

## How Improved to WC Based Hard Materials

Ahmet Yönetken<sup>1\*</sup>, Ayhan Erol<sup>2</sup>

<sup>1</sup>Afyon Kocatepe University, Engineering Faculty, Electrical Engineering, Afyonkarahisar /Turkey, e-posta: ayonetken@gmail.com

<sup>2</sup> Afyon Kocatepe University, Technology Faculty, Metallurgy and Materials Engineering, Afyonkarahisar /Turkey eposta:aerol@aku.edu.tr

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### Abstract

Tungsten carbide is known to have excellent corrosion resistance and high hardness within carbide ceramics. Due to their superior mechanical properties and wear resistance, tungsten carbide cutting tools containing Co binder have been the subject of many studies. There are a limited number of works regarding the use of Ni and Fe as a binder in tungsten carbide based composites, especially processing with microwave radiation. In this study, a composite cutting tool made of electroless nickel coated tungsten carbide ceramic powder was produced by microwave sintering. Two different tungsten carbide powder sizes of 2 µm and 10 µm were used for the production of composite cutting tool. The microwave sintering was carried out at two different temperatures of 1200 and 1400 ° C for 2 hours. Characterization of composite cutting tools was made by XRD, hardness, compression test and electron microscopy techniques.

**Keywords:** Powder Metallurgy, Ceramic–Metal Composites, Microwave, Sintering, Electroless Plating

### WC Tabanlı Sert Malzemeler Nasıl Geliştirilir

#### Öz

Tungsten karbür seramikler içerisinde mükemmel korozyon direnci ve yüksek sertliğe sahip olduğu bilinmektedir. Üstün mekanik özellikleri ve aşınma direncinden dolayı, Co bağlayıcı içeren tungsten karbür kesici takımlar birçok çalışmaya konu olmuştur. Tungsten karbür esaslı kompozitlerde, özellikle mikrodalga radyasyonu ile işlem yapan, Ni ve Fe'nin bağlayıcı olarak kullanımıyla ilgili sınırlı sayıda çalışma vardır. Bu çalışmada, elektriksiz nikel kaplı tungsten karbür seramik tozundan yapılmış bir kompozit kesici alet mikrodalga sinterleme ile üretildi. Kompozit kesici alet üretiminde 2 farklı tungsten karbür toz büyüklüğü 2 µm ve 10 µm kullanıldı. Mikrodalga sinterleme, 2 saat boyunca iki farklı 1200 ve 1400 ° C sıcaklıkta gerçekleştirildi. Kompozit kesici aletlerin karakterizasyonu XRD, sertlik, sıkıştırma testi ve elektron mikroskobu teknikleri ile yapılmıştır.

**Anahtar Kelimeler:** Toz Metalürjisi, Seramik-Metal Kompozitler, Mikrodalga Sinterleme, Akımsız Kaplama

## 1. Introduction

Tungsten is the abrasives used to make the carbides used in the production of hard materials wear resistant. For example, cemented carbides embedded in the cobalt (Co) metal matrix exhibit sufficient hardness and toughness that can cope with wear and also withstand vibration during cutting and processing. WC has so far been widely used on WC scribing tools and when abrasion resistance is desired (Clark and Sutton, 1996; Xiong, et. al. 2008; Dinesh,1998; Diger,et. al 1998). Hard alloys and carbide ceramics are used in the mining industry in a wide range of applications such as processing and drilling of metals due to their corrosion resistance under high pressure and temperatures as well as high hardness and wear resistance (Clark and Sutton, 1996; Xiong, et. al. 2008; Dinesh,1998; Diger,et. al 1998). When micro-and nano-scale WC particles are used in the production of composite, improvements were observed in the physical and mechanical properties of the composite structures. This indicates that the powder size is an important factor in the production of composite materials (Ban and Shaw, 2002; Upadhyaya and Bhaumik,1988; Taegong, et. al, 2008). Taegong et al. 2008, Ban and Shaw, 2002, also stated that the production of micro-sized WC-based composite materials can be successfully used in cutting, scratching and drilling materials with improved mechanical strengths.

The microwave (MW) sintering of WC containing Co has been extensively studied in literature (Ban and Shaw, 2002; Upadhyaya and Bhaumik,1988; Taegong, et. al, 2008; Ban and Shaw 2002; Breval et. al. 2005.). The comparison of MW sintering to conventional sintering showed that abnormal grain growth of WC following the

sintering do not happen and the formation of fine grains are promoted in MW sintered powders because of short processing times and lower sintering temperatures (Breval et. al. 2005). The introduction of MW radiation also resulted in the formation of neck growth at faster rate than other methods of sintering, which may be responsible mechanism for shorter and lower temperatures of processing (Demirskyi et. al., 2012; Chang and Chen, 2014;Wittmann, et. al., 2002;Guilemany et. al.,1993-1994). The use of Ni and/or Fe as a substitute for Co was also subject of many studies (Chang and Chen, 2014) and the coating with Ni is even more effective in terms of interface stability and wetting (Yönetken and Erol, 2010). Although Ni is added to improve the hot hardness and resistance against thermal cracking (Wittmann, et. al., 2002). there is strong evidence that corrosion resistance and rupture strength of WC with Ni and Fe binder composites are higher than Co containing WC composites except for volume shrinkage (Chang and Chen, 2014).

