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INFLUENCE OF THE LIQUID PHASE AND THE CARBON ON THE REACTIVE SINTERING IN MIXTURES W-Ni-C

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Reactive sintering in W-Ni-C elemental powders mixtures to develop the WC-Ni hardmetal was studied. WC monocarbide is formed in situ when the carbon content is suitable. A lower content of carbon gives rise to the W_2C hemicarbide, which reacts with the nickel to form the Ni_2W_4C mixed carbide. This compound weakens the material and partly consumes the nickel. If the carbon content is higher, a precipitation of carbon-graphite was observed which decreases the strength of the developed material. Thus, the choice of the carbon content makes it possible to control the microstructure and the densification of the cermet.

Keywords: Mixture W-Ni-C, tungsten carbide WC, hemicarbide W_2C, ternary carbide Ni_2W_4C, reactive sintering

1. Introduction

The tungsten carbide WC is valued for its high wear resistance and good thermal stability that earned him wide application in various industrial fields. It is used in the manufacture of cutting tools [1, 2] and drilling. However, its great intrinsic fragility limits its use as a structural material, but it is generally densified with metals acting as binders, which give it the necessary toughness.

In 1920, a tungsten carbide WC based composite was densified for the first-time using cobalt as binder. This material, called at the time "Hardmetal", combined the hardness of the ceramic WC and ductility of the binder metal.

Many works have since focused on the sintering of WC carbide with several metals, but cobalt is still considered the best binder.

The tungsten carbide, used in the preparation of these composites, is previously prepared by carburizing pure tungsten or by carboreduction of the trioxide WO_3. However, cost and performance requirements have directed research towards replacing cobalt with other metals or alloys [3] as well as other additions of refractory metal carbides such as TiC, TiCN, NbC, TaC, MoC [4, 5].

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Carburizing elements such as Ti, Ta and Nb have been used to synthesize hard metals by sintering the WC–(Ti, Nb, Ta)(C, N)–Co mixtures [6]. The study of the W-Co-C system allowed the establishment of the ternary diagram and revealed formation of M_6C and $M_{12}C$ carbides (where M represents Co and W) [7]. However, little work has concerned direct sintering of W, (Ni or Co) and C elemental mixtures.

The W–(Co, Ni, Fe)–C mixture has been studied in order to develop a hard metal by sintering [3]. The properties of hard metal WC-metal have been shown to depend on the binder phase composition [8, 9]. The hard metal is also obtained by spark plasma sintering of the nanostructured WC-Ni mixture syntisized by carboreduction of nickel nitrate hexahydrate and ammonium paratungstate [10]. Recent work has shown that the fineness of the particles of the nickel binder significantly improves densification during sintering [11].

Cermets from $Ti(C_{0.7}N_{0.3})$-WC-Ni systems have been produced by the technique of injection molding of powders and by sintering [12].

This work focuses on the reactive sintering of the W-Ni-C powder mixtures, rich in W. The aim is to ensure at the same time the carburizing of tungsten to form the WC carbide and its densification studied by anisothermal dilatometry with formation of a liquid phase based on nickel. The Hot Pressing was used to densifie the synthesised material because of poor compressibility due to the presence of graphite in the mixture. The sintered material was analyzed by X-ray diffraction (XRD) and examined by scanning electron microscopy (SEM).

2. Experimental process

Tungsten (W; Goodfellow, purity 99,9%), Nickel (Ni, Goodfellow, purity 99,9%) and graphite (C, Merck, purity 99,8%) powders were used. The average particle diameter, measured by laser particle size is 10 µm for tungsten, 5 and 20 µm respectively for the Nickel and Carbon. The mixtures were prepared by varying the proportion of Carbon, with a starting composition set at 6.13% (% wt.) of W, which corresponds to the Carbon content in the stoichiometric Tungsten monocarbide (WC). The nickel content is set at 6; 12 and 20% (% wt.) of the mixture. The compositions of samples are shown in Table 1.

