An Overview of the Microstructures Present in High-Speed Steel - Carbides Crystallography

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Abstract: The aim of the work was to prepare an overview about the microstructures present in high-speed steel, focused on the carbides crystallography. High-speed steels are currently obtained by casting, powder metallurgy and more recently spray forming. High-speed steels have a high hardness resulting from a microstructure, which consists of a steel matrix (martensite and ferrite), in which carbides of different crystal structure, chemical composition, morphology and size are embedded. These carbides are commonly named M_xC, where M represents one or more metallic atoms. These carbides can be identified by x-ray diffraction considering M as a unique metallic atom. In this work, it is discussed, in basis of the first principles of physics crystallography, the validation of this identification when it is considered that other atoms in the structure are substitutional.

Introduction

The microstructure of-high speed tool steels, in the annealing condition, is formed by martensitc or ferritic matrix and blocky M_xC_y type carbides, called primary carbides, formed during casting. After heat treatment (annealing, quenching and tempering), this matrix is strengthened by secondary precipitation of extremely fine carbides.

The function of the blocky carbides is to protect the matrix against wear and the secondary carbides to provide high hot strength. Besides, the high-speed steel requires high fracture toughness. Therefore, it is very important to control the type of existing carbides. Thus, a large number of studies had been undertaken to find ideal tool steel microstructures.

The conventional high-speed steel microstructure is not very homogeneous and presents some coarse carbide. Heterogeneous distribution of carbides and alloying elements reduces cutability; grindability, toughness and causes heat treatment problems. The high-speed steel produced by powder metallurgy (P/M) process using atomized prealloyed high-speed steel powders, presents more homogeneous microstructure. Advantages of this technique include uniform and finer microstructure, improved grindability and good cutting performance. The process using the hot isostatic pressing (HIP) produce near-net shape cutting tools, bearings and wear resistant parts, with disadvantage of a increase in the production costs and leading time. The spray-formed is an alternative process for high-speed steel obtention, allowing a more effective process as opposed to the P/M.

The aim of the present work was to prepare an overview of carbides identification in high-speed AISI M2 steel. A correlation between the identified carbides in the metallurgy field and the crystallography basis is attempted.

Carbides in metallurgy

The basic sequence of solidification of the high-speed steel can be described as: initially the melt solidify by the precipitation of the ferrite. In this stage the alloying atoms are dissolved in the ferrite, but the solubility of the carbon is quite low, then there is a large segregation of these atoms

in the melt. The austenite is formed by peritectic reaction as consequence of segregation. In subsequent cooling, occurs an increase of segregation of ferrite-stabilizing elements and the eutectic reaction starts forming the primary carbides. The MC, M_2C, and M_6C carbides are formed preferentially in the austenite grain boundaries. The eutectic reaction is influenced by the carbon content and by the cooling rate. Subsequently in the annealing treatment, at temperature above 900 °C, the M_2C metastable carbide decompose in M_6C and MC carbides [1]. Others carbide types can be formed, but they are rare, for example, $M_{23}C_6$, M_7C_3, and M_3C.

Table 1 show the average chemical composition of the most important carbides present in the AISI M2 high-speed steel. These data were collected from several publications [2-6]. The data accuracy depends on the used technique, the most common analysis was realized by electron microprobe analysis, energy and wavelength dispersion x-ray analysis.

Table1. Carbides average chemical composition present in high-speed steel [2-6].

Carbide type	Chemical composition mass%				
	W	Mo	V	Cr	Fe
M_6C	33.9 ± 3.9	23.8 ± 2.6	3.8 ± 0.9	4.3 ± 0.7	32.5 ± 1.3
M_2C	42.0 ± 6.6	28.9 ± 5.9	13.6 ± 1.3	6.8 ± 0.9	5.1 ± 2.6
MC	19.9 ± 6.7	12.7 ± 3.3	49.2 ± 5.2	4.2 ± 2.0	3.1 ± 1.8

The data analyses show that the MC carbide contains very small amounts of iron and consist essentially of vanadium, tungsten, and molybdenum. The amounts of tungsten and molybdenum depend of the steel composition. The M_6C carbide is rich in iron, tungsten and molybdenum; the amounts of vanadium and chromium dissolved in this carbide correspond approximately that present in the steel. In the annealing condition the M_2C carbide is rarely observed in high-speed steels.

The hardness of de MC carbide is in the range 2300 at 2500 HV, while the M_6C is 1400-1600 HV [2]. This hardness differences have been used to identify the carbide type. The morphology is another characteristic that can be used for carbide type identification. The M_6C carbide grows is the form of fish-bone. The fan-like morphology is characteristics of the mixture of the M_6C and MC carbides [7]. Besides the morphology the contrast in the scanning electron microscope is another manner to identify de carbides: M_6C are light grey to white, M_2C is dark grey, and MC is black [5].