In this study, the effect of sintering temperature and particle size of WC have been investigated using microwave radiation sintering. Composites consisting of electroless Ni coated WC powder were produced and physical, mechanical, metallographical and XRD studies were also carried out.

## 2. Experimental Method

Powder metallurgy method is used to obtain electroless Ni coated WC powder. Coated cores reduce the sintering temperature. It facilitates material production by reducing the amount of energy used. Electroless Nickel plating ensures homogenous coating. High density and low surface roughness are

achieved. In the first stage of the experimental studies, WC powders for the production of ceramic-metal composite were prepared to obtain a composition of 80% WC + 20% Ni following Ni electroless coating onto WC particles with two different sizes. WC powders were electroless Ni coated in a hydrazine hydrate chemical coating bath ( $N_2H_4.H_2O$ ), see Table 1. In this technique, the coating occurs as a result of the chemical reaction from which Ni is released and a

homogeneous deposition of Ni layer onto WC particles takes place without an electric current. During the manufacture of composites, Ni coating functions as a binder between ceramic powders as well as acts as a filler metal for the pores between powders (Yönetken and Erol, 2010). The size WC powders were chosen to be 2 and 10  $\mu m$  to investigate the effect of powder size of matrix on the bonding capacity and reduction of the pores within the matrix.

**Table 1.** Chemical composition of electroless Ni Hydrazine coating bath

Chemicals	Conditions
Tungsten Carbide (WC)	24g
Nickel Chloride ( $NiCl_2.6H_2O$ )	24g
Hydranize Hydrate ( $N_2H_4.H_2O$ )	20%
Distiled Water	80%
Temperature	90-95°C
pH Value	9-10
Weight after coating	29,437g

The WC powders were then compressed to the dimensions of 15 mm in diameter and 3 mm in thickness. The samples were cold compacted under 200 MPa pressure using hydraulic press and then were sintered at temperatures of 1200 and 1400 °C for 2 hours in Phoenix microwave oven (1500W) which was operated at a frequency of 2.45GHz. The temperature increase rate in the microwave oven was 10 °C/min. A mixture of 90%  $N_2$  + 10%  $H_2$  atmosphere was used during the sintering operation in microwave oven. The sintering parameters

were selected as a result of optimization of many sintering experiments at different temperatures and durations of which current parameters were the most feasible based on their microstructural features and hardness. Scanning Electron microscopy (SEM) study was carried out using LEO 1430 VP attached with Röntec EDX analyzer. For metallographic examination the bonded samples were cut to produce transverse sections through the joint region. The samples were prepared to a 1  $\mu m$  finish using diamond paste and not etched prior to

metallurgical examination in SEM. XRD studies were carried out using Shimadzu XRD- 6000 XRD analyzer with a wavelength of  $1,5440\text{\AA}$  within a range of  $2\theta = 5-90^\circ$ . XRD analysis was carried out on specimens sintered at  $1200^\circ\text{C}$ . Brinell hardness is defined in ASTM E10. This test is commonly used to test materials with a very rough surface having a coarse structure. Load, Ball Diameter and Application Time Depending on the type of material, the application time of the load is usually 10 seconds, except for soft metals. It is possible to determine the load to be applied in the Brinell hardness test according to the material type as follows.

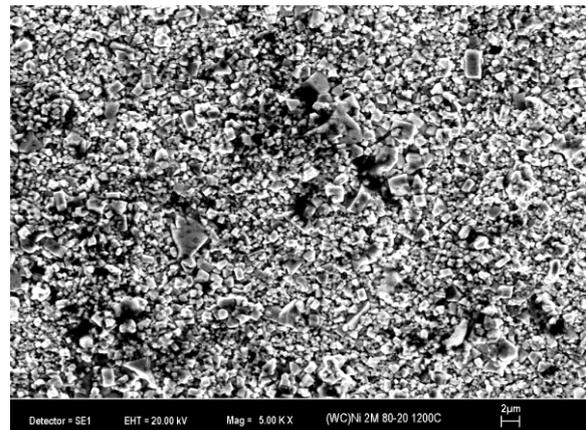
In the hardness test, firstly, it is necessary to make the surface of the material to be measured suitable for measurement. It is desired that the surface be smooth and shiny. Hardness tests were made using Shimadzu microhardness tester which is Brinell hardness machine with a load of 200g and time duration of 10 second. Compression strengths were measured with Shimadzu Universal Tensile Tester AG-IS of 100kN capacity with a crosshead speed of 1 mm/min.