The samples were first homogenized in a Turbula for 30 minutes and then poured into a 15 mm diameter graphite mold whose walls were covered with a layer of BN in order to limit the reaction with the powder. The whole was treated at a temperature of 1500 ° C under dynamic argon in a graphite resistor oven, equipped with uniaxial compression system. A pressure of 30 MPa was applied to the powder above 800 °C and maintained throughout the duration of the sintering. Prepared materials were cut and rectified then polished using diamond discs. A final polishing is carried out on felts, with diamond paste with a grain size varying from 0.25 to 9 µm. The phase composition was determined using X-ray diffraction (Bruker D8 Axes, using Cu-Kα radiation) with PDF-4 database. The scan angle is set from 15 to 90 degrees with a step size of 0.02 degree and an exposure time of one second per step.

In addition, micrographs and X mapping were performed using the JEOL 5600 LV scanning electron microscope. This device is coupled to energy dispersive spectroscopy system (EDS-X) allowing point analyzes of the microstructure. The mapping revealed the distribution of elements in the different phases of the sintered material.

A dilatometric study was carried out up to 1500 °C on small pre-sintered pellets at 900 ° C in a vacuum oven at 10^{-5} torr. For this, we used a SETARAM dilatometer allowing instantaneous recording of changes in sample length during heat treatment. We were able to clarify some kinetic aspects of densification.

Table 1

Compositions of the studied mixtures

Sample	% by weight of the element		
	W	Ni	C
A	93.87	-	6.13
A0	93	-	7
A1	87.87	6	6.13
A2	81.87	12	
A3	73.87	20	
A4	87	6	7
A5	10	80	10

3. Results and discussion

3.1. Influence of carbon on the microstructure

The formation of tungsten carbide (WC) from W-C mixture powders is dependent on the carbon content. Starting from the stoichiometric content of this carbide (6.13 wt. %), we obtain, after sintering, a mixture of WC and hemi-carbide W_2C. Once the carbon content is increased to 7%, the sintered product contains only the monocarbide WC. Thus, the carbon deficit leads to the WC + W_2C mixture. These results, in agreement with previous work [13], are illustrated in Fig. 1, showing the diffractograms of samples A and A0. In 1987, researchers developed a mathematical model describing the carburization kinetics of tungsten powders mixed with carbon and heated in hydrogen [14]. Work carried out on the carburization of tungsten [15] has shown that the W_2C hemicarbide is formed first by the reaction of W and C and then it evolves into WC. These same compositions were investigated with content 6, 12 and 20% (% wt.) of nickel. X-ray analysis of the sintered products shows that for all the compositions, one again obtains the formation of tungsten monocarbide (WC). However, the presence of the ternary carbide Ni_2W_4C and intermetallic compound Ni_4W are detected when the carbon content is less than 7 %.

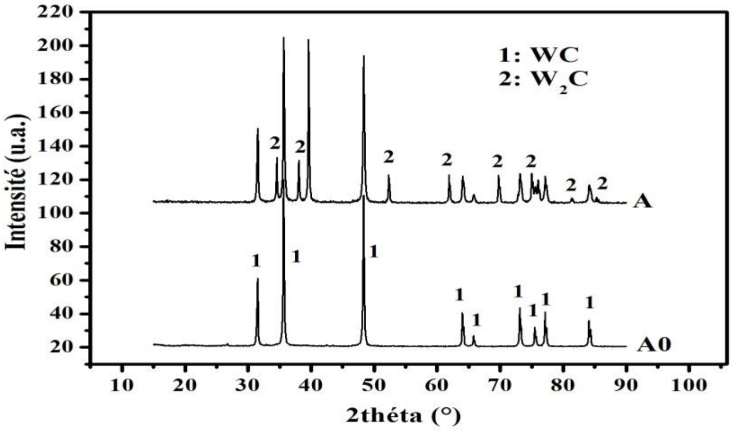


Fig. 1. XRD patterns of mixtures A and A0 sintered at 1500 ° C

Fig. 2 shows the diffractograms of samples A1 and A3, which highlight the coexistence Ni_2W_4C ternary carbide with tungsten monocarbide (WC) and Ni_4W compound. In addition, the amount of ternary carbide tends to increase when the carbon content decreases.

