using the DRSW test, the performance of conventional high-chromium hardfacing was worst. The authors explained it due to the presence of fine primary Nb-rich carbides randomly dispersed in an austenitic matrix containing very fine M_3C carbides. Therefore, to offer extra protection to a softer matrix, finer second hard carbides can be used, helping to avoid crack propagation.

It is not worthwhile that the use of hard abrasive particles, such as SiC, in pin-on-disc configuration did not bring any information regarding the wear resistance. The austenitic matrix can perform better in this system, but the reasons for that may not correlate with a specific component [31]. It is verified by Kazempour et al. [32], who tested four microstructures – ferrite, austenite, martensite, and tempered martensite - against SiC abrasive. They concluded that the as-welded (austenitic) matrix shows the highest wear resistance. This result was associated with the phase transformation induced by high-induced plastic deformation during the wear test.

This result from pin-on-disc was also found by Albertin and Sinatora [31] for austenitic cast iron. However, the austenitic matrix was not the best microstructure under ball mill tests than the martensitic ones. The real situation implies less plastic deformation, and the poor bearing support given by the austenitic matrix gave rise to a microcracking of M_7C_3 carbides during the ball milling. Therefore, to predict an abrasion performance from the pin-on-disc test should be taken carefully.

Fracture toughness can also be a control property for coatings with large volume fractions of carbides, such as hardmetal. However, the variation of abrasion resistance differs from that described in Figure 5. Fortunately, Roebuck et al. [33] presented this variation for WC-Co alloys (Figure 9).

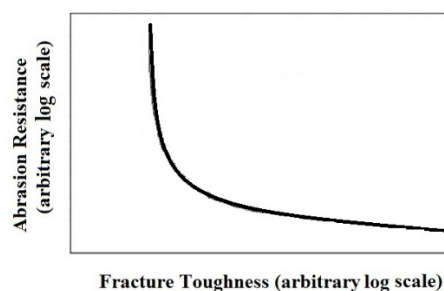


Figure 9. Variation of abrasion resistance with the fracture toughness (determined by indentation) of WC-Co alloys [33].

Figure 9 shows that the abrasion resistance drops continuously beyond a certain point with the increasing in WC-Co alloys' fracture toughness. The reason for that is the mean free path of metallic matrix governs the increase in this property, but the cutting action is preferable at this microstructural feature. Additionally, for a typical fracture toughness value, the increase in abrasion resistance depends much less on the fracture toughness, which means that the hardness approach discussed previously is predominant.

As a future trend, new developments of metallic matrix for hardmetal alloys are been proposed, such as the investigation performed by Testa et al. [34]. These researchers studied five WC-based HVOF coatings, three of them new alternatives for metallic matrix compositions (FeNiCrMoCu, NiMoCrFeCo, and FeCrAl). Unfortunately, they did not report the fracture toughness of coatings, and the abrasive wear testing was conducted using a hard abrasive (alumina), which is not representative for the current discussion. However, a promising result was observed for the FeNiCrMoCu matrix, which achieve the same level of abrasion resistance of WC-CoCr, but with a lower hardness (1020 vs. 1330 HV, respectively). They observed very similar wear mechanisms, but this finding can indicate that the composition's change can affect the fracture toughness of the coating.

4. Design Controlled by Dilution

An important variable to control during hardfacing process is the dilution. As the deposition aims to a low relation between cost and benefit, it is common to use low-carbon steel as substrate for abrasive wear situations. It will supply iron for the hardfacing during the processing.

To predict the volume fraction of carbides, Günther et al. [35] built a map for GMAW (gas metal arc welding) process, where the resulting microstructure of Fe-Cr-C alloy can be estimated. Their objective is to verify an additional hot-wire efficiency, then the wire feed ratio (v_{GMAW}/v_{HW}) was a crucial variable. They verified that a hypoeutectic microstructure occurred for dilution rates above 32% and ratios v_{GMAW}/v_{HW} above ~ 3 ; the eutectic was apparent for dilution rates between 20 and 35%, and the hypereutectic one was observed for dilution rates below 26% and v_{GMAW}/v_{HW} ratios below 1.8. This kind of study will be beneficial if applied to other hardfacing techniques.

Another exciting example of microstructure changing during the deposition of a hard constituent is Yano et al. [36]. They deposited chromium carbides onto NiAl alloy, using carbide powder of $Cr_{23}C_6$ stoichiometry with plasma transferred arc technique. The dilution effect combined with large amounts of carbide (> 30 wt.%) resulted in a microstructure composed of M_7C_3 carbides, as shown in Figure 10.

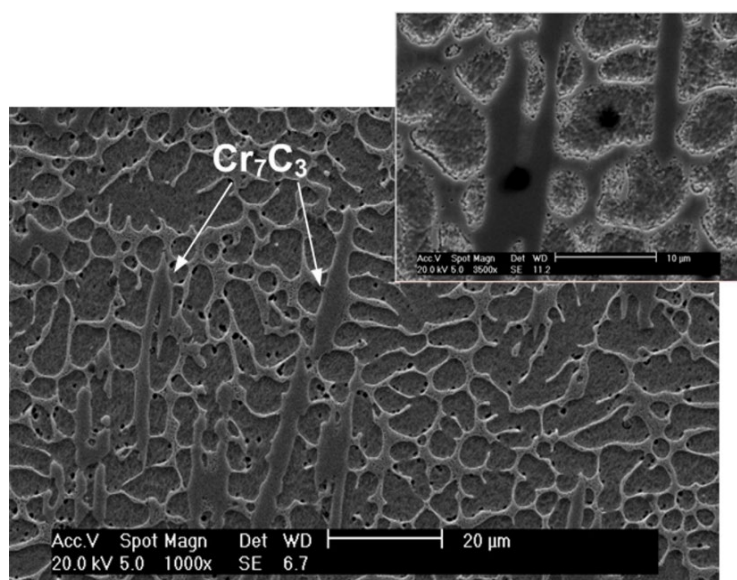


Figure 10. Resulted microstructure from PTA deposit of 45% wt. of chromium carbides onto NiAl alloy, processed with 100 A [36].

5. Summary

This review presented relevant strategies to obtain suitable microstructures resistant to abrasive wear. They are dependent on the volume fraction of the second hard phase, added primarily to increase the hardness. Besides aspects considering hardness, the fracture toughness, and the dilution level were treated as crucial approaches to defining a wear-resistant microstructure. In summary, the following aspects should be considered:

- carbide size is an essential microstructural characteristic for abrasive wear; it should be controlled to minimize the mean free path;

- the difference of hardness between the metallic matrix and carbide should be reduced; in the case of soft matrices, the incorporation of precipitated carbides can be a solution for that; and
- the volume fraction should be selected as a function of the system's severity and controlled using the dilution rate.

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