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# The Study of Properties of WC-Based and W-Based Composites Fabricated by Infiltration with Liquid Cu-Mn Binder

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**Abstract:** This study refers to the characterization of alloys WC-W-Ni, obtained from a process of sintering, by using fine powders infiltrated by an alloy Cu-Mn binder. This process is used to produce a carbide cemented high-speed cutting tools and drilling tools because of their high hardness, refractoriness and wear resistance. The study required, the determination of the sintering conditions of the infiltration. The operation of infiltration consists of heating the binder until the melting point 950°C to let it infiltrate by gravity, the mixture of metal powders respectively, W, WC, W+Ni, WC+Ni and WC+W, thus allowing the powder grains to drown in the binder while being densified during cooling. The characterization of powders is used to determine theirs physical properties, chemical composition, powder classes and specific surface. The present study investigates the possibilities of Cu-Mn alloys used as binder alloys in infiltration of WC-based and W-based powders. After infiltration, a microstructural and mechanical characterization of the sintered samples and infiltrant were conducted in order to include/understand the phenomena implied during the densification and infiltration.

**Key words:** Densification, infiltration, liquid phase sintering, binder phase, WC-W-Ni

## INTRODUCTION

Composite materials based on mixture of powders of WC, W and Ni is extensively used as matrix for the production of the mining and drilling tools (Cummings and Wicklund, 1980). The (WC-W- Ni) metal composites matrix were produced by infiltration with a tough binder metals copper-based, used as support material in diamond rock drillings bits. The purpose of the matrix is to form a strong chemical bond with the diamond grit and to hold it in place. It must be hard enough so that it will gradually expose new diamond cutting points as required by the tool (Caceras, 2002; Orban and Domsa, 1999; Domsa and Orban, 1999). In general, hard compound WC as well as W confer on materials hardness, the refractory character and corrosion resistance, while the metal phase, which is used as binder, brings tenacity and the aptitude for the plastic deformation (Boch, 2001). Nickel is often included to assist in sintering, due to the appreciable solubility for tungsten and it is added to provide fine grained corrosion resistant hard metals (Sriraman *et al*., 2007). These composites are produced by the powder metallurgy of which the densification is obtained by infiltration in liquid phase sintering.

This process gives certain advantages for the manufacturing of big sized tools and varied and complex forms. The infiltration consists in filling the pores of a mixture of free powders packed in a

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mould by a molten metal. This method for densifying a powder-metal skeleton that produces a final part of homogeneous composition without significant dimensional change, offering full-density sintering (Lorenz *et al*., 2004; Yulyugin and Kolesnichenko, 1999). The process of the infiltration begins with the fusion of the binder (infiltrant) metal Cu-Mn that allows it to fill the skeleton void space (open porosity) and later facilitates homogenization. It produced in two stages : the first stage is the fusion and the flow of infiltrant liquid, when the infiltrant and skeleton are separated physically prior to infiltration, the second stage is the densification when the molten infiltrant contacts the powder skeleton by the mechanisms of liquid phase sintering.

An ideal liquid phase sintering system has been defined as one in which the melting point of the infiltrant must be a inferior that of the powder skeleton and the solubility of the powder base in the infiltrant should be greater than that of the infiltrant in the base powder (Ryu *et al*., 2002; Lee and Kang, 2001). The infiltration with LPS is a complicated process that involves microstructural evolution through the action of several different mechanisms (Sung-Min and Kang, 1998; Michaud and Mortensen, 2007). The solid particles of the composite are rearranged under the action of the capillary forces. It causes shrinkage by elimination of porosity. The driving force of the rearrangement and the reduction of the interfacial energy, related to the reduction in the interfacial surfaces mainly solid/liquid/gas allow, at the end of the cycle, the densification of the mixture. The time of the operation is in general short and the temperature of work is very low than that of binder alloys (Yoon and Huppmann, 1979; Wu *et al*., 2003).

The earlier study use the bronze alloyed with Ni and the brass as the infiltrants alloys (Miroud *et al*., 2008; Constantinescu *et al*., 1993). For this study we selected new infiltrant copper-based alloy, it contains additions of Mn and small quantity of P. These elements improve the flow of the liquid phase, decrease the melting point of copper and increase the hardening of the matrix containing Cu. Interactions of this new binder with the basic powders, WC, W and Ni, are not yet clearly defined in the literature.

The present study investigates the possibilities of Cu-Mn alloys using as binder alloys in infiltration of WC-W-Ni powders by the optimization of the operating parameters of the infiltration in liquid phase such as, time, temperature and atmosphere of sintering. A microstructural and mechanical characterization (hardness profiles are established) of the sintered samples and binder alloys was necessary in order to understand the phenomena implied during the densification and to determine the influence of chemical composition of the infiltrated phase on the densification.

## MATERIALS AND METHODS

### Grades of Powders

The powders selected for this study of the effect of infiltrating liquid Cu-Mn on the morphological evolution of the particles, are classified in three groups:

- P1 and P2 are pure W and WC powders, respectively. They correspond successively to W, WC that we later characterized. The results from these infiltrations will give initially the individual and separated effect of each of the powders immersed in a molten liquid Cu-Mn
- M1, M2 and M3 are binary mixtures of the basic powders. Their compositions are shown in Table 1
- M4 is a three-phase mixture, is a mixture of the powders : Ni5 wt. %; W5 wt. % and WC (base)

### Process of Infiltration

The infiltrations, of the metal binder in fusion, are carried out in a graphite mould (Fig. 1) constituted of two parts laid out one on the other. The lower half-mould serves to contain the mixtures

