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Microstructural Evolution of Composite 8 WC-(Co, Ni): Effect of the Addition of SiC

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Abstract. Tungsten carbide (WC) based cemented carbides, also called hardmetals, are a family of composite materials consisting of carbide ceramic particles embedded in a metallic binder. They are classified as metal matrix composites (MMCs) because the metallic binder is the matrix that holds the bulk material together [1]. WC based composites are used in applications where a good combination of hardness and toughness are necessary [2]. It is usual to add more components to tailor the microstructure of the WC-(Co, Ni) system. The hardness for the cemented carbides based on nickel, increases significantly because of the addition of reinforcements like SiC nano-whisker [3]. In this work, the SiC was considered as an additional component for the composite WC-8(Co, Ni). Four mixtures were prepared with SiC contents ranging from 0 to 3.0 wt%. These mixtures were pressed (200 MPa) and green samples with 25.2 mm of diameter and 40 g were produced. Sintering was carried out in Sinter-HIP furnace (20 bar). Two sintering temperatures were investigated, i.e. 1380 and 1420ºC, and the sintering time considered was 60 minutes. The relative density, hardness, linear and volumetric shrinkage were determined. Microstructural evaluation was investigated by optical microscopy and scanning electron microscopy (SEM-FEG). The results showed that the addition of SiC promoted higher densification and grain size growth. The hardness was higher for samples with SiC, so solid solution hardening of the binder was more effective than WC grain size growth.

Introduction

WC-Ni composites are of great importance in the manufacturing industry. The term "composite material" appeared in the twentieth century, which means a component with two or more individual constituents, metals, ceramics and polymers [4]. By this definition, any material consisting of two components, such as ceramic WC and nickel powder with different physicochemical properties, can be treated as a composite material. WC-Ni composites are used in hydraulic as sealing rings for mechanical seals and for other applications [2, 5]. The benefit is also seen in the mechanical industry, such as compression tools for magnetic materials, wear resistance and abrasion tools for corrosive atmospheric environment in the chemical and food industry [5]. Experimental tests with WC-Ni composites indicate that the replacement of Co in the binder phase with Ni is a very good alternative. Ni is considered to be a material with excellent plasticity and satisfactory resistance to corrosion at high temperatures. Compared with the traditional composite WC-Co, the composite WC-Ni has better corrosion resistance and oxidation behavior [6].

It has been studied the effects of the addition of metallic silicon in WC-10Ni composite (wt.%) and it was found that the hardness and fracture toughness were higher when compared with a similar composite, WC-10Co [7]. Many researchers compared WC properties with nickel and cobalt on the concluding is similar properties. The cobalt and nickel properties are very similar, except for their crystal structure [8]. The allotropic cobalt has a packed hexagonal crystal structure (HCP) up to

450°C and the nickel structure is face-centered cubic (FCC). The Ni and Co, along with varying proportions of carbides, are used to improve the wear resistance by combining the metal carbide with a binder to form a composite coating WC- (Co, Ni). Cobalt is very expensive, toxic and has low corrosion resistance [9], that is why many researches aiming to find alternatives, for example, a suitable binder phase that substitute it [10]. During the sintering of the WC-Ni composite occurs the growth of WC particles due to the dissolution of small particles of WC and in the liquid phase. During sintering, carbon and tungsten particulates precipitation on the surfaces of larger carbides and abnormal grain size growth occurs, reducing the performance of the product. Therefore, the abnormal growth of WC particles should be avoided [11]. The mechanism for the abnormal grain size growth is not completely understood and a lot of research on the prevention of abnormal growth of the carbides were performed [12, 13]. The hardness for the WC-Ni can be improved with the addition of *SiC nanowhiskers* reinforcements. This increase can also be attributed to a solid reinforcement in the solution, binder phase of nickel silicon [14].

