Materials Research. 2021; 24(5): e20210054
DOI: https://doi.org/10.1590/1980-5373-MR-2021-0054

Analysis of Milling Efficiency of the Vanadis® 8 Tool Steel with Additions of Vanadium and Molybdenum Carbides

Elioenai Levi Barbedo[a]*, Pedro Henrique Gonçalves[a], Marcela Silva Lamoglia[a], Agata Mayara Paula Pontes[a], Bruna Horta Bastos Kuffner[a], Guilherme Ferreira Gomes[a], Gilbert Silva[a]

[a]*Universidade Federal de Itajubá (UNIFEI), Itajubá, MG, Brasil*

Received: January 19, 2021; Revised: May 16, 2021; Accepted: June 11, 2021.

The Vanadis® 8 is a tool steel used in the manufacture of dies, punches and tools. It has a high carbon content combined with chromium, molybdenum and vanadium, and presents good performance in its mechanical properties. Usually, its chips obtained by machining are sold to companies that use remelting. However, this technique is considered expensive and harmful to the environment. Therefore, this work aimed to analyze the efficiency of the addition of vanadium carbide (VC) and molybdenum carbide (Mo_2C) in the high energy ball milling of the Vanadis® 8 steel. Microstructural analysis were performed in the pure steel and with 3% of VC and Mo_2C additions. The milling parameters used were: speed of 350 rpm, ball-to-powder weight ratio of 15:1 and times of 4, 8 and 12 hours. The results indicated that the Vanadis® 8 steel milled with VC presented the best microstructural results in all of the conducted tests.

Keywords: *Vanadis® 8 Tool Steel, Carbides, High Energy Ball Milling, Powder Metallurgy.*

1. Introduction

Tool steels are iron-based alloys, with different properties from carbon steels, due to the presence of alloying elements in their chemical composition. Alloying elements such as tungsten, vanadium, molybdenum, chromium, cobalt, silicon and nickel, offer characteristics that determine the application of each tool steel. Examples of tools that can be produced with these steels comprehend: drills, taps, minting, dies, interchangeable inserts, cutting tools, folding, spinning or even dies for hot and cold working[1,2].

Facing the challenges generated by the search and development of high-performance tool steels, hybrid mechanical properties such as high hardness and high wear resistance in line with high toughness, have been a constant target of researches that seek to obtain solutions to increase the durability of tool steels, which in most cases are subjected to extreme working conditions[3-5].

One of the most important steps in the development of high-performance materials is the understanding of the structural, atomic and molecular interaction levels. This understanding helps to define the mechanical properties to be obtained for these materials. However, with the fractional knowledge about structural interactions, only through characterization it is possible to determine the triangle (structure, interaction and property), in order to work, evaluate and develop new materials[6,7].

In this context, the Vanadis® 8 SuperClean appeared, an alloy produced by the powder metallurgy (PM) route, composed of chromium, molybdenum and vanadium, with a high carbon content (2.3%), composition not found in any other tool steel obtained by conventional casting. Vanadis® 8 has mechanical properties of high wear resistance, high hardness, high compressive strength and high toughness. It is optimized for cold working applications, suitable for tools such as dies, stamping punches and forging, mill knives, among others[8-10].

Vanadis® 8 steel compared to other conventional steels, has a refined microstructure with carbides distributed homogeneously in the matrix[11,12]. This microstructure may vary according to the heat treatment performed. The heat treatments used in Vanadis® 8 allow a reduction in the amount of austenite retained and modify the behavior of the carbides precipitation, all with the aim of increase the mechanical strength and ensure dimensional stability[13]. The only process that allows the production of a material with these characteristics is the powder metallurgy, where the manufacturing steps consist of the obtainment of the powders, pressing and sintering[14,15].

Among the milling processes, the high energy ball milling proved to be efficient in the production of metallic powders. The comminution of the material occurs from the impact generated by the milling spheres, in contact with the powders over high rotation speed. This milling method was initially used in the mechanical alloying (MA) technique, whose objective is the creation of metallic alloys starting from powders. In recent years, the milling process has been used to reuse metallic materials through mechanical milling (MM)[16-19].

*e-mail: levibarbedo@unifei.edu.br

Composites with metallic matrix are the most produced by powder metallurgy using high energy ball milling. In these materials, usually the ductility of the metal is combined with the high hardness and resistance to high temperatures of ceramic particles[20,21]. The carbides found in the Vanadis steel family are MC and M_7C_3. The MC carbides have a spherical morphology and are distributed inside the grains, while the M_7C_3 have a plate-like morphology in the grain boundaries[22].

In Vanadis® 8, carbides of the MC type are predominantly present[23]. In this way, due to the high economic value that Vanadis® 8 SuperClean presents, it is expected to reuse its chips generated by machining, with the purpose to promote a research that gives sense to intelligent practices and that explore more innovating processes for recycling of new materials.

Thus, this work aims to evaluate, through high energy ball milling, the efficiency of the VC and Mo_2C carbides addition in the reduction and homogenization of Vanadis® 8 particles. For this, three different experiments were carried out to analyze the most viable configuration between the arrangements: In powders of Vanadis® 8 without carbides and with additions of 3% of VC and Mo_2C.

2. Experimental

Table 1 shows the chemical composition of the Vanadis® 8 SuperClean tool steel, obtained from the Uddeholm company.

To verify the efficiency of the addition of carbides in the high energy ball milling of the Vanadis® 8 steel, molybdenum carbide (Mo_2C) and vanadium carbide (VC) were used. Table 2 shows the density, hardness and elastic modulus of the Vanadis® 8 steel and the VC and Mo_2C[8,24] carbides.

The material used in this study was donated by the Uddeholm company. The casted material was received in the condition as annealed to facilitate the machining process. The Vanadis® 8 steel was then machined under low rotation speed and without the use of lubricants to avoid oxidation and contamination. The equipment used to obtain the chips was a machining center model Romi Discovery 560.

The average size and morphology of the chips were characterized using an Olympus® SZ61 stereoscope. For the high energy ball milling process, it was used a Noah-Nuoya planetary ball mill, model: NQM 0.2 L (Yangzhou Nuoya Machinery CO). To the milling process, three different compositions were studied: the first corresponded to chips of Vanadis® 8 steel pure and to the others, were added vanadium carbide (VC) and molybdenum carbide (Mo_2C) with a proportion of 3% by weight of the total chip mass. Initially the chips, carbides and stainless steel balls were weighed with ball-to-powder ratio of (15:1). After weighing the milling spheres, argon gas 5.0 was inserted inside of the milling containers to avoid any type of oxidation. The mill was programmed with a rotation speed of 350 rpm and a total time of 12 hours. In the break of 4 and 8 hours of milling, a small amount of sample was removed from each condition for characterization.

The microstructural characterization was performed using a scanning electron microscope (SEM) Carl Zeiss EVO MA 15 in the secondary electron mode (SE), to analyze the particles morphology, size and distribution, as well as

Table 1. Chemical composition of Vanadis® 8 tool steel (% by weight).

Chemical Element	Vanadis® 8 steel
C	2.3
Si	0.4
Mn	0.4
Cr	4.8
Mo	3.6
V	8.0

Table 2. Density, hardness and elastic modulus of the Vanadis® 8 steel and the VC and Mo_2C carbides.