### 3. Experimental Results And Discussion

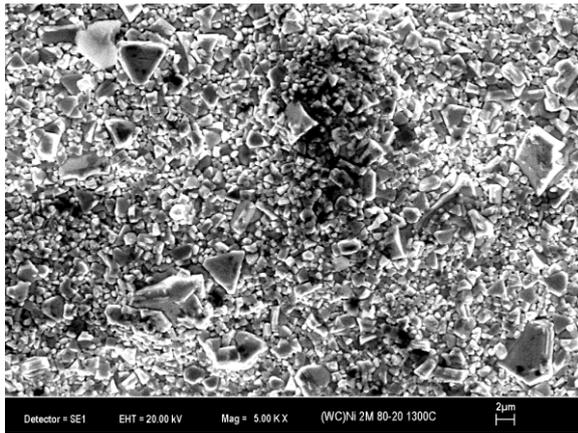
#### Metallographic Analysis

As shown in Figure 1 and Figure 2, as the initial size of WC powder decreased, the degree of porosity appears to be reduced by the formation of a close contact between powders. A homogeneous distribution of Ni coated powders of different sizes forming the composite was obtained with both 2 and 10  $\mu\text{m}$  size WC powders. In the ceramic-metal composite specimen, a complete wetting and

resulting joining between powders were achieved by sintering at high temperatures, eliminating some of the pores by filling them up with Ni present on the WC powders. This may have a positive effect on the mechanical properties of the composites. As can be seen in Figure 2a and b, in the 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite system at both temperatures of sintering, a distribution of coarser pores are observed within the matrix compared to 2  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  as shown in Figure 1a and 1b. A network of pores are easily seen in Figure 2a and a dramatic change from 2  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite in the distribution of WC powders in 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  are clearly visible due to the presence of longitudinal powders of  $(\text{WC})_{\text{Ni}}$  as a result of sintering at high temperature of  $1400^\circ\text{C}$ . Ni coating may have acted as a wetting agent and engulfed smaller powders, causing a decrease in total volume. Such a contraction within the matrix can lead to the formation of a network of pores as seen in Figure 2. The grain size of the composite produced in Figure 1 was less than 1  $\mu\text{m}$ . The particle size of the composite produced in Figure 2 was less than 6  $\mu\text{m}$ . The density and stiffness values of the composite produced in Figure 1 also support this.



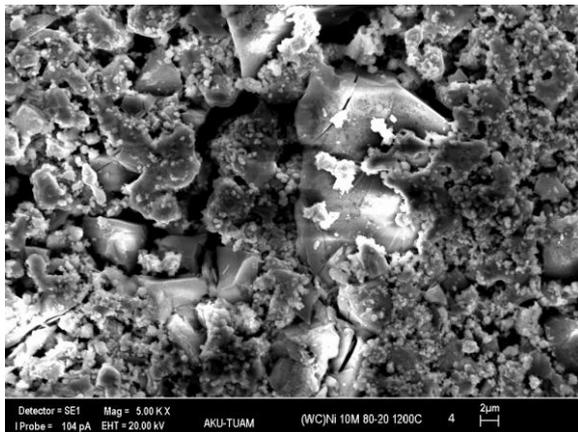
a)



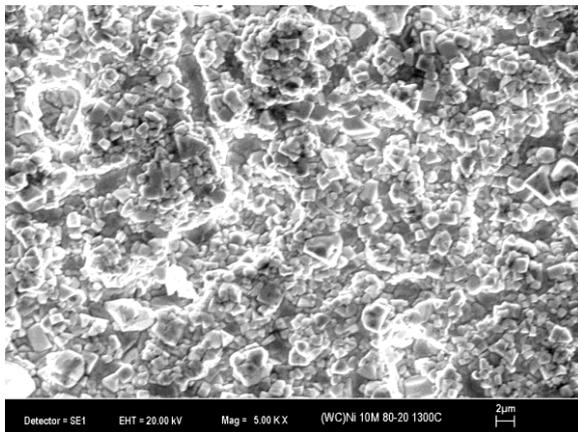
b)

**Figure 1** SEM image of  $(WC)_{Ni}$  composite produced with 2  $\mu m$  powders,

a) 1200 °C, 5KX      b) 1400 °C, 5KX



a)



b)