The carbides formed during powder processing are called primary carbides. At the micrograph this carbides are identify because they show a blocky form. After the annealing treatment, occurs the formation of the secondary carbides, which are extremely fine. The average blocky carbides size is around 3 μm, but they can vary from 0.1 to 10 μm. The secondary carbides are usually present in plate shape with average diameter of the order of 3 to 10 nm and the thickness is about 1 to 2 nm [4]. Hence, these secondary carbides cannot be observed in the scanning electron microscopy. At this point is necessary to make some considerations:

1.	The analysis of the secondary carbides is very difficult because their size and shape. They are even very small for transmission electron microscopy using the traditional thermoionic electron source. It's easier to analyze them with a field ionic microscopy.
2.	For energy dispersion analysis, the accelerating voltage necessary to excite de K and L lines of the interest elements, results in the contributions of part of the matrix surrounding the analyzed particle, affecting the chemical composition determination of them.
3.	Special importance has to be given in the determination of the quantity of the chromium, because of the proximity of the $FeK\alpha$ line to the chromium absorption edge, results in fluorescence.
4.	The carbon concentration in the phases has been calculated taking into assumption the exact stoichiometry between carbon and metal in the carbides.

The metallurgical definition of ferrite phase is a phase of iron atoms which crystalline structure is body centred cubic and martensite is a phase of iron and carbon atoms with a body centred tetragonal structure. These different structures are attributed to the deformation of de cubic structure of the ferrite phase caused by an atom of carbon localized in the octahedral site of the reticule. An important characteristic of the martensitc phase is the hardness. Hence, many researchers considered it the ideal microstructure of high-speed steel, but others consider that the ferrite matrix is the ideal because its high ductility [8]

Crystallography of the carbides

The study of carbides crystallography present in steels, in fact, is still very incipient. One of the possible causes for disagreement in compounds identification occurs between metallurgists and crystallographers. For the crystallographer the study of the crystalline structure must be undertaken using a mono crystalline sample with typical chemical composition. Now, for the metallurgist this identification is based mainly on the phase diagram and chemical composition may vary. Table 2 shown a summary of identified crystalline carbides structure as proposed by Kulmburg [8].

Table 2: Crystalline structure of carbides, adapted from Kulmburg [8].

Carbide type	Iron content	Crystalline structure
M_3C	High	Orthorhombic
$M_{23}C_6$	High	Cubic (complex)
M_7C_3	High	Hexagonal
M_6C	High	Face centred cubic
M_2C	Low	Hexagonal
MC	Low	Face centred cubic

Many proposals regarding the chemical composition of carbides, in the metallurgy, using the notation M_xC_y were prepared. The main characteristic of these proposals is that, it agrees with the crystalline structure describe in Table 2, independent on the chemical composition. In the point of view of crystallography physics, the crystalline structure is defined by one of the Bravais reticules and by a base that repeats in each point of the reticule. Thus, it is not possible to make an affirmative that the Table 2 is completely correct because the crystalline structure is dependent on the metallic atom.

In the ICSD [9] and ICDD [10] databases of the data crystallographic and the data of the diffraction pattern, respectively, is possible to find many types of carbide with different stoichiometry, that unable the correlation between these databases and the carbides proposed in Table 2. But, is this data that is used in the identification of the carbides by x-ray diffraction technique. The data in these databases illustrate that the carbides can show many crystalline structures and some data phases are very old referring to compounds with a typical stoichiometry. But the interesting fact is that those data have been collected trough the development of the metallurgical researches, indicating again that the data in the Table 2 cannot be totally correct.

X-rays diffraction is the technique more widespread, used for identification of the crystalline phases in polycrystalline sample, but there is some constraint to this approach. The first is that the compound must be in the any database, because the identification is realized by comparison with a phase identification put forward in the database. Some authors have been identifying steel carbides, using specifics standards but named by metallurgic notation as (M_xC_y). In this approach it is supposed that the atoms of metallic elements occupied the positions of the

metallic atoms in the crystalline structure, in a substitutional manner. But, it has been observed that many times, the atom size is not considered. However the question is: is this structure physically correct? The carbon is a small atom; hence, it occupies the voids in the iron structure. In the body centred cubic reticulate, there are two types of voids. The large void is known as tetrahedral, situates at position 1/2 1/4 0 in the iron structure and has a 0.36 Å diameter. The small void, known as octahedral, is situated at the 0 1/2 1/2 position and has a 0.19 Å diameter. In the carbide structure, the carbon occupies the octahedral position, nevertheless, occurs the distortion of the lattice, because this carbides are known as interstitial compound or Hägg compound, that are long-range ordered structures [11].