Indeed, on the XRD patterns of sample A4 (Fig. 3), only the WC diffraction peaks are visible, while those of ternary carbide are non-existent. In addition, a solid solution of nickel is highlighted. Controlling the carbon content in the initial mixture thus allows direct carburization of the tungsten during the sintering. A carbon deficit favors the formation of ternary carbide that results from the reaction of nickel with the hemicarbide W_2C. The last is unstable and transforms into tungsten carbide WC when there is sufficient carbon. In the presence of cobalt also the compounds Co_3W_3C and $Co_3W_9C_4$ are formed in the sintered product [13]. In the case of supersaturation, unaltered free graphite remains in the structure formed by the WC carbide alone and the nickel-based binder phase. In WC-Ni mixtures sintered with low Ni contents, a precipitation of graphite has been demonstrated [11]. However, very friable graphite behaves like micropores, which can initiate cracking of the material and would not be desirable in the microstructure. H. Suzuki [8] showed that the tensile strength of the WC-Co alloys increases with the carbon content and reaches a maximum when the free graphite begins to appear in the microstructure. However, for materials working wear, graphite is appreciated for its solid lubricant properties. Obtaining the two-phase structure (WC-binder) by sintering of W-Ni-C mixture is therefore quite feasible, but it assumes, as we have demonstrated precise control of the total carbon content.

For the carbon content of stoichiometric WC is 6.13% (% wt.), this quantity practically generates the ternary carbide Ni_2W_4C. Carbon is probably consumed partly by the reduction of surface oxide films of metal powders and by the reaction with oxygen adsorbed by the sintering installation. This leads to a carbon deficit that promotes the formation of W_2C hemicarbide, which then reacts with the nickel to form the ternary carbide. These results are in accordance with the work of Dina V. Dudina and al. [16] which demonstrated the formation of the compound Ni_2W_4C in the sintered Ni-W-C mixture. J. Zackrisson [17] also showed the formation of the ternary carbide for low carbon contents.

Ternary carbides are renowned for their high hardness, which explains the high microhardness values recorded on the spot sintered carbides mixed [2]. However, the formation of ternary carbide can be a disadvantage because it consumes Nickel initially intended for the densification of the monocarbide WC particles. In a previous study [13], we showed the presence of the ternary carbide $Co_3W_9C_4$ coexisting with the WC monocarbide for a carbon deficit compared to the stoichiometric WC content.