Table 1: Mixtures of powders used for the infiltration

| Grades | M1 | M2 | M3 | M4 |
|---|---|---|---|---|
| Mixture wt. % | 70W-30Ni | 70WC-30Ni | 70WC-30W | WC-5W-5Ni |

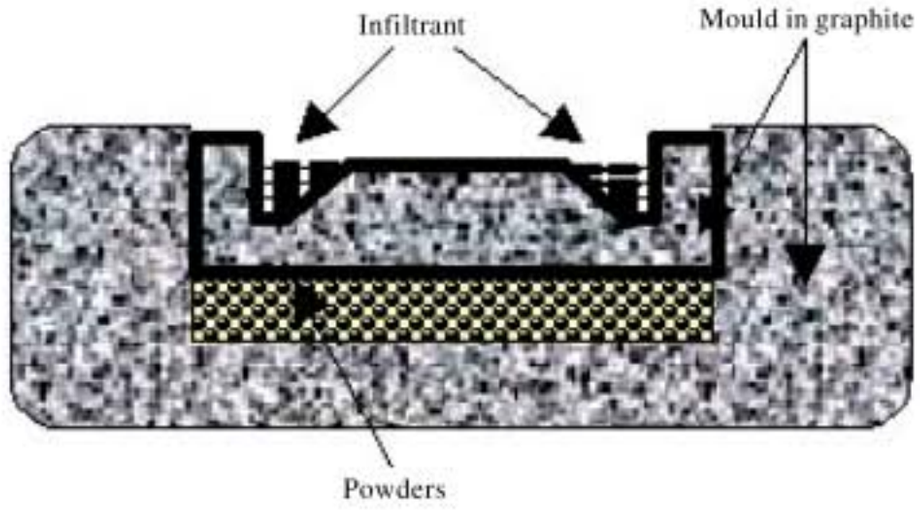


Fig. 1: Schematic representation of the infiltration process

of powders to be infiltrated and the higher half-mould is used to contain the metal binder which will be fed in sufficient quantities in the powders which are in the various cavity during its fusion. The sintering of the samples is carried out under an atmosphere of hydrogen in an industrial electric furnace (furnace BOREL).

**Optimization of the Sintering Cycle Parameters**

The values of these parameters were determined and fixed starting from the results obtained by our preliminary tests. The temperature of the isothermal stage was fixed at 950°C. It corresponds to the melting point of infiltrant alloy to which is added a temperature of value 80°C in order to maintain alloy in the liquid state all along cycle (Handbook, 1992). A duration of 30 min of the stage was given after having observed that it allowed at the same time a good infiltration and a good densification of the sample*s*. The speed of heating was fixed at 5°C $min^{-1}$. The cooling of samples is done in the furnace by turning it of after having stopped it. The choice of the atmosphere of hydrogen was dictated by the fact that it prevents the oxide film formation on the powder grains and accelerates, at the same time, sintering and the densification (Huppmann and Riegger, 1979).

**Characterization**

The basic powders WC, W and Ni were characterized by determinating of their apparent densities after compression measured in accordance with the standards ISO 3923 and ISO 3953. Their size and the distribution granulometry is obtained by the method of dry sifting following the standard ISO 4497. Specific surface or surface total of particles per unit of powder mass is determined by the method BET (Brunauer, Emmett and Teller). The chemical analysis for each powder and the analysis of carbon are obtained respectively by X-rays fluorescence spectrometry and by carbon analyser type LEYBOLD. The crystallographic nature of the basic powders is observed using a Siemens X-rays diffraction analyzer D5000 type equipped with a copper anticathode. Samples for metallographic examination were prepared according to the standard metallographic procedure. The observation of the morphology of the various phases formed in the binder Cu-Mn and of their distribution in the sintered samples are obtained using a JEOL JSM 6830 Scanning Electron Microscope (SEM) equipped with a detector EDS. The hardness of the various phases which are formed in the samples and microhardness profiles established in the direction of the infiltration are measured by the test of Vickers HV0,1. The load applied is of 100 g and 15 sec application time.

## RESULTS AND DISCUSSION

### Characteristics of WC, W and Ni Basic Powders

Table 2 and 3 shows the results of the chemical analysis of the three powders of bases which are WC, W and Ni. The analysis confirms the purity of the powders W, WC and Ni which is respectively about 99, 590, 98, 554 and 99, 748 wt. %. The analysis also confirmed, the presence of other chemical elements in very small quantity such as: Ca, Cr, Fe, Mo, Co and Si. This presence of the elements is due to the industrial manufacturing processes.

The morphology of the powders observed by MEB is presented in Fig. 2a-c. The X-ray diffraction spectra of the basic powder WC are shown in Fig. 2d. The analysis indicates that the powder WC is constituted of two phases of hexagonal structure. Initial phase WC and a second eutectic phase $W_2C$. The presence of this second phase is obtained during the elaboration of WC powder because during the carburizing step, the tungsten hemicarbide $W_2C$ is formed like intermediate phase. This phase is undesirable because it presents at the same time a very high hardness and a great brittleness.