Material	Density (g/cm^3)	Hardness (HRA)	Elastic Modulus (GPA)
Vanadis® 8	7.46	64	230
VC	5.71	91	268
Mo_2C	8.20	89	227

in the backscattered electron (BSE) and energy dispersive spectroscopy (EDS) modes, to evaluate the chemical composition and mapping of the samples. In order to evaluate the volumetric distribution and the average particles size, it was used a Microtrac Bluewave S3500 laser granulometer. It uses the optic analysis model based on Mie Spreading Theory, which offers in its report the results with values represented by 3 to 7 significative digits. Another equipment used in the research was the X'pert PRO model BV® x-ray diffractometer with CuKα radiation and interval of 10-90 ° of scanning and step of 0.02 ° for 1.5 seconds. The analyses were made on the material received and during the milling intervals.

In addition to the tests of SEM, XRD and particles distribution by laser granulometry, another method to calculate the efficiency of the high energy ball milling is by calculating the size of the crystallite. Just like micro-deformation and particles size are related to the width of the diffraction peaks, the crystallite size can be estimated using the Scherrer Equation 1[25].

$$D = \frac{K.\lambda}{\beta_L.\cos\theta} \tag{1}$$

Being: D the crystallite size (nm) in one direction (h, k, l), K the Scherrer constant; λ the wavelength of the radiation used; β_L the width at half height of the peak also known as full width at half maximum (FWHM) and θ the Bragg angle called of the diffraction angle.

The theoretical method to estimate the material percentage of crystallinity with the results obtained from the XRD was also performed. For this, initially an adjustment in the diffractogram curve was performed by the Rietveld[26,27] method, using the GSAS software®. Subsequently, the calculation was made by simple separation of area.

GSAS® allows the obtainment of the curves by calculating the crystalline and non-crystalline areas of the material. With the data obtained, it is possible to calculate the percentage of the crystalline phase using the Equation 2[27], with the OriginPro 9.0 software®.

$$\%C=\left(\frac{A_C}{A_C+A_A}\right).100 \quad (2)$$

Being: %C the percentage of crystalline phase, Ac the crystalline area and Aa the amorphous area.

3. Results and Discussion

3.1. Analysis of the powders morphology

In a ductile-brittle process, during the milling, the particles of the powders are subject to plastic deformation, and fracture with the absence of cold welding, due to the high capacity of the Vanadis® 8 to absorb plastic deformation. In the first milling stage, ductile particles suffer deformation, while fragile particles, fragmentation[16,28].

The Figure 1, obtained by scanning electron microscopy (SEM) shows the morphology of Vanadis® 8 steel without the addition of carbides. In Figure 1a, with 4h of milling, it can be seen that the particles presented acicular morphology and heterogeneous size with variation in a range of 60 µm to 1000 µm. In Figure 1b with 8h of milling, it is noted that the particles tend to decrease their size due to the fracture during the high energy ball milling process. Because of the constant impact, these particles presented a less angular shape compared to the milling time of 4h. With the increase in the milling time from 8 to 12h (Figure 1c), it is observed that the particles acquired a more rounded morphology, with average size of 600 µm. Therefore, there is a typical behavior for fragile components, where the particles are fragmented during the milling and their sizes are continuously reduced.

The Figure 2 shows the micrographs of the Vanadis® 8 steel with the addition of molybdenum carbide. In Figure 2a, it can be seen that the particles milled for 4h presented heterogeneous morphology. The largest particles showed acicular morphology with an average size of 800 µm, while the smaller particles showed flaky morphology and size around 10 µm. For the milling time of 8h (Figure 2b), it was observed that the particles exhibited a more homogeneous and rounded morphology, with size of 800 µm. By increasing the milling time from 8 to 12h (Figure 2c), it was noted a reduction in the particles size, which presented a variation around 50 and 400 µm. One explanation for this is that, as a consequence of the increase in the milling time, there was a greater energy stored, so the particles reduced to smaller sizes and presented a more rounded morphology[29].

The Figure 3 shows the micrograph of Vanadis® 8 with the addition of vanadium carbide. With 4h of milling (Figure 3a), it was observed that this carbide was more efficient in the fracture and consequently, the decrease in the particles size was better when compared to the other samples. The particles presented rounded morphology, where the average size reached was of 400 µm for the largest particles and 10 µm for the smallest ones.

With 8h of milling, in Figure 3b, it can be seen that there was a greater reduction in the particles size, where the largest particles showed an average size of 400 µm, intermediate size of 60 µm and smallest size of 10 µm. The largest particles exhibited spherical morphology, and the smallest, flaky morphology.

In Figure 3c, with 12h of milling, it is observed a greater homogenization of the particles. Figure 3d also refers to the milling time of 12h, with a greater magnification for better visualization and analysis of the particles morphology. As it can be seen more clearly in Figure 3d, the particles presented irregular morphology and high volume of clusters, due to the fact that they possess small granulometry and tend to agglomerate.

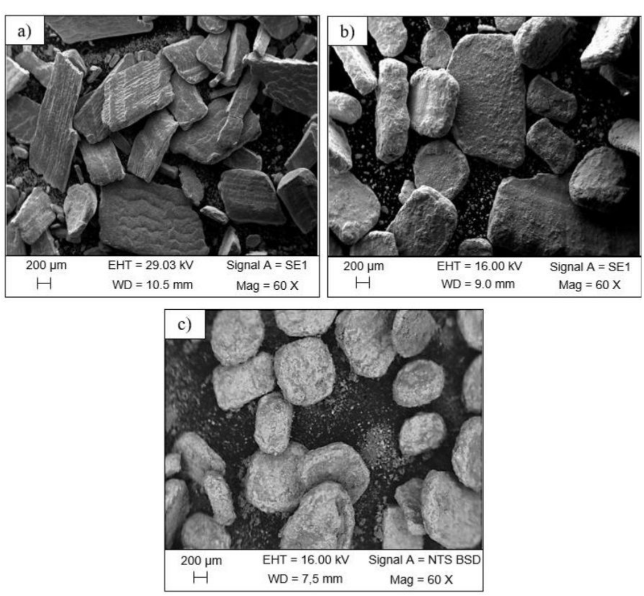

Figure 1: SEM micrographs of the Vanadis® 8 steel without carbides addition and milled for: (a) 4 hours (b) 8 hours (c) 12 hours

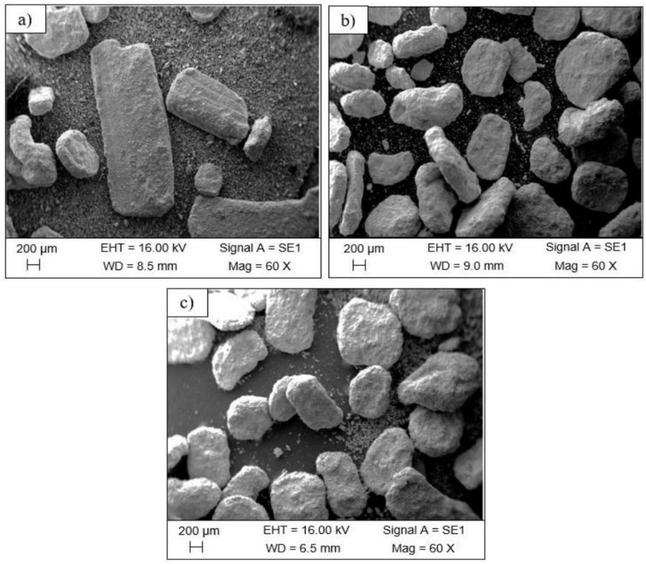

Figure 2: SEM micrographs of the Vanadis® 8 steel with Mo_2C addition and milled for: (a) 4 hours (b) 8 hours (c) 12 hours