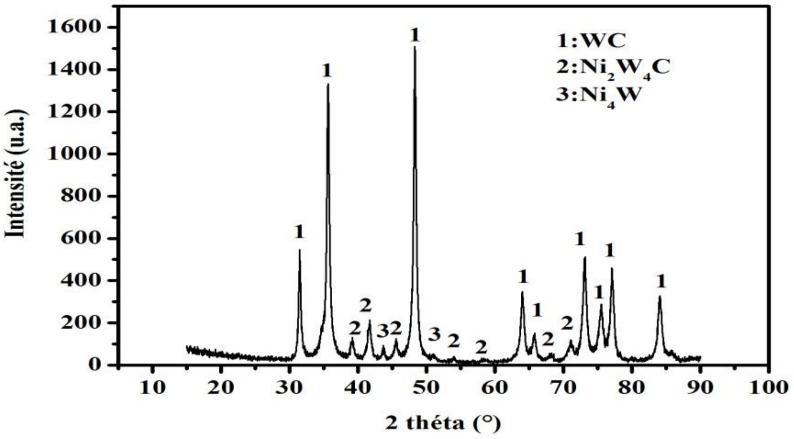


Fig. 2. XRD patterns of A1 mixture sintered at 1500 °C

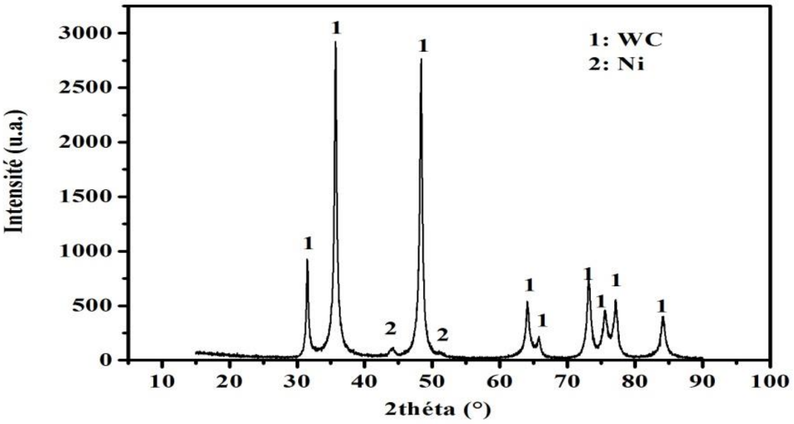


Fig. 3. XRD patterns A4 mixture sintered at 1500 °C

3.2. Effect of carbon on densification

The dilatometric study of samples A1 and A4 at increasing temperature, made it possible to locate the beginning of the phenomenon of densification in the vicinity of 1100 °C which continues until 1400 °C where an acceleration of the withdrawal is recorded up to 1500 °C. The dilatograms illustrated in Fig. 4 show a relatively higher densification rate for the carbon-rich mixture (A4) than for A1 having a lower content of this element. It therefore appears that when the carbon content is 7% (mixture A4), the sintered product consists of a WC-Ni cermet (Fig.3) and its densification is relatively better as shown in Fig. 4.

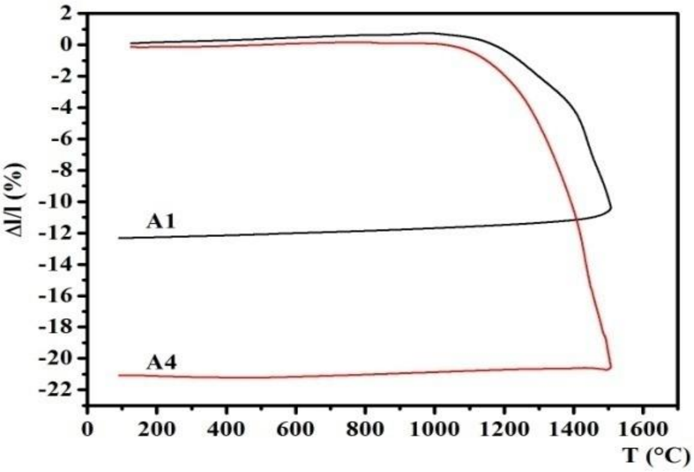


Fig. 4. Anisothermal dilatograms of mixtures A1 and A4

On the other hand, a Carbon deficit (mixture A1) causes the formation of the tungsten hemicarbide W_2C, which reacts with nickel to form the mixed carbide Ni_2W_4C. This mobilizes an amount of Nickel and consequently decreases the densification rate as shown in Fig. 4 (for mixture A1 relatively to the mixture A4).

3.3. Influence of Nickel content

The mixtures A1 and A3 (containing respectively 6 and 20% Ni and 6.13% C) were analyzed by XRD after sintering at 1500 °C. The mixed carbide Ni_2W_4C was detected in a relatively higher quantity in the mixture richer in Nickel. Fig. 5 shows the diffractograms of the sintered products, which reveal relatively intense diffraction peaks of Ni_2W_4C carbide for the Nickel-rich mixture. In addition, the analysis highlights the formation of the intermetallic Ni_4W predicted by the Ni-W Phase diagram [18]. It therefore appears that the elevation of the nickel content is in favor of the formation of a larger amount of the mixed carbide. This result is similar to the case of W-Co-C mixtures where the formation of the ternary carbide $Co_3W_9C_4$ was revealed during a carbon deficit in the mixture [13].