The major difficulty in the study of the crystalline carbides structure is their obtention, mainly, in the one stoichiometry. Generally, is obtained a mixture of carbides, e.g., VC, V_2C and other non-stoichiometries [12]. These studies were only realized when the material was of the technological awareness, for example silicon carbide. Another factor is that the scattering amplitude of the carbon with respect to the metallic atoms is very weak for the x-rays, thus, it is necessary to use neutron diffraction for the study of this material [13]. In the case of the metallic atoms with scattering amplitude very close, the crystallographic information can be obtained using careful x-rays measurements and appropriate wavelength choice.

This review permitted to survey the necessity of more researches is this field, for carbides crystallography structure refinement. In this context the authors of this paper intended to use the Rietveld method for refinement of carbides structures present in the AISI M2 high-speed steel. This work is part of a major study, which claims to apply the Rietveld method in the refinement of the crystalline structure for M_6C and MC carbides in the high-speed steel type AISI M2, and their quantification.

Results

Fig.1 shows the diffraction pattern of the high-speed steel type AISI M2 obtained by the conventional, powder metallurgy and spray formed processes. The identified phases, by comparison to standards contained in the ICCD e ISCD database, are presented in Table 3.
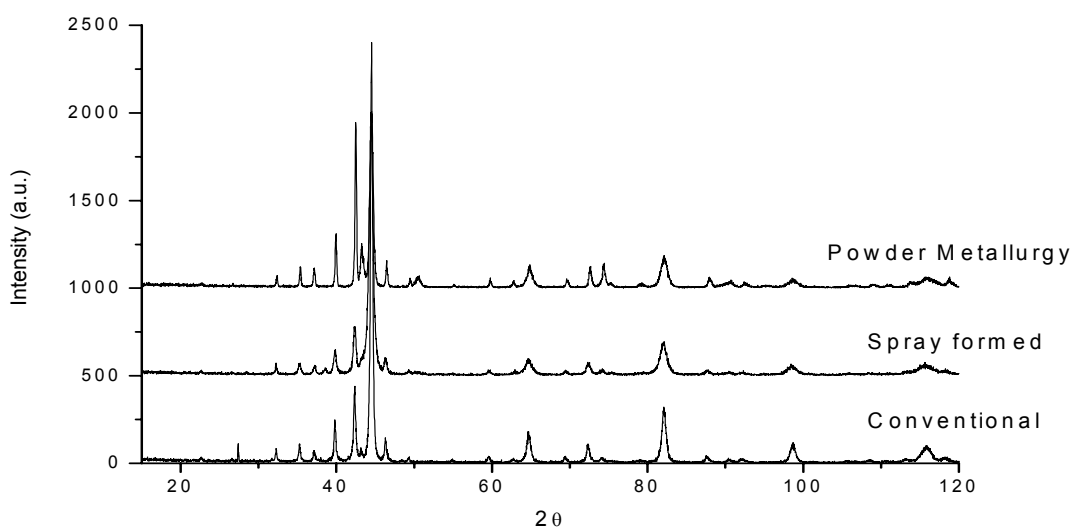

Figure 1. X-ray diffraction patterns of AISI M2 high-speed steels obtained by conventional, powder metallurgy and spray forming techniques.

Table3: Phases identified from diffraction pattern showed in Figure 1.

Carbide Type	Metallurgy	XRD	Database
MC	FCC	VC (FCC)	ICSD 22263
		V_8C_7 (primitive)	ICSD 85953
M_6C	FCC	Fe_3W_3C (FCC)	ICDD 41-1351
			ICSD 43230
		Fe_2Mo_4C (FCC)	ICSD 76135

The crystalline phases presented in Table 3 were chosen by the crystal structure expected by metallurgy, despite other phases has been possible to be used for the identification of the crystalline phases of the diffraction patterns showed Figure 1. The diffraction patterns showed in the Fig.1 indicate the presence of other phases.

Conclusion

The main aim of a future work will be to demonstrate that the x-ray diffraction is a technique useful for the quantification of the carbides present in steels, using Rietveld method. Many steps are necessary for to obtain this result and most difficult must be eliminated. For this reason, some consideration below are drawn:

1)   The crystalline structure of the MC and M_6C are face centred cubic, which reduce the precision of the Rietveld method, however is necessary to use many wavelength for minimize this effect.

2)   Monochromator is used for collecting data for Rietveld refinement due to resolution, but this implicate in intensity loss. The solution of this problem is to use synchrotron radiation source for x-ray diffraction.

3)   The position of the carbon atom in the structure can only be determinate by simultaneous powder x-ray and neutron diffraction refinement. This fact is very important because the MC carbide can show ordered structure.

4)   The refinements allow the identification of preferential sites for substitution in the metallic structure.

5)   The broadening of lines referent at the matrix indicates that the structures show several defects: microcrystallines, microstrain, fault stacking, etc.

6)   Once the crystalline structure is refined using the synchrotron radiation and neutron diffraction, the spectra collected from conventional x-ray tube can be confronted and the data quality assessed. This result allows to establish if it is possible the quantification of carbide by Rietveld method for everyday analysis using conventional diffractometers.

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