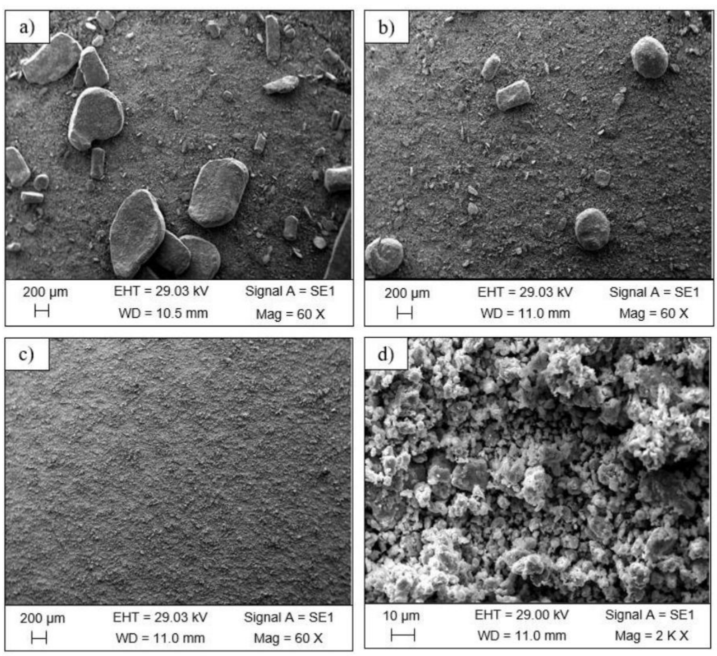

Figure 3: SEM micrographs of the Vanadis® 8 steel with VC addition and milled for: (a) 4 hours (b) 8 hours (c) 12 hours (d) 12 hours with magnification of 2000x

The vanadium carbide proved to be the most efficient addition to the milling process of the Vanadis® 8 steel, since, the steel milled with this addition, obtained the smallest particles size for 12 h of milling, where most of the particles presented size of 10 μm. The presence of nanometric particles can also be seen. It proves how the milling time is an important parameter to obtain submicrometric and nanometric particles in the process of mechanical milling. However, it is noteworthy that particles with very small size present ductile behavior, being not possible to reduce their size furthermore. This phenomenon is called of comminution limit[16].

3.2. Laser granulometry analysis

The granulometric analysis comprises representation of the equivalent average size of particulate material (adopted in this work as average diameter) and the frequency in which it occurs in a certain size range, that is, of its populations, which represents the fine, average and coarser particles. It is mandatory to obtain information about the granulometric distribution of the powder, since materials with identical average sizes can present different distributions. The particles size distribution influence directly the packaging of these particles. Each peak of the Gaussian corresponds to a population of different particles size, and the greater is the number of populations, more efficient the packaging tends to be[30,31]. The analysis of the particles size distribution of the milled samples of Vanadis® 8 steel was performed under the following conditions: without carbide (as reference) after milling times of 4, 8 and 12 hours (Figure 4a, 4b and 4c), with vanadium carbide after 4, 8 and 12 hours of process (Figure 5a, 5b and 5c) and with molybdenum carbide after 4, 8 and 12 hours of milling (Figure 6a, 6b and 6c). Analyzing the samples according to the terminology of[31,32], it was identified that for all of the conditions, polymodal distributions were obtained.

For the samples of Vanadis® 8 steel milled without the addition of carbides, with 4 hours of processing (Figure 4a), an increase in the asymmetric trimodal distribution was observed, with populations of fine particles from 10.12 to 66.54 µm (representing 19.2% of the total volume of particles), median particles of 396.40 µm (representing 36% of the total volume of particles), and coarse particles of 725.10 µm (representing 36% of the total volume of particles). In the samples milled during 8 hours, there was also an increase in the asymmetric

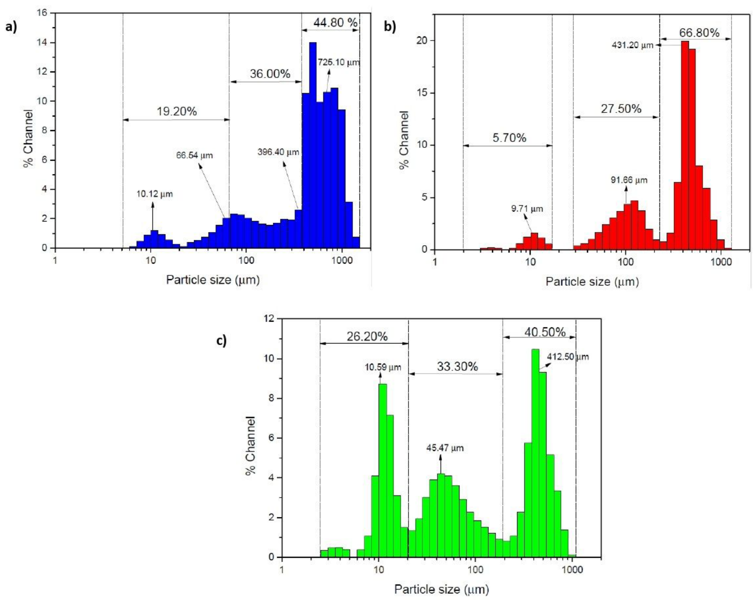

Figure 4: Granulometric distribution of the Vanadis® 8 milled without carbides addition for (a) 4 hours (b) 8 hours (c) 12 hours

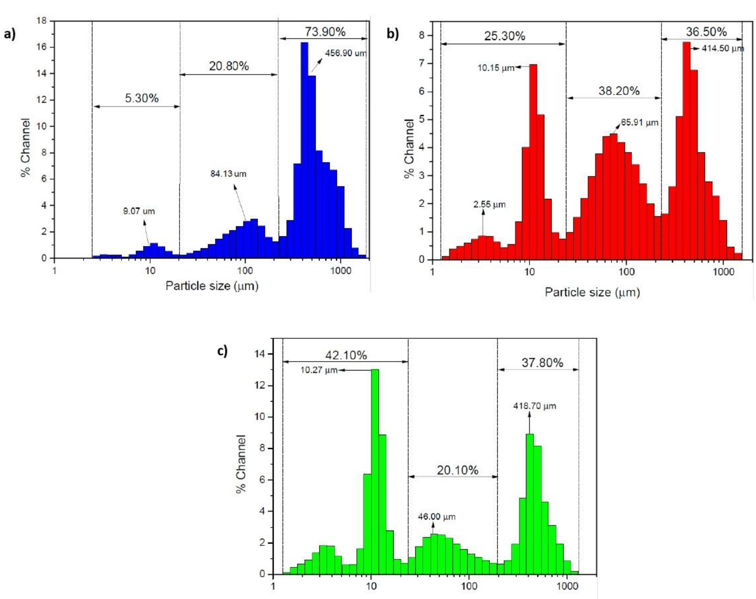

Figure 5: Granulometric distribution of the Vanadis® 8 milled with VC addition for (a) 4 hours (b) 8 hours (c) 12 hours