Experimental Procedure

Figure 1 shows the manufacturing stages of the tested samples. The mixture WC-8 (Co, Ni) having an average particle size of WC of 3.5 µm was purchased from UNIWIDIA Co. mixed and homogenized in a high energy attritor mill, using cemented carbide balls, for 8 hours. Figures 3 (A) and (B) show micrograph samples of WC-8(Co, Ni) sintered at 1420ºC, and Table 1 shows the chemical composition obtained from *Energy Dispersive X-ray Spectroscopy* (or EDS) of the area as in Fig. 3 (A). In the micrographs, it was observed the predominance of WC particles (light gray), nickel and cobalt (dark gray region), and generally a homogeneous microstructure with uniform distributed particles.

Table 1 - Chemical composition (EDS) of WC-8 composite (Co, Ni).

Element	[norm. wt.%]
W	88.9
Co	4.1
Ni	3.9

Particulates SiC were purchased from Imerys Fused Minerals Co, TREIBACHER, ALODUR® micro grain size, 1200 mesh, black silicon carbide type for abrasives, grain shape, density of 3.22 g/cm^3. The particle size ranged from 1.0 to 7.0 µm (80% de 1.0 µm). Its chemical composition is given in Table 2.

Table 2 - Chemical composition of the silicon carbide powder (SiC) provided.

Element	SiC	C free	Si	Fe
[norm. wt.%]	97.47	0.25	1.8	0.48

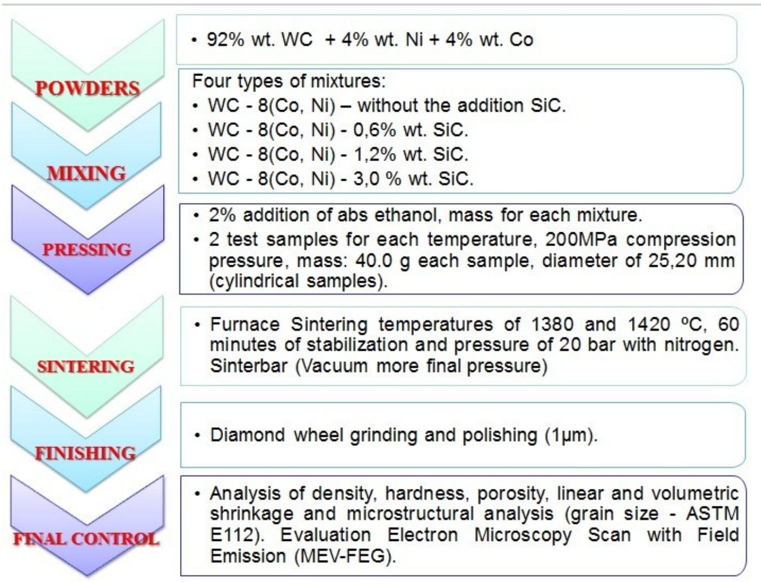


Figure 1 - Experimental procedure of the sample processing route.