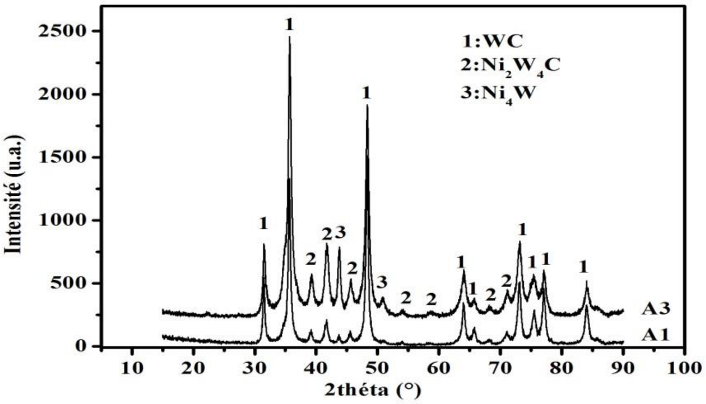


Fig. 5. XRD patterns of mixtures A1 and A3 sintered at 1500 °C

The dilatometric study has shown that with increasing nickel content, the rate and speed of densification become important. Indeed, Fig. 6 shows this shrinkage is 24% for the A3 mixture containing 20% Nickel. The acceleration of densification is marked by higher slopes of the dilatograms of mixtures with a high Nickel content.

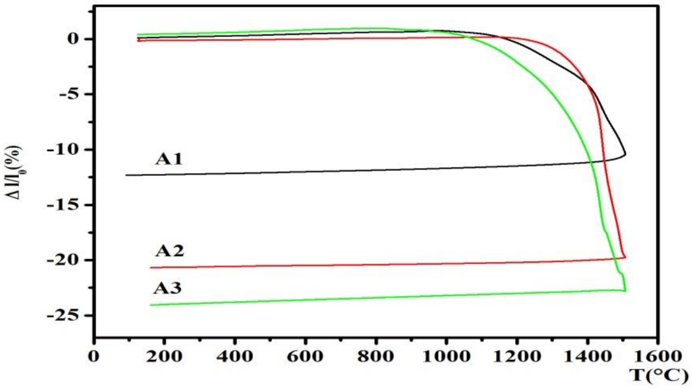


Fig. 6. Anisothermal dilatograms of mixtures A1, A2 and A3

When the mixed carbide Ni_2W_4C is not formed, the quantity of liquid phase remains sufficient to densify the material by liquid phase sintering. Otherwise, this carbide consumes part of the Nickel, which consequently reduces the densification rate during sintering. It therefore appears that it is possible to avoid the formation of mixed carbide by using an appropriate carbon content of the starting mixture.

4. Study of the binder phase Ni-(W, C)

A5 mixture, composition of Ni-10%W-10%C (% wt.), was homogenized and brought to fusion at 1500 °C under argon for 30 minutes. After cooling, the developed material is characterized by XRD and analyzed by scanning electron microscopy. The XRD pattern (Fig. 7) revealed the formation of the tungsten monocarbide WC in a solid solution of Nickel.

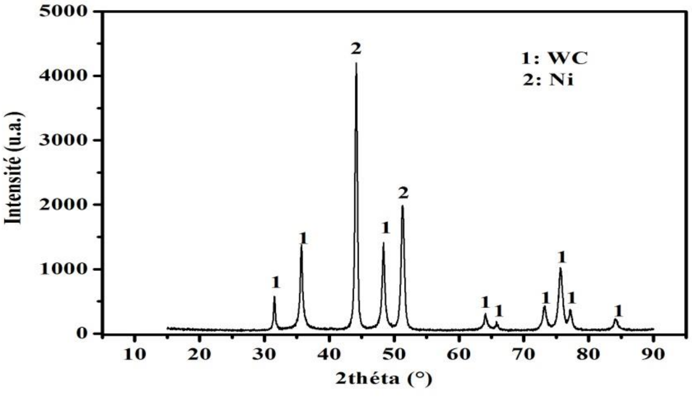


Fig.7. Diffractogram of the A5 mixture after melting at 1500 °C

In fact, a shift of the Nickel peaks towards small angles is observed, which is explained by an increase in the lattice parameter by dissolution of the tungsten in the Nickel. The Ni-W phase diagram predicts a solid solution of tungsten in nickel, the concentration of which increases with the temperature [18].

4. 1. Observation SEM

The microstructure (Fig.8) obtained by SEM, shows faceted tungsten carbide dispersed in the nickel matrix and black colored graphite revealed at the grain boundaries.