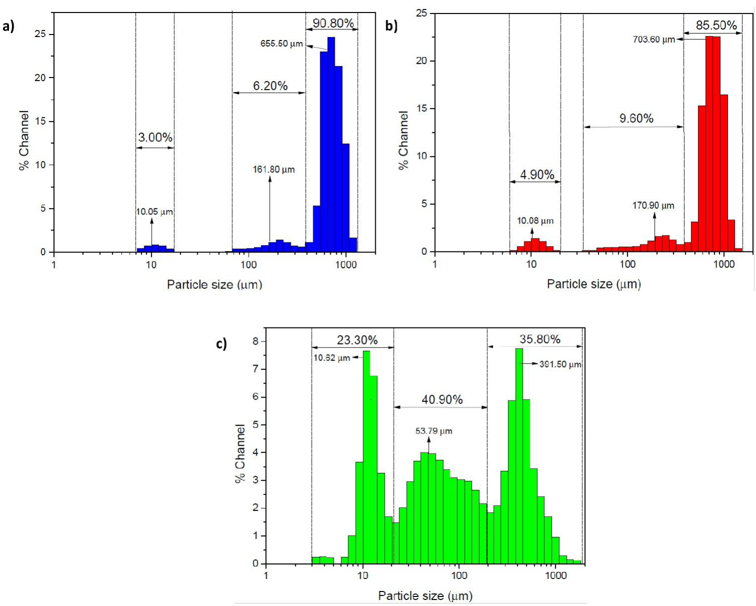

Figure 6: Granulometric distribution of the Vanadis® 8 milled with Mo_2C addition for (a) 4 hours (b) 8 hours (c) 12 hours

distribution (Figure 4b), with a predominance of coarse particles populations, with size of 431.20 µm (representing 66.80% of the total volume of particles), populations of fine particles of 9.71 µm (representing 5.70% of the total volume of particles) and median particles of 91.66 µm (representing 27.50% of the total volume of particles). Already the samples milled through 12 hour (Figure 4c) presented a discontinuous trimodal distribution, with populations of fine particles of 3.32 to 10.58 µm (representing 26.20% of the total volume of particles), median particles of 45 to 47 µm (representing 33.30% of the total volume of particles) and coarse particles of 412.50 µm (representing 40.50% of the total volume of particles). These results indicated that, for this condition, there was a higher proportion of coarse particles.

The samples milled with the addition of vanadium carbide, showed polymodal distribution, in which the samples with 4 hours of processing (Figure 5a), presented an increase in the asymmetric trimodal distribution, with fine particles of 9.07 µm (representing 5.30% of the total volume of particles), median particles of 84.13 µm (representing 20.80% of the total volume of particles) and coarse particles of 456.90 µm (representing 73.90% of the total volume of particles). The samples milled for 8 hours (Figure 5b), presented asymmetric trimodal distribution, with fine particles of 2.55 to 10.15 µm (representing 25.30% of the total volume of particles), median particles of 65.91 µm (representing 38.21% of the total volume of particles) and coarse particles of 414.50 µm (representing 36.50% of the total volume of particles). However, the samples milled for 4 hours showed the largest coarse granulation, and the samples milled for 8 hours presented coarse and median particles populations in almost the same proportion, which indicates that the milling times of 4 and 8 hours were not as efficient as the distribution presented for 12 hours (Figure 5c). In this, there was a continuous polymodal distribution with four populations, with a higher concentration of fine and medium particles, being the fine particles of two populations from 2.92 to 10.27 µm (representing 42.10% of the total volume of particles), the medians particles with 10.27 µm (representing 20.80% of the total volume of particles), and the coarse particles with 418.70 µm (representing 37.80% of the total volume of particles). This type of polymodal distribution is the most efficient for the packaging of particles, according to the works of Funk and Dinger[30].

In the samples milled with the addition of molybdenum carbide, the distribution behavior for 4 hours of milling (Figure 6a) and for 8 hours (Figure 6b) were similar, with 3 populations with fine particles of 10.05 µm (representing 3.00% of the total volume of particles) and 10.08 µm (representing 4.90% of the total volume of particles), median particles with 161.80 µm (representing 6.20% of the total volume of particles) and 170.90 µm (representing 9.60% of the total volume of particles) and coarse particles with 655.50 µm (representing 90.80% of the total volume of particles) and 703.60 µm (representing 85.50% of the total volume of particles). Both exhibited asymmetric discontinuous trimodal distribution, where most of the particles presented coarse granulometry. The distribution for the samples milled for 12 hours (Figure 6c) was symmetrical trimodal, where the proportion of fine particles was of 10.62 µm (representing 23.30% of the total volume of particles), of median particles was of 53.79 µm (representing 40.90% of the total volume of particles) and of coarse particles was of 391.50 µm (representing 35.80% of the total volume of particles). This milling time demonstrated the most equal proportion between the populations. However, regardless of the type of trimodal distribution found in the samples, the most efficient result for the packaging of the particles was found in the samples with the addition of vanadium carbide and 12 hours of milling. It happened because this condition presented a polymodal curve with four populations, and this variety of particles size favors the packaging, which generates an excellent compression of the powders with reduced porosity. Consequently, it decreases the internal defects of the material.

The Figure 7 represents the average size of the particles obtained by laser granulometry, according to the milling time and composition used. The samples without and with carbide additions had the same reduction behavior. It means that, with the increase in the milling time, the reduction was progressive and it can be explained due to the contact between the particles as they were defragmented.

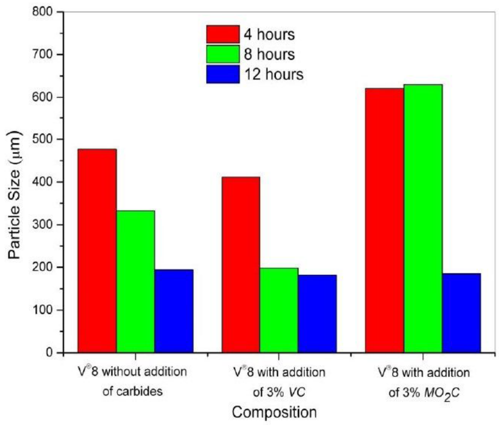

Figure 7: Volumetric fraction of particles versus milling time of Vanadis® 8 with and without carbides addition

The most effective reduction in the particles was with the addition of vanadium carbide (VC), explained due to the high hardness of this carbide in comparison with the chips and the molybdenum carbide, since that, with the milling process, the carbides are "penetrated" in the Vanadis® 8 particles, causing microcracks that with the milling time, propagate and assist in the comminution of the particles.

The same effect can be explained for the samples with the addition of molybdenum carbide. However, with 8 hours of milling, there were no great reductions in the particles size, when compared to the other samples. The effect of the molybdenum carbide in the particles reduction was significant for 12 hour of milling, where the final average size was approximately equal to the others. Of all samples, the reduction in the average particles size was more effective with vanadium carbide (VC). However, there were no expressive differences in the average size of the particles subjected to milling times of 8 and 12 hours.

3.3. Microstructural evolution in the ductile-brittle Vanadis® 8 steel system

The maximum time of 12 hours used to check the efficiency of the carbides addition in the high energy ball milling of the Vanadis® 8 steel was justified by the classification of the process as ductile-brittle (ductile steel and brittle carbide) with the absence of cold welding.