Table 2: Chemical analysis of the basic powders in weight (%)

| | Elements | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Powders | W | Ni | Ca | Cr | Fe | Zn | Mo | Co | Si |
| W | | 0.097 | 0.100 | 0.037 | 0.094 | 0.031 | | | |
| WC | | 0.031 | 0.093 | | 0.311 | | 0.090 | | 0.080 |
| Ni | | | | | 0.022 | | | 0.170 | 0.060 |

Table 3: Quantity of carbon in the powders W, WC and Ni

| Powdres | W | WC | Ni |
|---|---|---|---|
| carbon (weight %) | 0.05 | 3.94 | 0.07 |

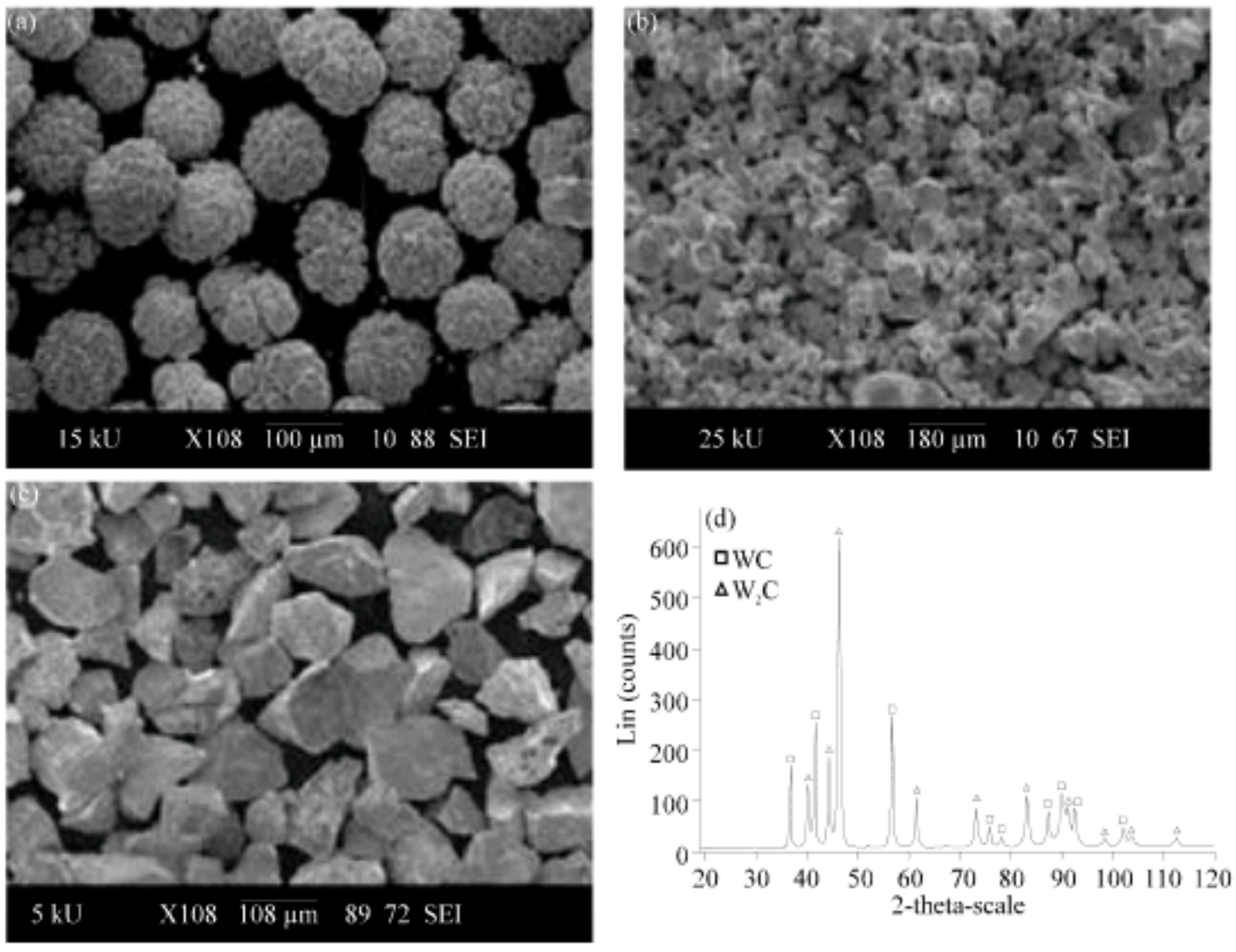


Fig. 2: SEM image of Ni powder (a), W powder (b), WC powder (c) and (d) X-ray diffraction analyse of WC powder

The granulometric distributions of three powders W, WC and Ni (Fig. 3) gives for each powder, two classes of majority sizes are observed: class 63-75 microns and class 106-150 microns. For the powder of WC, a third majority class is highlighted: class 150-212 microns. The values of apparent density after compressing and the specific surface of powder WC is largest. This is directly dependent on its irregular and faceted form, contrary to that of the nickel powder whose form is symmetrical is rounder (Table 4). Specific surface is a very significant parameter has a notable influence on the process of sintering and the values obtained depend especially on the form and the size of the grains of the powder.

**Microstructure of Infiltrant Cu-Mn Before and After Infiltration**

The infiltrant used in this study is an alloy containing copper and manganese in proportions 70.26 and 29.08 wt. % respectively with a very weak phosphorus at 0.66 wt. %. The presence of phosphorus in alloy comes from the copper phosphide which is used for stripping of copper and does not have action on the mechanical properties but on the other hand it lowers thermal and electric conductivities (Ryu *et al*., 2002). Figure 4 shows the morphology obtained by optical microscope of infiltrant in initial state. The infiltrant structure corresponds to a dendritic structure distributed with nonspecific orientations. The fine dendritic phase is within a matrix copper-manganese. This structure

Table 4: Apparent densities and the surface specific of the powders W, WC and Ni

| | Powder | | |
|---|---|---|---|
| Variables | W | WC | Ni |
| Apparent density before compressing (g $cm^{-3}$) | 6.43 | 7.87 | 5.61 |
| Apparent density after compressing (g $cm^{-3}$) | 7.84 | 8.78 | 6.22 |
| Specific surface ($m^2$ $g^{-1}$) | 0.341 | 0.409 | 0.031 |