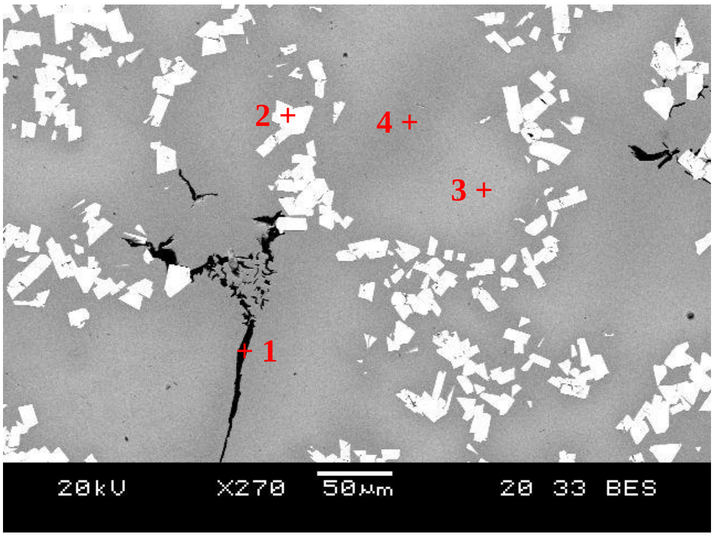


Fig. 8. SEM observation of the A5 mixture after melting at 1500 °C

The backscattered electron mode makes it possible to reveal a white phase (carbide) rich in tungsten and a matrix rich in nickel, relatively darker. In addition, the matrix shows a color contrast which is explained by an inhomogeneity of its concentration. This phase appears bright in areas where the concentration of tungsten, a relatively heavy element, is higher. On the other hand, in the neighboring zones of the tungsten carbide, this phase appears darker because it has partially precipitated the tungsten which forms the WC carbide by reaction with the Carbon.

To show the distribution of the elements between the different phases, we have established an X map shown in fig. 9. This figure confirms that the binder phase is relatively rich in tungsten because it appears in two different colors for tungsten.