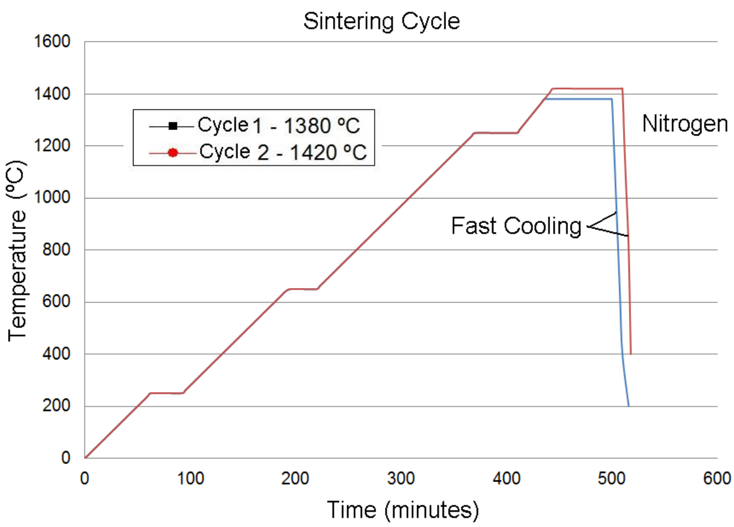
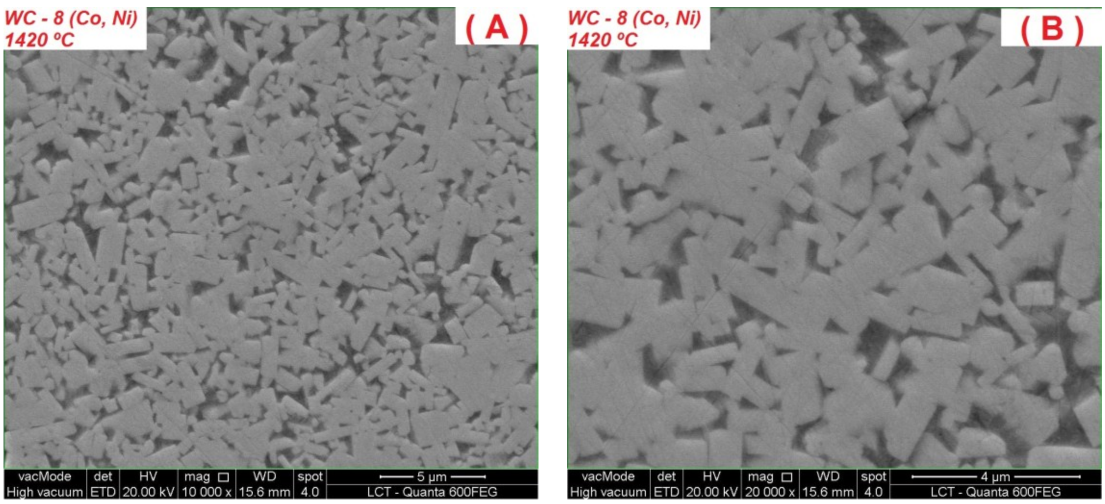


Figure 2 - Sintering cycle test specimen for cycle 1 (1380ºC) and cycle 2 (1420ºC).

The SiC was added to each mixture WC-8 (Co, Ni) using an industrial blender with 4 liters of liquid naphtha, for 30 minutes, to reach the desired mass balance, as shown in Fig. 1. After the homogenization, the naphtha was removed by drying.



Figures 3 (A) and (B) - Analysis by SDS WC- 8 mixture (Co, Ni) without SiC at 1420°C.

Analysis by EDS showed the predominance of WC particles (light gray), nickel and cobalt (dark gray region). In general, a homogeneous microstructure with uniform distributed particles was obtained. Figures 4 (A) and (B) show the powder after mixing with 1.2 wt.% addition of SiC. The BEI - Backscattered Electron Image (backscattered electrons) showed the presence of the SiC particles that is darker in (A) and in case (B), much larger than other constituents are.