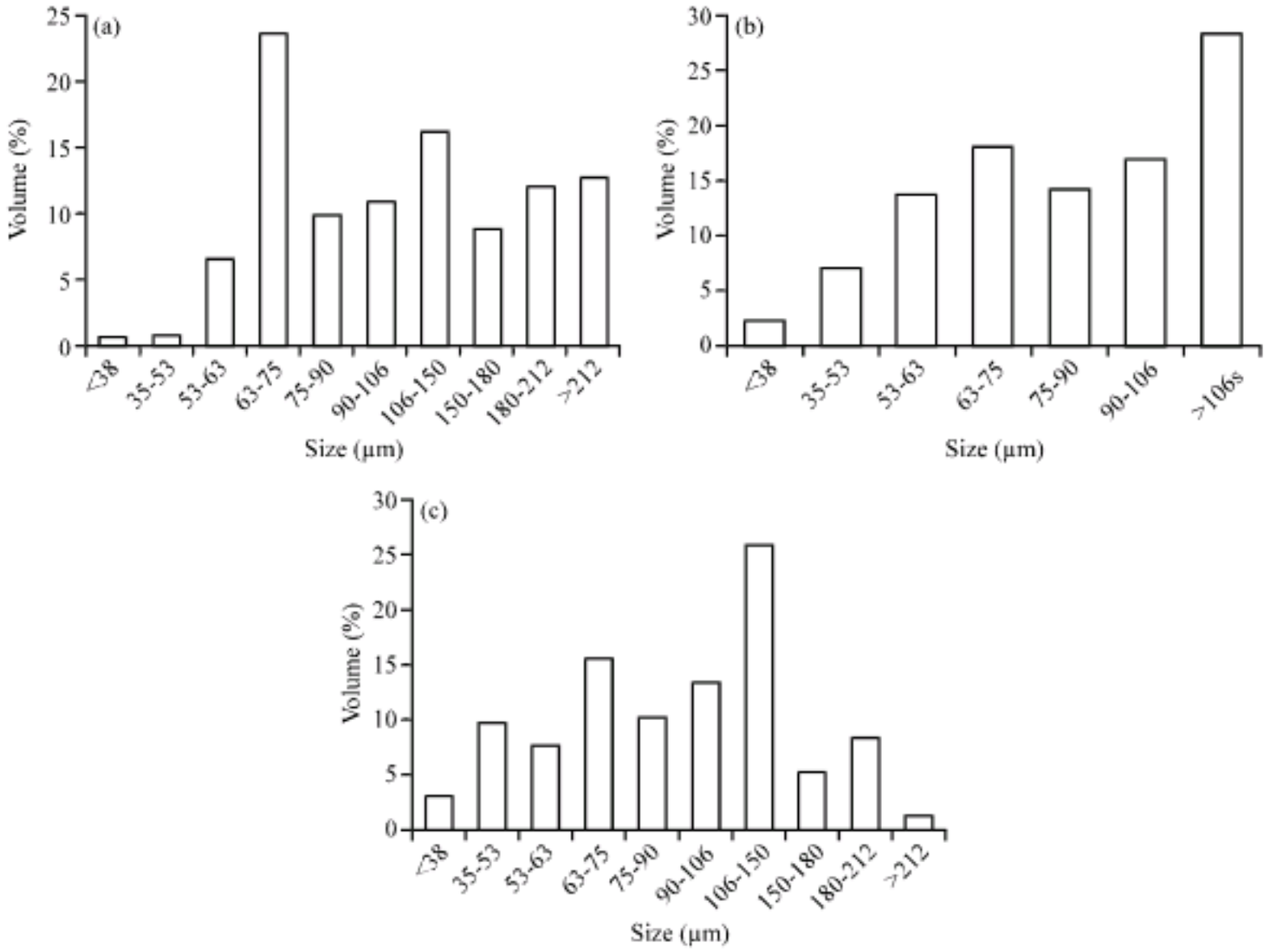


Fig. 3: Granulometric histogram of distribution for powders (a) WC, (b) W and (c) Ni according to the average size