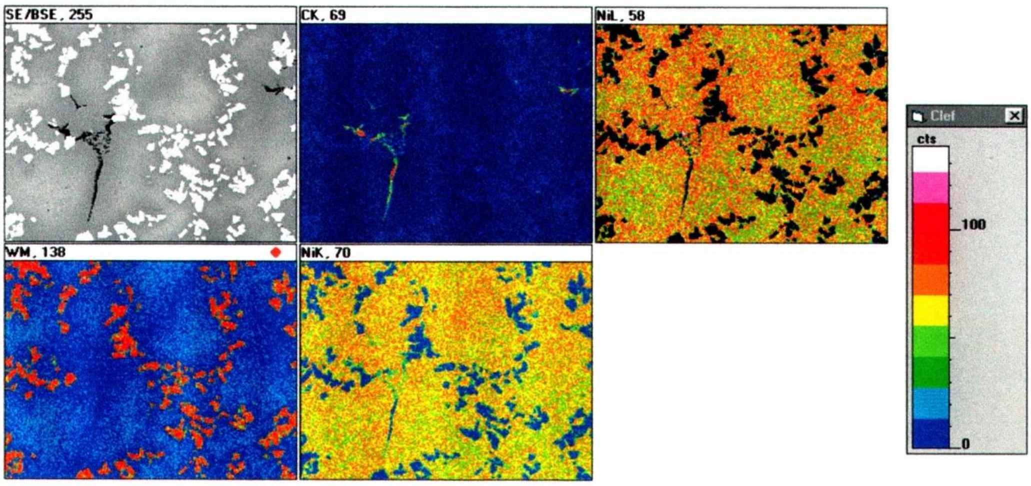


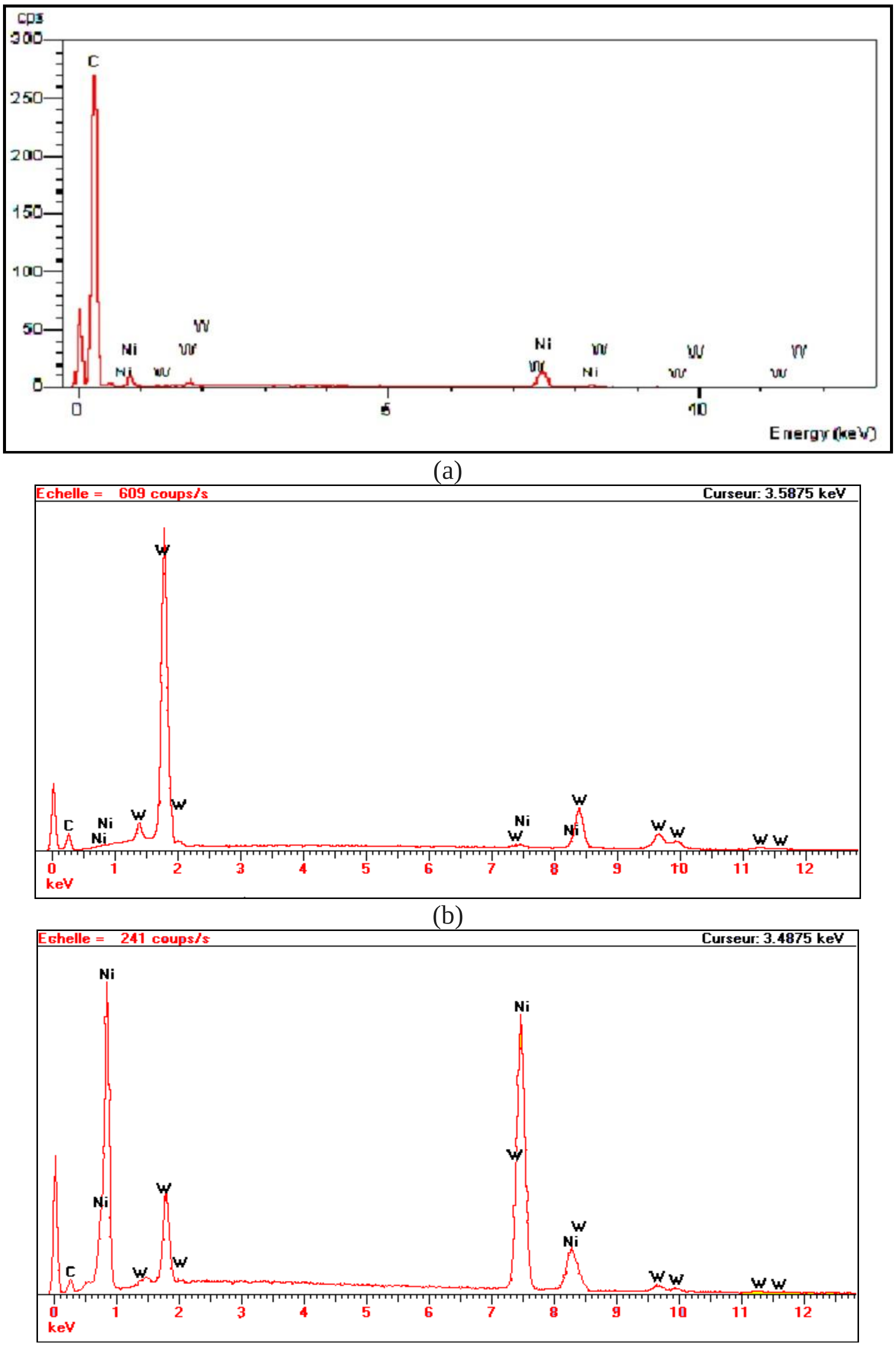
Fig. 9. X mapping of the mixture A5 after melting at 1500 °C

The tungsten rich areas are whitish while the relatively poor areas are blue near the tungsten carbides due to precipitation during cooling. The monocarbide WC, in a known geometric shape, is concentrated at the grain boundaries. It appears red in the mapping for Tungsten and blue for Nickel. The black phase of needle-shaped appears green and red on the carbon map. This phase can only be a precipitation of free carbon but not revealed by X-ray diffraction, probably because of its amorphous structure or its relatively low content. It can be concluded that the hardness of the binder phase will depend on its cooling rate, which allows precipitation of the carburic phase from the Nickel binder phase.