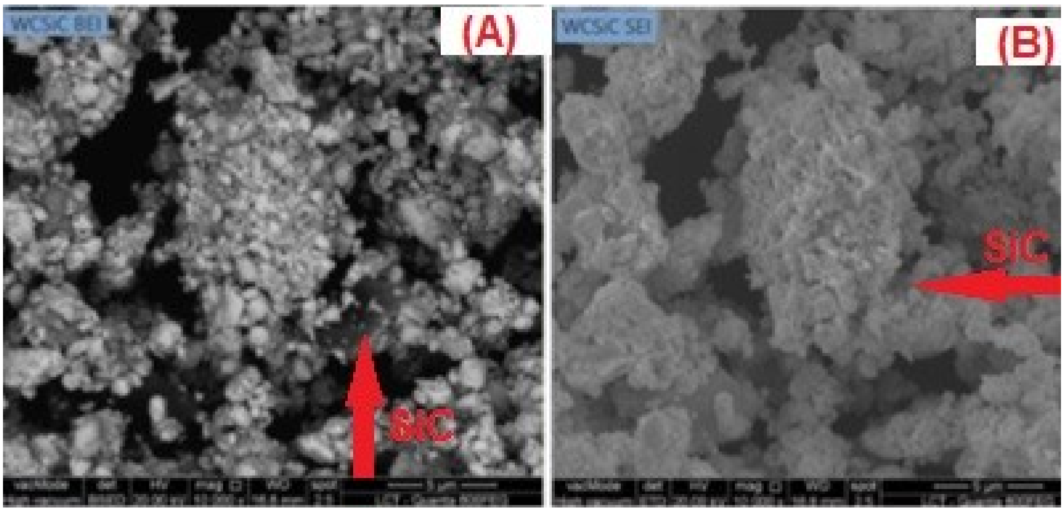


Figure 4 (A) BEI and (B) SEI - SiC identification on WC-8 mixture (Co, Ni) -1.2 wt.% SiC.

The samples were compacted with 200 MPa in a steel die (single action) with a cemented carbide core, with a diameter of 25.20 mm, and mass of 40.0 g for all the samples. For convenience and recommendation of ASTM E3-01, preparation of specimens is in the range 12-25 mm for material with cylindrical features and, in relation to height, it must not exceed what is necessary for convenient handling during polishing, ranging from 9 to 13 mm for measures to green or sintered.
The sintering cycles were performed in a single vacuum furnace with graphite resistance at 1380ºC and 1420ºC with 2.10^{-2} mbar, an average heating rate of 10°C/min and a step for stability of the microstructure of 60 minutes, and then a rapid cooling by introducing nitrogen, reaching a pressure of 20 bar, as shown in Fig. 2. This final step is known as “SinterBar”. After sintering, samples were ground and polished with diamond grinding wheels of the resinoid type, and then polished with diamond paste 1 µm and the revelation of the microstructures was performed with Murakami electrolytic etch. In this test, we used the *Axio Vision Release 4.9.1* program to measure linear intercept using circular lines, an automatic interception method. The circular intercepts procedures are most suitable for use as manual procedures fixed routines for estimating particulate sizes in quality control as described in ASTM E82.
The hardness tests, Rockwell A scale were conducted in a Durometer Galileo model by applying a load of 60 kgf with a conical tip with diamond 120º, according to the standards ASTM B 294 and ISO 3738. Based on this procedure, 10 tests were performed on each specimen for reliability of results. The density of the sintered samples were determined by the Archimedes method according to ASTM B 38 and MPIF-95 standard. The linear and volumetric shrinkage were measured in accordance with ASTM B-610 standards, MPIF Standard 44 and ISO 4492.

Results and Discussion

Table 3 shows the chemical compositions of the four mixtures and their respective hardness, obtained density, linear and volumetric shrinkage and finally the grain size of WC particles. In addition, this table presents the theoretical density of each chemical composition of the composite. Figures 5 to 8 show this values as a graphical representation.

Table 3 - Details and properties for the sintered samples.

Nº. Cycle	Composição química (wt.%)				T (ºC)	Hardness (HRA)	Theoretical Density (g/cm³)	Density (g/cm³)	Linear Shrinkage (%)		Volumetric shrinkage (%)	WC grain size (μm)
	WC	Ni	Co	SiC					Diameter (mm)	Height (mm)		
1	89.0	7.0	4.0	0.0	1380	88.2	14.75	14.70	21.15	14.72	43.63	4.4
2					1420	87.9		14.60	21.45	18.52	47.81	5.0
1	88.5	7.0	4.0	0.6	1380	88.9	14.45	14.50	24.44	20.52	38.08	4.8
2					1420	88.6		14.50	25.69	24.43	40.8	5.2
1	87.8	7.0	4.0	1.2	1380	88.4	14.15	12.80	21.45	19.21	28.19	5.7
2					1420	88.0		14.00	25.87	22.78	31.57	6.2
1	86.0	7.0	4.0	3.0	1380	-	13.30	9.35	12.50	8.30	5.40	-
2					1420	-		10.08	15.30	14.15	1.50	-