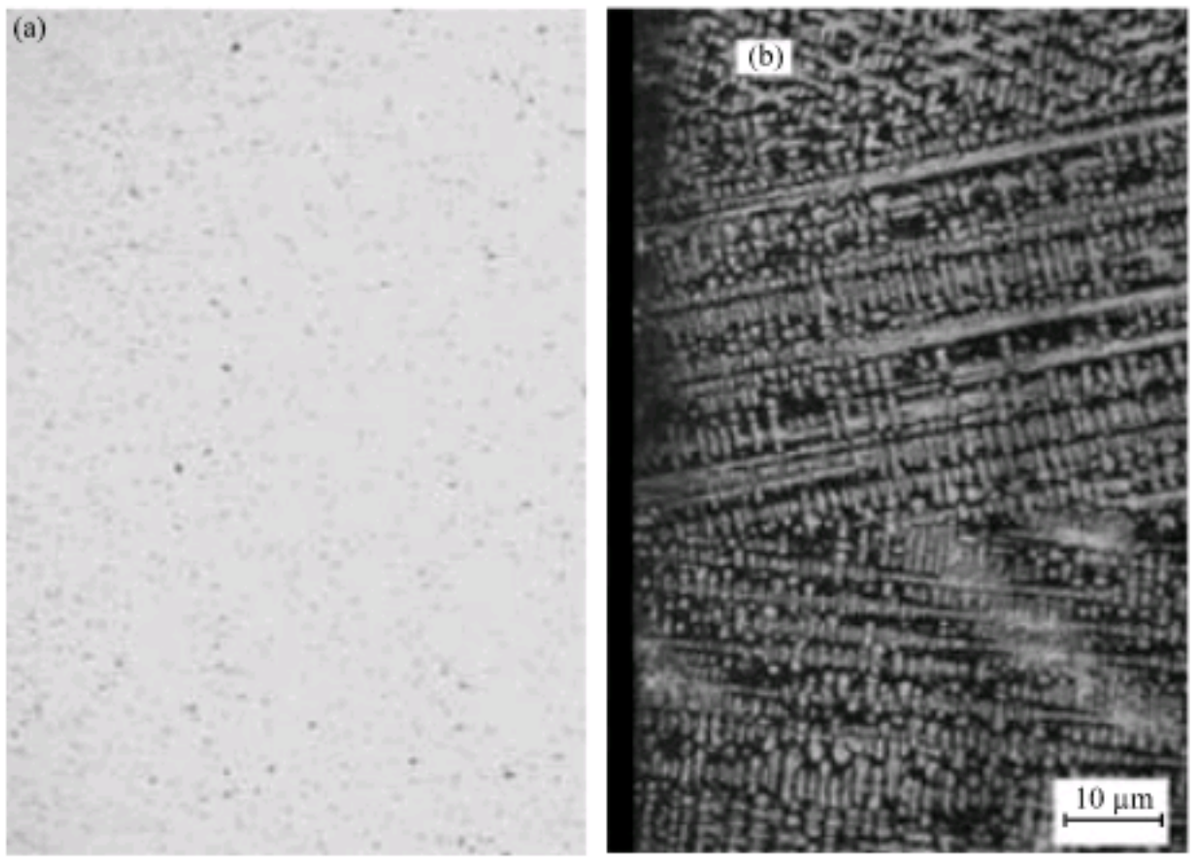


Fig. 4: Optical microstructure of infiltrant: (a) not attacked and (b) attacked with Nital

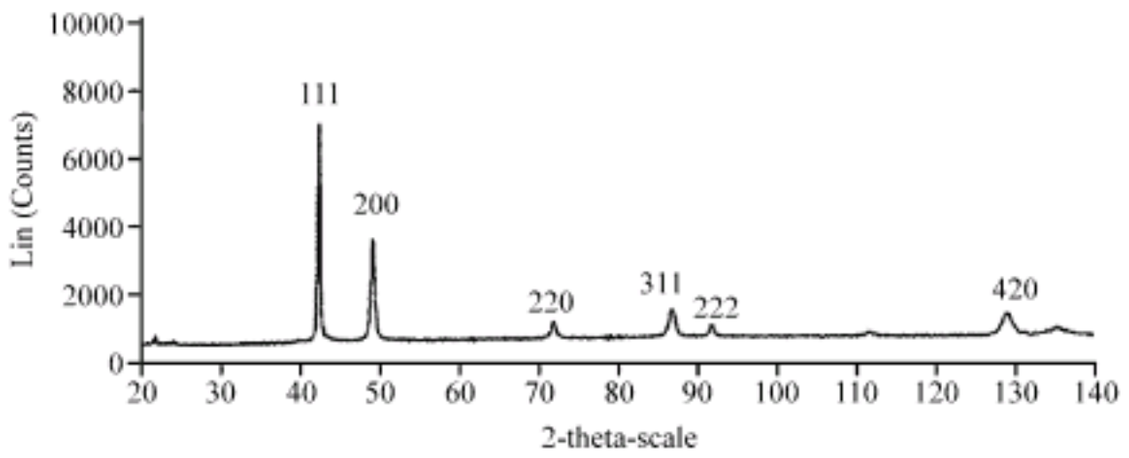


Fig. 5: The X-ray diffraction analyse of infiltrant Cu-Mn

is never chemically homogeneous, the impurities like phosphorus are located in the parts solidified last and accumulate in the vicinity of the defects and the pores. It was noted that the element P is with percentages high at the level of the dendritic ramifications and at the level of the grain boundaries. The result of the analysis by X-ray diffraction of infiltrant in the initial state are shown in Fig. 5. The examination of these results highlights the predominance of the copper cubic structure phase.

After infiltration of the powder samples, a residual quantity of the infiltrant remains in their higher part. Microstructural observation by the optic of the infiltrant after infiltration were carried out in this part. The initially dendritic microstructure did not completely disappear but the imposed thermal cycle generated a compact microstructure after solidification composed of a majority solid Cu-Mn solution with a very high porosity (Fig. 6). The presence of the phase eutectique Cu-$Cu_2O$ distributed on the surface of the sample is observed.

**Microstructural Characterization of the Sintered Composites**

Figure 7a-f shows the microstructures of the grades P1, P2, M1, M2, M3 and M4 obtained by sintering with infiltration of the binder Cu-Mn in liquid phase. The different sintered grades present all a good densification, with the presence on the samples surface a very weak porosity. This result is the consequence of good infiltration.


Fig. 6: Optical micrograph showing microstructure of infiltrant after sintering (attacked with Nital)

Figure 7a show the morphology of the W powder in P1 which changed its form completely. Initially with polygonal form to a round form, confirming thus, the interaction of the W powders with the binder by dissolution (Fig. 8a).