The Figure 8 shows the microstructural evolution of the high energy ball milling in a ductile-brittle system, where

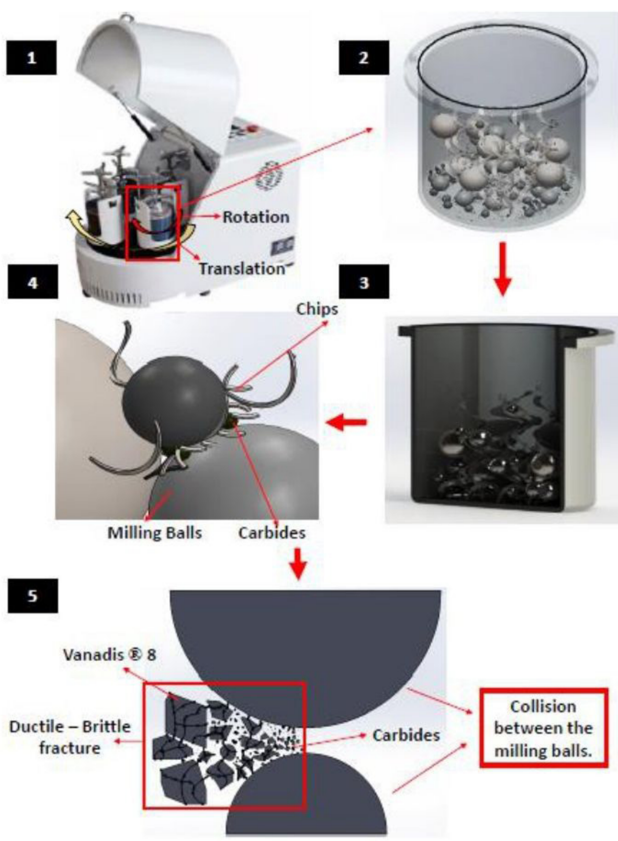

Figure 8: Scheme of the Vanadis® 8 milling system with carbides addition

it is observed that the impact between the milling spheres promotes the collision of the particles of the ceramic material with the metallic material, resulting in a region of generalized stresses in the ductile particles, which leads to rupture, by combining the ductile-brittle process[16,28]. In addition, this form of analysis has the purpose of meeting economic aspects, since that this type of study can be extended to other high energy ball milling processes, with the objective to reuse other types of materials, with high economic value added.

3.4. X-ray diffraction (XRD) and scanning electron microscopy (SEM) tests

Figure 9 shows the x-ray analysis of the casted sample (in annealed state). To find the phases present in the material, it was used the X'Pert High Score Plus® software. With the results obtained by the identification of the peaks in the diffractogram, the optical microscopy and the SEM in the energy-dispersive detector mode (EDS), it was found that the Vanadis® 8 steel consists of a ferritic matrix (Fe-α) with MC-type carbides distributed homogeneously (Figure 10).

Carbides of the MC type are rich in vanadium. In comparison, the authors[23] conducted a research with the same material. Small divergences were noted between the graphs, such as the slope of the peaks and small detachments with respect to the angle of the phases. However, the graphics were very similar and showed that only two phases present in the material can be conformed: ferrite (Fe-α) and vanadium carbide (VC).

In addition, with the Rietveld refinement performed with the aid of the X'Pert High Score Plus® software, it was possible to quantify 18.2% of vanadium carbide of the MC type distributed in a ferritic matrix. In comparison with the study[33], which found 18% of vanadium carbide using the quantification of phases through SEM/EDS images, with assistance of the Thermo-Cal® software, these results are very close.

Figure 11 shows the diffractograms of the powders obtained after 12 hours of milling, specifically of the three compositions under study: chips grounded without the addition of carbides, with addition of VC and finally, with addition of Mo_2C. Comparing these conditions with the diffractogram of the casted material, it is observed that even with a few hours of milling, there was an enlargement and a reduction in the height of the diffraction peaks.

These changes in the diffraction peaks are characteristic of the amorphization of the original crystalline structure. In the high energy ball milling process, continuous shocks between the milling spheres and the particles of the material occur, and as the processing time increases, severe deformations of the crystalline structure occur until it is completely destroyed.

According to Figure 11, it can be observed that the peaks with lower intensities (43.28°; 62.87° and 75.40°) are practically amorphous. For those with higher intensities (37.25° and 44.60°), it is noted a considerable enlargement. The probable disappearance of these peaks would be possible to see after long hours of milling.

3.5. Calculation of the crystallite size

With the data obtained after the Rietveld refinement of the diffractograms, the crystallite size was calculated using the Scherrer method[25]. Since the microdeformation and the size of the particles are directly related to the width of the diffraction peaks, it is possible to predict by the crystallite size calculation the tendency of the process to amorphize, since the smaller is the crystallite size, the greater is the deformation of the lattice parameter of the crystalline structure.

Table 3 shows the values of the crystallite size of the two present phases identified in the Vanadis® 8 steel milled for 12 hours. The average crystallite calculation was performed

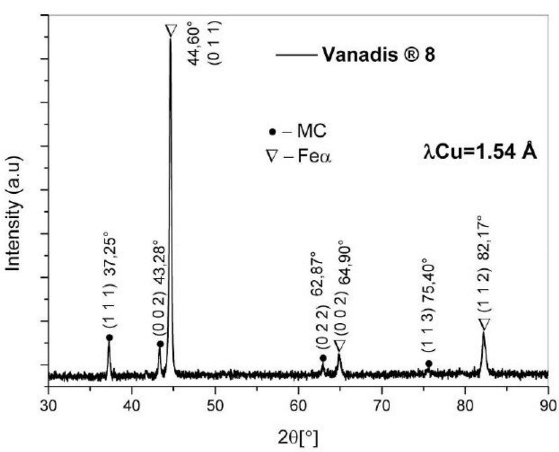

Figure 9: Diffractogram of the Vanadis® 8 as casted in annealing state

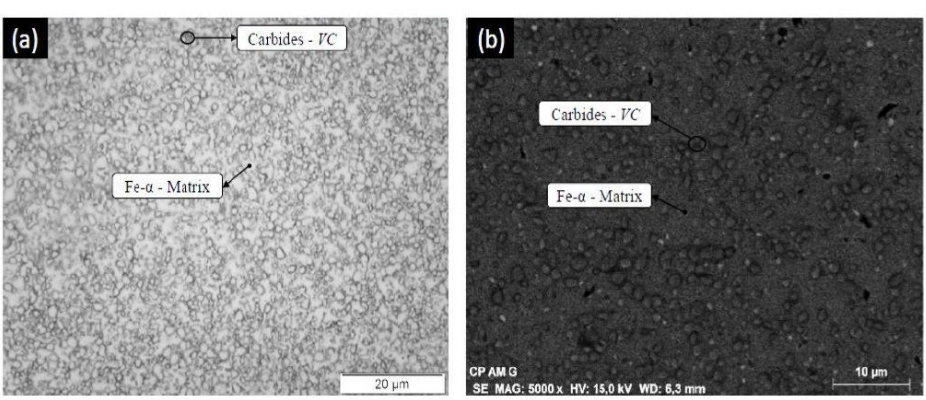

Figure 10: Micrographic analysis of the Vanadis® 8 as casted (a) Optical microscopy after etching with Nital 4% (1000 x) (b) SEM / EDS

Table 3. Results of crystallite size of the Vanadis® 8 pure and with VC and Mo_2C after 12 hours of milling.