The microstructural characteristics of the sintered specimens were taken by an optical microscope, according to ASTM B657 and ISO 4499. The microstructures of these composites WC-8 (Co, Ni) are classified according to the binder phase content and size particulate and may be fine, medium or coarse, by a direct comparison of overlapping images. In the measurement of the average size for each sample according to ASTM E82, it is recommended to follow the intercept procedure for all structures that have uniform equiaxial grains.

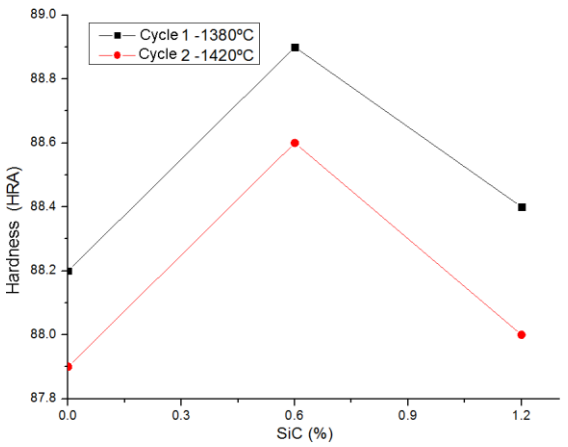


Figure 5 - Hardness as a function of addition of SiC and sintering temperature.

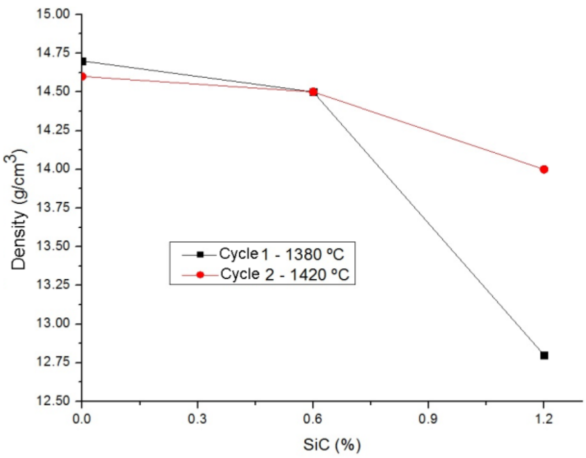


Figure 6 - Density as a function of addition of SiC and sintering temperature.

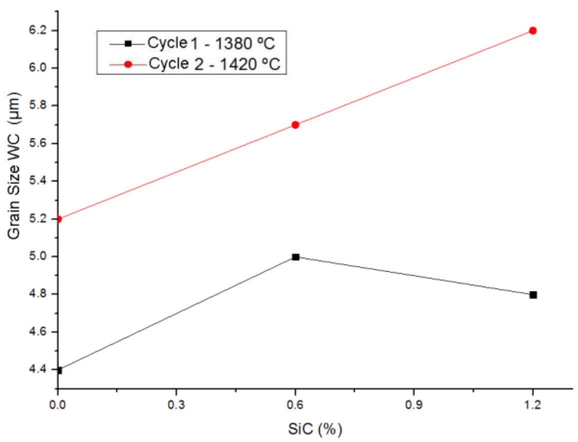


Figure 7 - WC grain size growth as a function of addition of SiC and temperature.