4.2. EDS- X Analysis

EDS-X analyzes were performed at the points indicated by numbers 1, 2, 3 and 4 on the micrograph of Fig. 8. The analysis at point 1 (Fig.10a) shows a large Carbon peak indicating that the targeted black phase is free graphite. A small amount of Nickel from neighboring regions is also highlighted. In point 2, the analysis shows peaks of tungsten and Carbon, which confirm that the white phase is the tungsten monocarbide (Fig.10b). In contrast, nickel peaks are not detected on the same spectra. The analyses at points 3 and 4 (Fig. 10c and 10d) reveal peaks of Nickel, Tungsten and Carbon. However, the Tungsten peaks are relatively more intense at point 3, which shows that the binder phase is a solid solution of Tungsten and Carbon in Nickel. Its concentration is not uniform due to the precipitation of WC carbide.

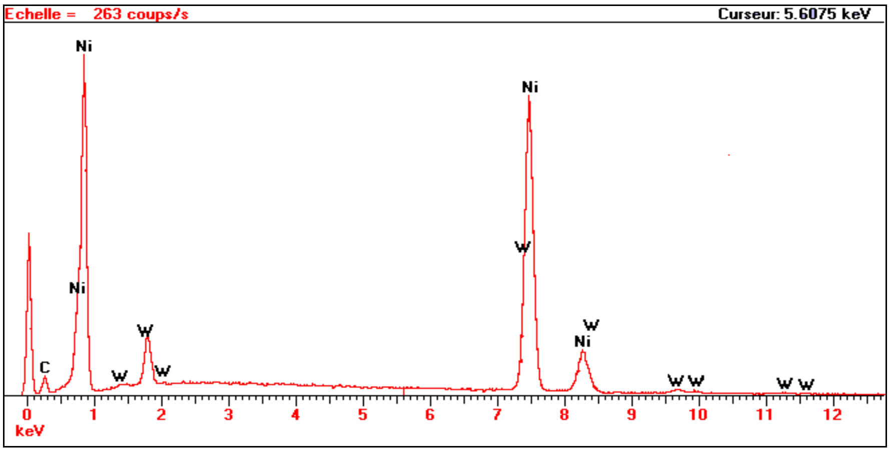
The micrograph in Fig. 8, obtained in backscattered electrons, shows this dark gray phase in the areas close to the carbides appearing in white. On the other hand, in the distant ranges of carbides it has a relatively lighter color. This explains an inhomogeneity of its concentration due to the phenomenon of precipitation of the dissolved components (carbon and tungsten). This is also confirmed by the X mapping presented in Fig. 9.



(a)

(b)

(c)



(d)

Fig. 10. Spot analysis in mixture A5 after melting at 1500 ° C

5. Conclusion

For cemented carbides, Cobalt is considered the best binder, especially for WC tungsten monocarbide. Due to the high cost of cobalt, its partial or total replacement by nickel was studied. High mechanical properties of the binder phase are linked to the precipitation of carbide during cooling. Indeed, Ni-W diagram shows the existence of a solid solution based on nickel tungsten whose concentration increases as a function of temperature. On cooling, the Ni-W equilibrium diagram predicts tungsten precipitation between 1497 and 1047 ° C. In the absence of Carbon, tungsten and Nickel form intermetallic combinations Ni_4W and NiW. However, mixed with a suitable Carbon content, a reaction with Tungsten gives rise to the WC monocarbide alone. It appears that a Carbon content of 7% makes it possible to obtain the WC-Ni cermet by reactive sintering of the W-Ni-C mixture. An excess of Carbon causes the precipitation of the free graphite, which reduces the sintered material properties.

On the other hand, any Carbon deficit leads to the formation of the W_2C hemicarbide that in turn reacts with Nickel to form the ternary carbide Ni_2W_4C. Thus, the choice of the carbon content of the W-Ni-C mixture makes it possible to prevent the formation of the ternary carbide, which is harmful in cemented carbides due to its fragility and its negative effect on densification during sintering.

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