State	Crystallite size – Feα (nm)				Crystallite size – MC - type carbides (nm)			
	1	2	3	Mean	1	2	3	Mean
Sample as received	36.1	39. 6	44.4	40	38.8	39.6	43.1	40.5
Without adding Carbides - 12 h	7.4	8.1	9.1	8.2	6.8	6.9	7.5	7.1
Addition 3% VC - 12 h	5.8	6.1	6.9	6.3	23.4	23.9	26.1	24
Addition 3% Mo_2C - 12 h	8.1	8.8	9.9	8.9	15.9	16.2	17.7	16.6

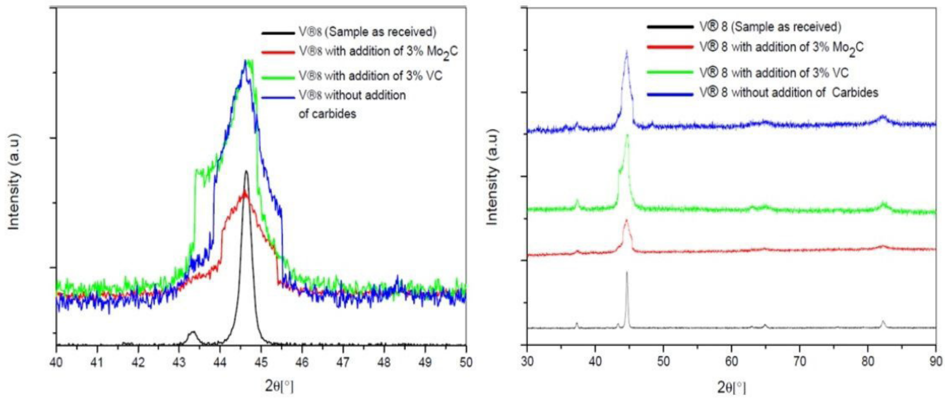

Figure 11: Diffractograms obtained from the Vanadis® 8 chips milled for 12 hours under different conditions

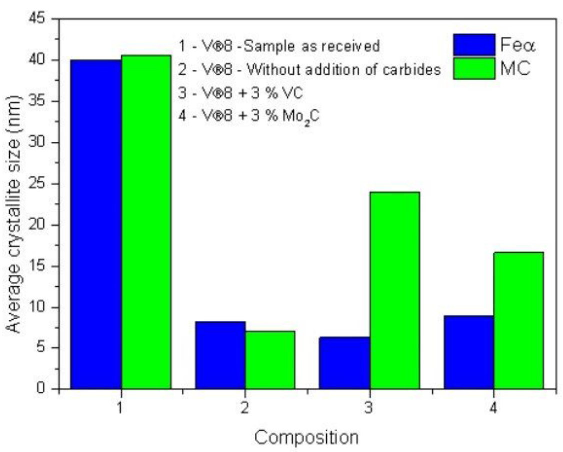

Figure 12: Average crystallite size of the Vanadis® 8 pure and with additions of VC and Mo_2C after 12 hours of milling

using the data from the three most intense peaks and best adjusted by the Rietveld refinement.

As it can be seen in Figure 12, by comparing the sample of the casted material with the samples that were submitted to the high energy ball milling process, a significant decrease in the size of the crystallite after milling was observed, which confirms the microdeformation, the enlargement and the decrease of intensity noted in the x-ray diffraction peaks. Regarding the Fe-α phase, the crystallite size was smaller for the condition with vanadium carbide addition.

These values confirm the particles size distribution obtained in the laser granulometry test, showing a greater reduction in the average particles diameter, justifying, therefore, that the vanadium carbide was the most efficient addition to reduce the degree of crystallinity, and, consequently the most productive condition. However, for the MC phase (carbides rich in vanadium), the condition with addition of vanadium carbide did not present the smallest crystallite size. A possible justification for this is related to the addition of vanadium carbide, since that it may have different crystalline and dimensional characteristics, from the eutectic carbides of the MC type present in the material matrix. Consequently, the condition of Vanadis® 8 with addition of 3% of VC suffered a widening of the peaks angles referring to half height (FWHM) and as a result, it happened an increase in the crystallite size according to the Scherrer equation[25].

3.6. Analysis of the percentage of crystalline phases

In addition to the results of laser granulometry and calculations for average crystallite size, another technique that can be used to identify the most efficient condition is the theoretical method of percentage estimation of crystallinity of the material, starting from the XRD data. In this research, the simple area separation method was used[34,35]. The calculation foresees the separation of the crystalline and non-crystalline contributions.

Figure 13 shows the XRD of a hypothetical sample. The graph didactically represents the difference between the curves of the crystalline phase and the amorphous phase[36]. The crystalline phase curve was provided by the XRD data of the sample, while an adjustment curve for the non-crystalline phase was generated by the Rietveld refinement. It can be done by softwares such as GSAS ®, which uses the adjustment based on least squares method. In general, adjustments less than 1 mean incorrect adjustments and divergence of the

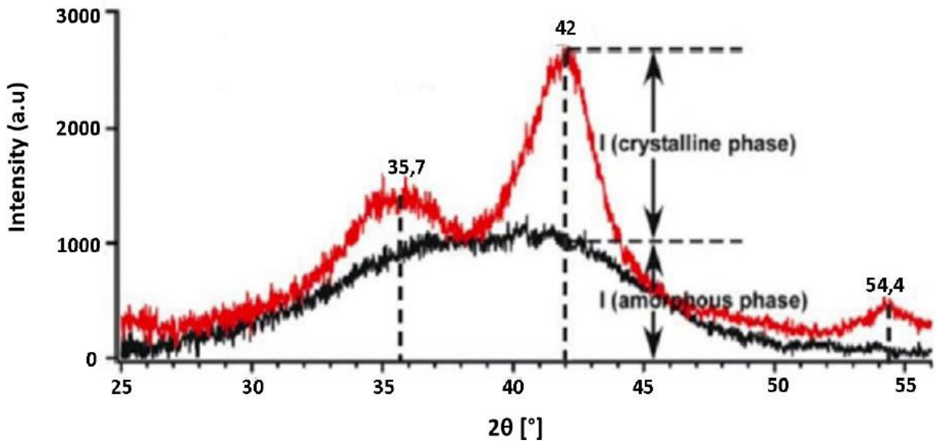

Figure 13: Diffraction profile of a hypothetical sample, crystalline phase and amorphous phase