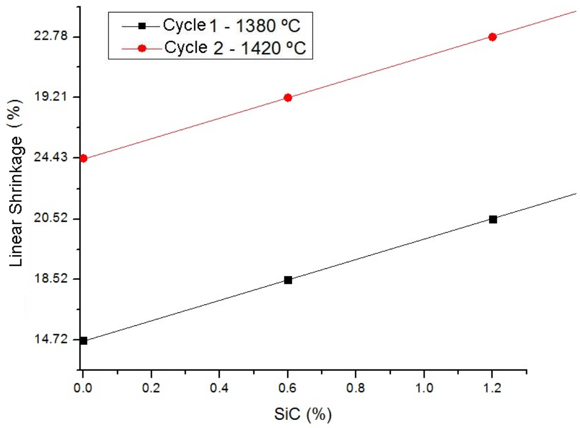
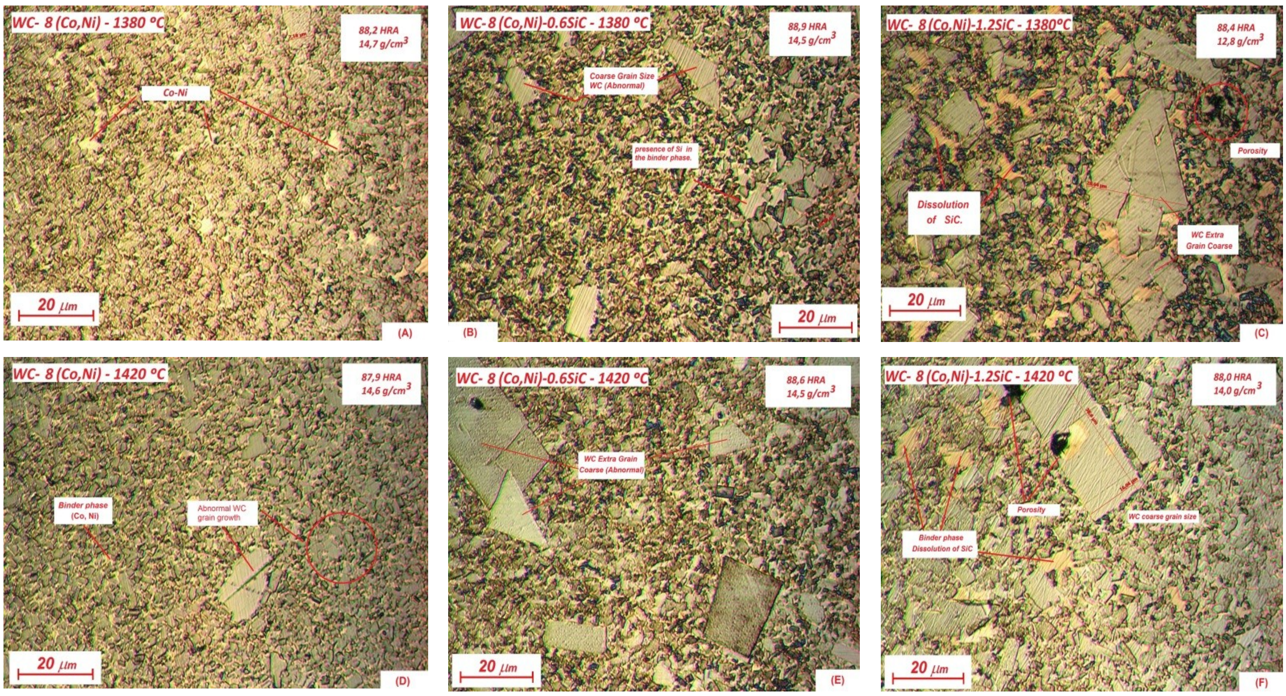


Figure 8 - Linear Shrinkage compacted height as a function of addition of SiC and temperature.

There was no sintering evidences for WC-8(Co, Ni)-3.0 wt.% SiC composites, that presented low densification, low linear and volumetric contractions. Regarding the hardness and microstructural characterization, the samples showed to be as pressed. So, it was not possible to determine hardness. The microstructure was not evaluated for these samples.
In Figs. 9 (A) to (F), the microstructures of the composites are shown for temperatures of 1380ºC and 1420ºC. These images were captured in the optical ZEISS microscope, with a magnification of 1000x (IFSP-SPO).