The powder WC in the P2 grade (Fig. 7b) has a faceted morphology and constitutes a skeleton due to the bridging together between grains WC, in certain cases to the formation of contacts WC-WC. This structure is almost identical to that observed in the classical structure of sintered alloys WC-Co (Petersson, 2004). M1 and M2 (Fig. 7c, d) rich in Ni present a strong content of binder phase. There are no direct contacts between the powder particles of W/W or WC/WC. Vijayakumar *et al*. (1988) and Massalski (1990) show that the intersolubility between W and Cu is almost zero. The addition of Ni to the powder of W (M1 grade) allowed a significant dissolution of tungsten and to increase the quantity of Ni in the liquid binder (Fig. 8b). Moreover, we observed that the particles of W have an irregular spatial distribution and are divided into fine entities. The densification process of this grade can be explained as follows: the binder melts, infiltrates and distributes completely around the particles of W. The capillary forces directed by the formed initial skeleton impose on the mobile particles a redistribution and a regrouping around this skeleton (Liu *et al*., 1995; Shen *et al*., 2005).

The presence of Ni in high quantity, allows infiltrant liquid to attack the particles of W at the level of the junction points which form the strong points of the skeleton and makes them mobile. This mobility prevents the formation of the agglomerates and allows a good densification with a better distribution of the chemical elements (Upadhyaya and German, 2001). Contrary to the dissolution of tungsten in contact with Cu-Mn infiltrant in the presence of nickel, the dissolution of tungsten carbide (nuance M2) in the infiltrant phase is practically impossible otherwise with quantities very weak. It seems that the thermodynamic and kinetic conditions imposed during the process of sintering and the presence of Ni with a high rate supported the formation of intermetallic compounds Mn-P.

We observed in certain zones of the sample (M1 nuance) the presence of old grain boundaries probably of nickel, with a precipitation at the level of these joints a rich phase in phosphorus and manganese. The EDS microanalysis indicated that this phase contains 71.63 wt. % Mn and 28.37 wt. % P, which corresponds to the stoichiometry of the given compound $Mn_3P_2$ whose presence is random and not localized (Fig. 9a). Another phase was observed in M2 (Fig. 9b). The analysis agrees with the given compound of $Mn_2P$ type.

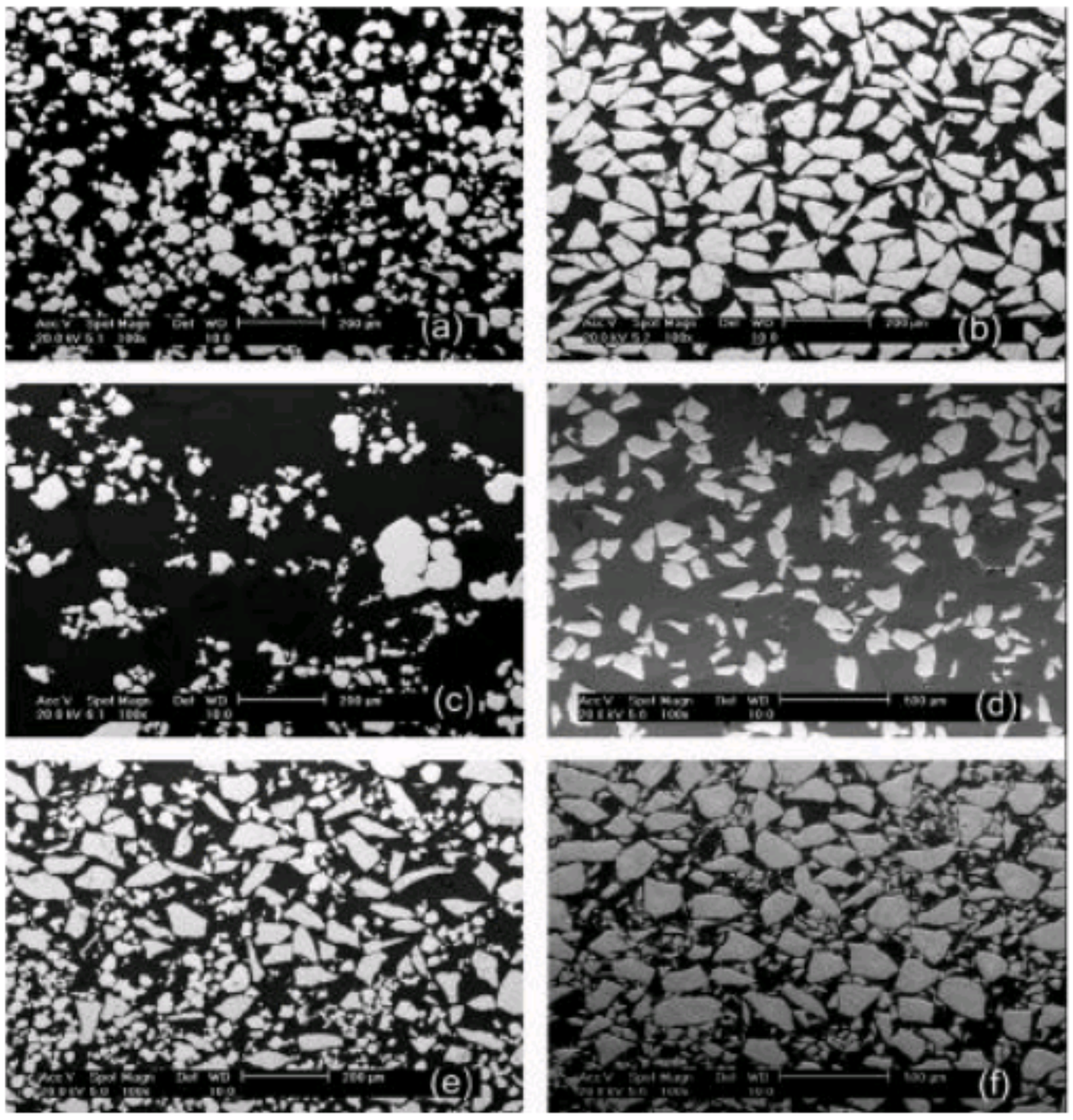


Fig. 7: SEM micrographs of the samples after infiltration respectively (a) P1, (b) P2, (c) M1, (d) M2, (e) M3 and (f) M4