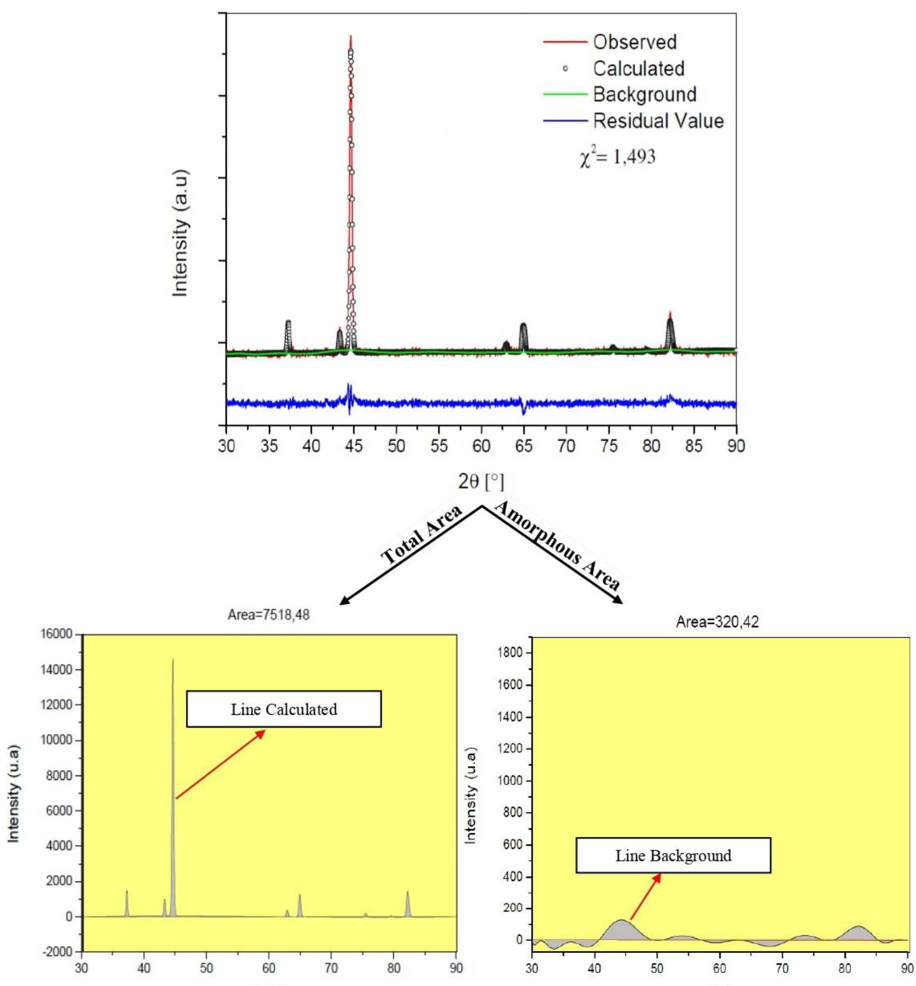

Figure 14: Refinement and obtainment of the curves to calculate the percentual estimation of crystallinity (sample as received)

refinement. Already adjustments greater than 1.5 indicate inadequate adjustment or the existence of a local minimum. Thus, the adjustment must be as close as possible to 1[37].

As an example, in Figure 14 it can be seen the results of the adjustment curves performed by the Rietveld refinement with the GSAS® in the casted sample. Basically, the software

Table 4. Percentages of crystallinity of the Vanadis® 8 pure and with VC and MO_2C after 12 hours of milling.

State	Crystalline phase area (au)	Amorphous phase area (au)	% Crystallinity
Sample as received	7198	320	96
Without carbides addition - 12 h	5432	1957	73
Addition of 3% of VC - 12 h	5766	2329	71
Addition of 3% of Mo_2C - 12 h	8563	1102	89

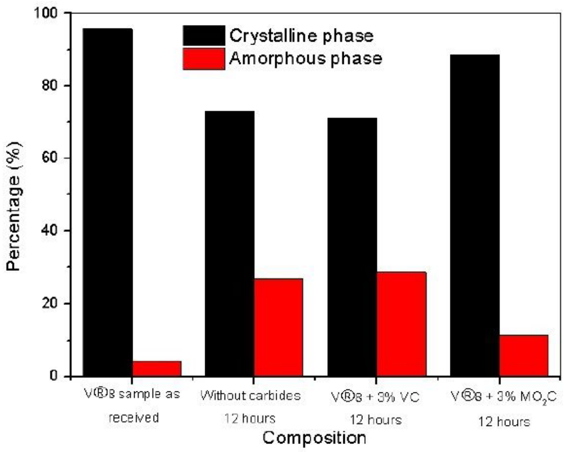

Figure 15: Percentage of crystallinity of the Vanadis® 8 after 12 hours of milling

generates three curves. The first is the value calculated by the refinement, the second curve is a baseline of polynomial adjustment (line background) and the third, a residual curve, being this third represented by the difference between the curve observed by the XRD and the curve calculated by the software.

According to the method of crystallinity percentage estimation by area separation, the relative crystallinity of the material can be calculated by the relationship between the peak areas, represented by the curve of the value calculated by the adjustment and the baseline areas. Therefore, for all of the compositions, the same procedure was performed, in order to compare the evolution of the amorphization due to the high energy ball milling process. In addition, as example, all of the areas were calculated using the OriginPro® 9 software[37]. Table 4 and Figure 15 show the results of the crystallinity calculation according to the Equation 2, for each condition used in this research.

From the results obtained in Figure 15, it was possible to observe that the casted sample, as expected, reached by the calculations almost 100% of crystallinity. However, in order to understand the results of crystallinity for the other configurations, it is necessary to observe Table 2 with the hardness of the Vanadis® 8 material and the carbides used in this study.

In contrast to the casted sample, the addition of 3% of vanadium carbide showed the best performance in terms of amorphization of the material, proving to be the best condition among all the others analyzed in this work. This happened because, when compared to the molybdenum carbide (Mo_2C) and the Vanadis® 8 steel, the vanadium carbide (VC) presented greater hardness (Table 2). With this, these particles are considered more efficient for the destruction of the crystalline planes, which is represented by the widening of the most intense peaks and the disappearance of the less intense peaks of the XRD graphs (Figure 11). Thus, as the VC was the most efficient carbide for the reduction of the steel particles, consequently the percentage of crystalline phase for this configuration was lower[38-40].

The configuration of the mixture of Vanadis® 8 with the addition of 3% molybdenum carbide (Mo_2C) showed the lowest performance regarding to the percentage of crystalline phase. From an intuitive point of view, this is not logical, because according to Table 2, molybdenum carbide (Mo_2C) has the second highest hardness. However, what may have happened according to Figure 7, is that at the beginning of the high energy ball milling process with the addition of Mo_2C, the Mo_2C particles were either aggregated or agglomerated. The agglomerates have an irreversible adhesion, being the main responsible for the creation of cold welding. Aggregates, on the other hand, are a group of particles linked together by windows. In high energy ball milling with particles size reduction, very fine particles have a strong tendency to agglomerate due to the cohesive relationship between the surface area and its volume (Wander wall window). Another point is that the capillarity window due to humidity can also be responsible for the formation of aggregates. Therefore, both aggregate and agglomerate are undesirable, as they have a negative effect on reducing particles and, consequently, low performance for increasing the amorphous phase[40-42].

Comparing the condition with addition of vanadium carbide with the condition without carbides, the results were close. The answer to this can be explained by two factors: material and processing ratio. The first one is that the Vanadis® 8 steel, despite being a tool steel suitable for cold working with excellent wear resistance, has characteristics of excellent ductility and toughness. It makes the Vanadis® 8, a steel that should behave like totally fragile material, to have a ductile-brittle behavior. However, since it is a steel with high hardness and tenacity, there is a difficulty for the vanadium carbide particles to generate fractures in the chips of Vanadis® 8, requiring higher energy in the process for better reduction and amorphization of the particles.

4. Conclusions

The analysis of milling efficiency of the Vanadis® 8 tool steel with additions of vanadium and molybdenum carbides have been studied. The results indicated that:

- The high energy ball milling process was efficient to reduce the size of the chips of the Vanadis® 8 steel obtained by the machining process, with and without the addition of carbides.

- The addition of 3% vanadium carbide provided greater efficiency in reducing the particles of the Vanadis® 8 steel.
- With respect to milling time, the microstructural results indicated that the best milling time was of 12 hours.
- Although the addition of VC was more efficient compared to the conditions without carbide and with Mo_2C addition, for all of the tests, the results were very close to each other.

5. Acknowledgements

The authors would like to thank the FAPEMIG for financing this research and the company Uddeholm for the material donation.