Figures 9 - Microstructure of the composites for temperatures of 1380ºC and 1420ºC.

Figure 10 (a) shows a microstructure for WC-8 (Co, Ni) -1.2 wt.% SiC sintered at 1420ºC. It is possible to observe a distribution of tungsten carbides ranging from 0.5 to 5 µm. It was observed a high Si concentration in the binder phase, Table 4, indicating dissolution of SiC.

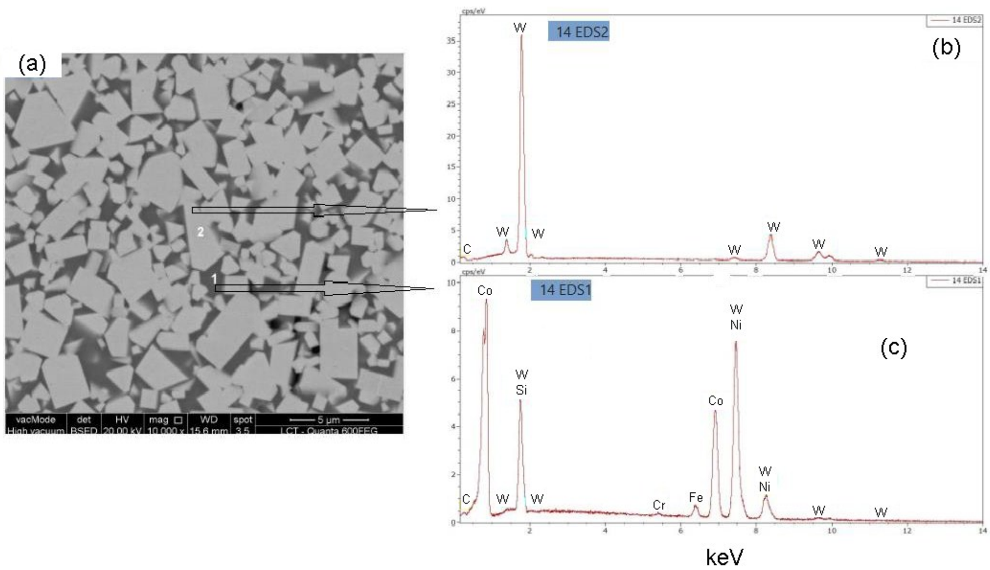


Figure 10 - (a) EDS spectrum, region 1 and 2, WC-8(Co,Ni) -1,2 wt.%SiC; (b) sample revealing W and C elements; (c) It was observed, a high Si concentration in the binder, indicating dissolution of SiC, revealing W-Ni, W-Si, Co.

Table 4 - Chemical composition of EDS region 1 and 2, Fig. 10(c) and (b) mixing with 1.2 wt.% SiC.

Chemical Composition (wt%)							
Sample/Region	C	Si	Cr	Fe	Co	Ni	W
Fig. 10 (b) EDS 2	5.44	-	-	-	-	-	94.56
Fig. 10 (c) EDS 1	4.87	5.24	0.38	2.16	27.47	51.54	8.35

Conclusions

A significant grain size growth of WC was observed when sintering at 1420ºC, considering mixtures without the addition of SiC, resulting in a decrease of hardness. The presence of Si in the binding phase after sintering suggested dissolution of the SiC. It was observed in the mixture with 0.6 wt.% SiC a significant increase of hardness (better result), for the sintering temperature of 1380ºC. In the microstructures for 1.2 wt.% SiC, the samples showed abnormal WC grain size growth that should be related to the change in the WC solubility in the binder. Abnormal grain growth was observed in samples sintered at temperatures higher than 1420ºC.

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