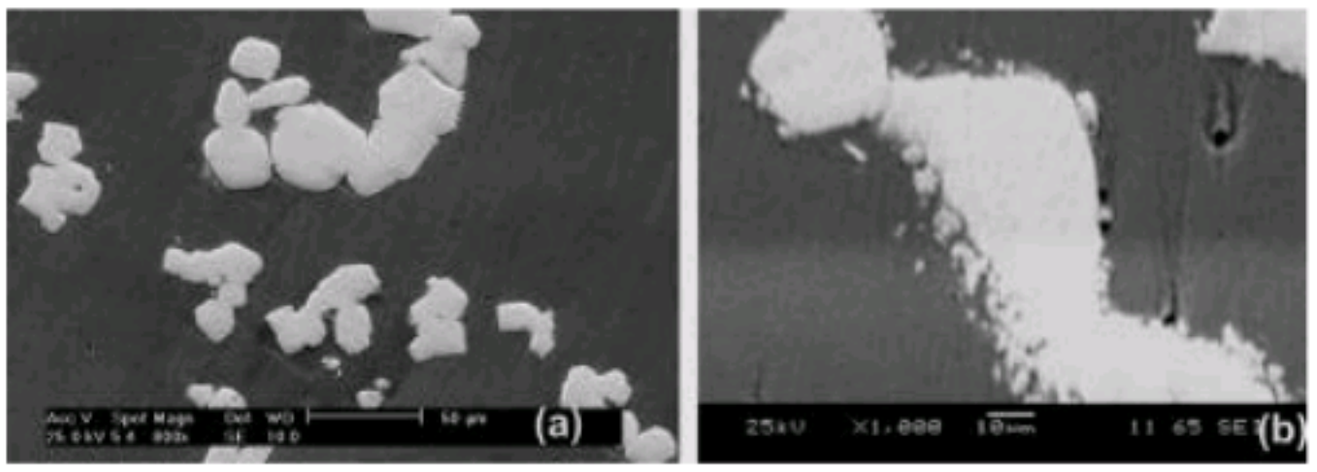


Fig. 8: SEM image showing (a) the morphology a round form of the W powder in P1 grade, (b) a significant dissolution of W with presence of Ni

In M3, the particles of WC are surrounded by fine particles round representing the phase of W in dissolution in the binder (Fig. 7e). The dissolution of W in this grade is partial and is established around the junctions of the skeleton of WC, by forming agglomerates. During the infiltration, the capillary forces accelerate the mobility of the fine particles of W which are distributed around the

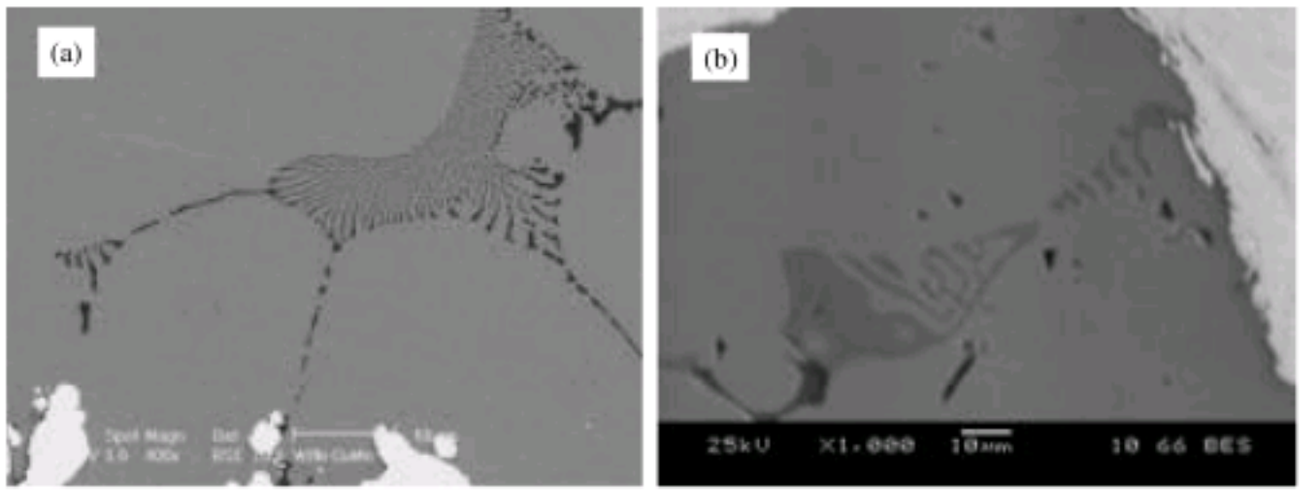


Fig. 9: BSE micrographies of intermetallic phase: (a) $Mn_3P_2$ in M1 grade, (b) $Mn_2P$ in M2 grade