6. References

1. Højerslev C. Risø-R-1244(EN): tool steels. Roskilde: Risø National Laboratory; 2001. 25 p.
2. Roberts GA, Kennedy R, Krauss G. Tool steels. Materials Park: ASM International; 1998. 364 p.
3. Abdul Rahim MAS, Minhat MB, Hussein NISB, Salleh MSB. A comprehensive review on cold work of AISI D2 tool steel. Metall Res Technol. 2018;115:1-12.
4. Podgornik B, Sedlaček M, Žužek B, Guštin A. Properties of tool steels and their importance when used in a coated system. Coatings. 2020;10(3):1-17. http://dx.doi.org/10.3390/coatings10030265.
5. Mussa A, Krakhmalev P, Selte A, Bergström J. Development of a new PM tool steel for optimization of cold working of advanced high-strength steels. Metals. 2020;10(10):1-18.
6. Brostow W, Lobland HEH. Materials: introduction and applications. New York: John Wiley & Sons; 2016. p. 3-9.
7. Evans ND, Gentleman E. The role of material structure and mechanical properties in cell–matrix interactions. J Mater Chem. 2014;17(17):2345-56.
8. Uddeholm. Vanadis 8 SuperClean. 2016. p. 1-12.
9. Huang KT, Chang SH, Yeh PT. Microstructures and mechanical properties of TaC added to Vanadis 4 tool steel through vacuum sintering and heat treatments. ISIJ Int. 2017;57(7):1252-60.
10. Narasimhan KS. Recent advances in ferrous powder metallurgy. Adv Perform Mater. 1996;3(1):7-27.
11. Baykara T, Bedir HF. Effects of heat treatment on the mechanical properties of the Vanadis 4 extra and Vanadis 10 tool steels. J Mar Sci Eng. 2017;6:1-3.
12. Sobotova J, Jurci P, Adáme J, Priknerová P, Prikner O, Šuštaršič B, et al. Diagnostics of the microstructural changes in sub-zero processed Vanadis 6 P/M ledeburitic tool steel. Mater Technol. 2013;47:93-8.
13. Jurči P, Dománková M, Hudáková M, Ptačinová J, Pašák M, Palček P. Characterization of microstructure and tempering response of conventionally quenched, short-and long-time sub-zero treated PM Vanadis 6 ledeburitic tool steel. Mater Charact. 2017;134:398-415.
14. Mahesh K, Sankaran S, Venugopal P. Microstructural characterization and mechanical properties of powder metallurgy dual phase steel preforms. J Mater Sci Technol. 2012;28(12):1085-94.
15. Narasimhan KS. Recent advances in ferrous powder metallurgy. Adv Perform Mater. 1996;3(1):7-27.
16. Suryanarayana C. Mechanical alloying and milling. Prog Mater Sci. 2001;46(1-2):1-184.
17. Ozdemir I, Ahrens S, Mücklich S, Wielage B. Nanocrystalline Al–Al_2O_3p and SiCp composites produced by high-energy ball milling. J Mater Process Technol. 2008;205(1-3):111-8.
18. Schulz MJ, Kelkar AD, Sundaresan MJ. Nanoengineering of structural, functional and smart materials. Boca Raton: CRC Press; 2009. 740 p.
19. Akçamlı N, Küçükelyas B, Kaykılarlı C, Uzunsoy D. Investigation of microstructural, mechanical and corrosion properties of graphene nanoplatelets reinforced Al matrix composites. Mater Res Express. 2019;6:115627.
20. Zawrah MF, Zayed HA, Essawy RA, Nassar AH, Taha MA. Preparation by mechanical alloying, characterization and sintering of Cu–20 wt.% Al_2O_3 nanocomposites. Mater Des. 2013;46:485-90.
21. Ahamed H, Senthilkumar V. Role of nano-size reinforcement and milling on the synthesis of nano-crystalline aluminium alloy composites by mechanical alloying. J Alloys Compd. 2010;505(2):772-82.
22. Chang SH, Yeh PT, Huang KT. Microstructures, mechanical properties and corrosion behaviors of NbC added to Vanadis 4 tool steel via vacuum sintering and heat treatments. Vacuum. 2017;142:123-30.
23. Toboła D, Cyboroń J, Łętocha A. Selected properties of Vanadis 8 tool steel after grinding and hard turning. Mechanik. 2017;90(10):864-6.
24. MatWeb. Material Property Data - MatWeb. Blacksburg, VA; 2020.
25. Langford JI, Wilson AJC. Scherrer after sixty years: a survey and some new results in the determination of crystallite size. J Appl Cryst. 1978;11(2):102-13.
26. Kumar L, Kumar P, Narayan A, Kar M. Rietveld analysis of XRD patterns of different sizes of nanocrystalline cobalt ferrite. Int Nano Lett. 2013;3(1):1-12.
27. Bish DL, Howard SA. Quantitative phase analysis using the Rietveld method. J Appl Cryst. 1988;21(2):86-91.
28. Akçamlı N, Şenyurt B. B4C particulate-reinforced Al-8.5 wt% Si-3.5 wt% Cu matrix composites: powder metallurgical fabrication, age hardening, and characterization. Ceram Int. 2021;47(5):6813-26.
29. German RM. Powder metallurgy science. Metal Powder Industries Federation. 1984;1:1-279.
30. Funk JE, Dinger DR. Predictive process control of crowded particulate suspensions: applied to ceramic manufacturing. New York: Springer; 1994. 823 p.
31. Dinger DR, Funk JE. Particle-packing phenomena and their application in materials processing. MRS Bull. 1997;22(12):19-23.
32. Davis RM, McDermott B, Koch CC. Mechanical alloying of brittle materials. Metall Trans, A, Phys Metall Mater Sci. 1988;19(12):2867-74.
33. Tidesten M, Medvedeva A, Carlsson F, Engström-Svensson A. A new cold work PM-grade combining high wear resistance with high ductility. BHM Berg- Huttenmann Monh. 2017;162(3):117-21.
34. Ribotta PD, Cuffini S, León AE, Añón MC. The staling of bread: an x-ray diffraction study. Eur Food Res Technol. 2004;218:219-23.
35. Le Bail A. Whole powder pattern decomposition methods and applications: a retrospection. Powder Diffr. 2005;20(4):316-26.
36. Carolino AD. Estimativa do percentual de cristalinidade de polímeros semicristalinos derivados da anila através dos padrões de raios X [dissertion]. Manaus: Federal University of Amazonas; 2017.
37. Larson AC, Dreele RBV. General structure analysis system. Los Alamos, NM: Los Alamos National Laboratory; 1994. 185 p.
38. Ahvenainen P, Kontro I, Svedström K. Comparison of sample crystallinity determination methods by X-ray diffraction for challenging cellulose I materials. Cellulose. 2016;23(2):1073-86.
39. Mendonça CSP, Dias ANO, Melo MLNM, Ribeiro VAS, Silva MR, Oliveira AF, et al. Evaluation of high-energy milling efficiency in stainless steel with addition of vanadium carbides.

Int J Adv Manuf Technol. 2018;95(5-8):3093-9. http://dx.doi.org/10.1007/s00170-017-1297-7.
40. Dias ANO, Oliveira LA, Mendonça CSP, Junqueira MM, Melo MDLNM, Silva G. Comparative analysis of niobium and vanadium carbide efficiency in the high energy mechanical milling of aluminum bronze alloy. REM Int Eng J. 2018;71(1):59-65.
41. Zhang Q, Saito F. Mechanochemistry in nanoscience and minerals engineering. Berlin: Springer-Verlag; 2008. p. 122-5.
42. Bailon-Poujol I, Bailon JP, L'Espérance G. Ball-mill grinding kinetics of master alloys for steel powder metallurgy applications. Powder Technol. 2011;210(3):267-72.