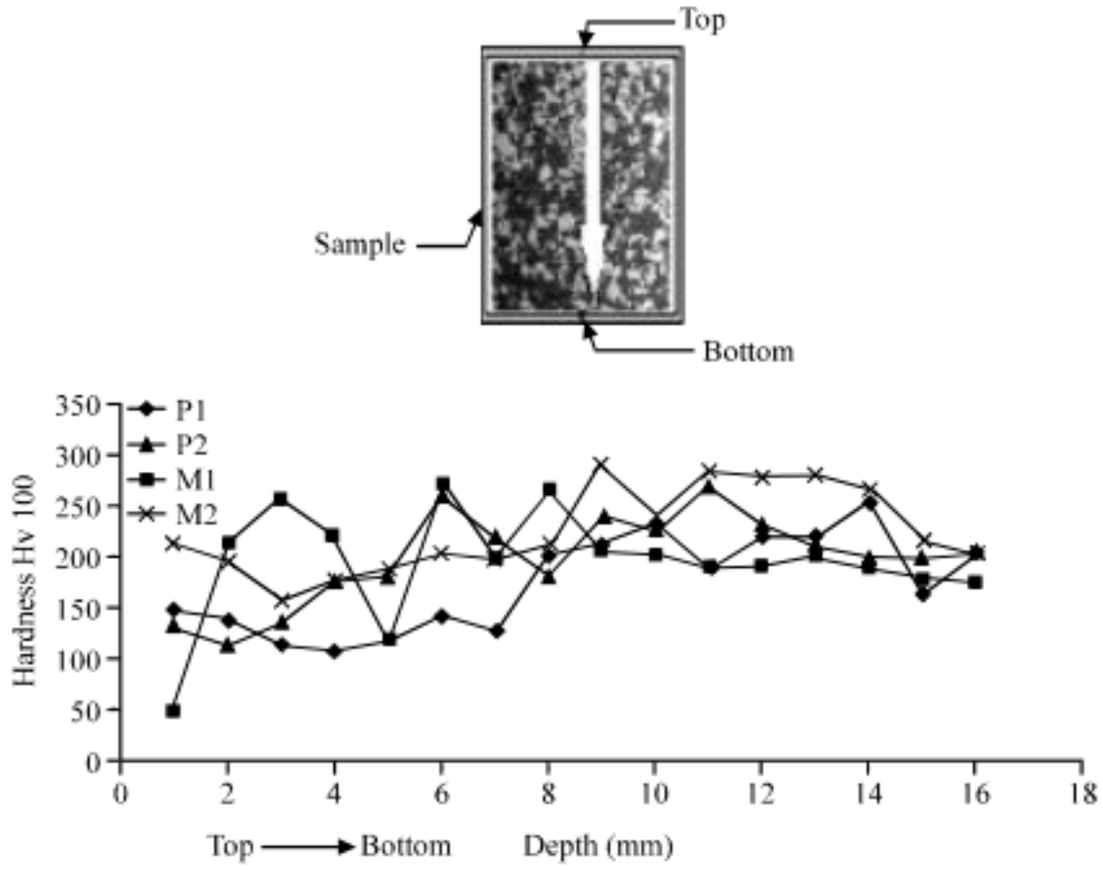


Fig. 10: Profiles of HV 100 hardness of the binder phase according in direction of infiltration of samples P1, P2, M1 and M2 (top of the sample towards the bottom)

particles of WC. The mass fraction of the binder seems more significant compared to P1 and P2, which prevents the formation of the skeleton. The microstructure of M4 is almost identical to M2 because of the small quantities of the elements W and Ni present in the mixture (Fig. 7f).

**Characterization of Hardness**

Figure 10 presents the profiles of microhardness of the binder phase according to the direction of infiltration for the infiltrated samples P1, P2, M1 and M2 (top of the sample towards the bottom). These profiles make it possible to know the hardness of each phase present in the surface of the composite especially the binder phase and to determine the degree of influence of the chemical element nickel on the various mixtures. The average hardness measured of infiltrant before the infiltration in an initial state is 154,5 Hv and the hardness of phases WC and W are respectively 1954 and 504 Hv.

The hardness profile of the P1 presents several values of hardness of the binder phase, whose the value average is 224,4 Hv. This value higher than that of infiltrant. This can be attributed to the partial

dissolution of the tungsten which confers to the binder matrix a significant hardness. The fluctuations observed can be directly related to the importance of dissolution. Indeed, in certain zones where the dissolution of tungsten was important, hardness reached is maximum 253, 25 Hv.

The hardness of the binder phase measured for P2 is almost identical to that of P1. In spite of the insolubility of the WC in copper, two hypotheses can be formulated to explain this high hardness compared with that of infiltrant. The first lies in the possibility of a weak dissolution of WC and/or $W_2C$ in the Cu-Mn liquid phase and thus of an enrichment of the binder with W. The second is the decarburization of WC and/or $W_2C$ during the high temperature treatment. For the nuances M1 and M2, the profiles of hardness are more stable and the calculated average values are respectively 255,7 and 253, 5 Hv. In these nuances, the presence of nickel can play a role for obtaining of these high values because it facilitates the dissolution of tungsten in the liquid phase thus the enrichment of the binder with W. The partial dissolution of nickel in the liquid phase Cu-Mn enriches binder with the Ni, which increases the whole of the mechanical properties of copper, in particular hardness. All the profiles of hardness give values of low hardness in the top part of the samples because of presence in excess of infiltrant in this zone.

## CONCLUSION

The use of this method of sintering with infiltration in liquid phase for fabrication of wear resistant hard materials assure a higher densification and appears the most advantageous. The elaboration of the materials required the optimization of the determining parameters of sintering such as, time, temperature and atmosphere of sintering to knowing: 30 min with 950°C and under hydrogen. The various sintered and infiltrated nuances W, WC, W-Ni, WC-Ni and WC-W present all a good densification and also observed on the samples a very low porosity. A good homogenisation and distribution of the chemical elements Cu and Mn in the nuances. These results are the consequence of the good infiltration. The presence of nickel in the nuances M1 and M2 increased the dissolution of tungsten what made it possible to raise the hardness of their binder phases.

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