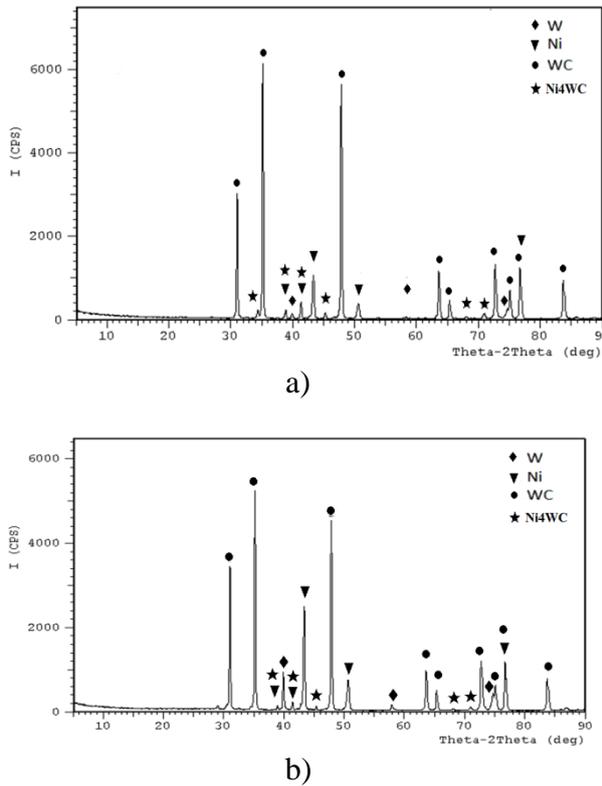
**Figure 2** SEM images of  $(WC)_{Ni}$  composite produced with 10  $\mu m$  powder,

a) 1200 °C, 10  $\mu m$ , 5KX      b) 1400 °C, 10  $\mu m$ , 5KX

### XRD Analysis

Figure 3a and b present the XRD analysis results of the electroless Ni coated  $(WC)_{Ni}$  composites. The WC phase, which was the main addition in the composite, has evidently the highest peak intensity over the other phases present in the XRD analysis in both  $(WC)_{Ni}$  composites. However, peak intensities in the 2  $\mu m$   $(WC)_{Ni}$  composite (Figure 3a) are lower in general compared to 10  $\mu m$   $(WC)_{Ni}$  composites (Figure 3b). In both specimens, detected elements and compounds in the matrix are Ni, W, WC and  $Ni_4WC$ . Peak intensities of both WC and Ni appear to be higher than remaining elements and compounds. The presence of Ni and W peaks in XRD analysis of 10  $\mu m$   $(WC)_{Ni}$  composite is an important result of high temperature sintering and corresponding reactions taking place between WC and Ni. The Ni layer on the surface of WC reacts with substrate WC particle at high temperatures. The interface reaction between Ni and WC diffusion couple takes place and  $Ni_4WC$  is formed. The information regarding this phase is very limited. The reaction of WC with Ni may later result in dissociation of WC into W and C and due to the difference in solubility of C in Ni and W in Ni at the temperatures of interest. In addition to  $Ni_4WC$ , the formation of carbon rich Ni phase is also promoted at high temperatures (Singleton, and Nash, 1989) and the solubility of Ni in W is very low (Okamoto, 1991). Although W can contain upto 10 at% of Ni, the amount of Ni is possibly not sufficient to form Ni rich W. Indeed, XRD analysis at 1400 °C shows that the amount of  $Ni_4WC$  phase is lower than in 1200 °C but

the amount of W is increase, which may be the result of Ni enriched with C (possibly in liquid state), leaving the surface rich in W. The lower surface area of particles in 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite may be due to particle surface area effect which limits the amount of peaks coming from smaller volume of element or compounds.



**Figure 3.** XRD analysis results of a) 2  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  b) 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composites

**Density of  $(\text{WC})_{\text{Ni}}$  Composites**

The temperature dependent change in the density of the sintered samples is given in Table 2. SEM images and the density figures indicate that the change in density in both specimens at different temperatures was insignificant and very close in value. The density values are also very similar to studies regarding WC-Co composited by Agrawal et. al., 1999 and Yönetken and Erol, 2010..The thickness of Ni layer can have an influence on the density; as it increases the number of

pores can drop to a limited extend since but the density measured would be lower than the theoretical density of  $(\text{WC})_{\text{Ni}}$  that is nearly  $14.28 \text{ g/cm}^3$ . The shape distribution of powders in 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite appears to be irregular unlike of 2  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite, which may have a slight effect on the number of pores and hence their density at both temperatures. The composite samples were produced with a density of 95% after microwave sintering.

**Table 2.** Temperature dependent changes in the density of  $(\text{WC})_{\text{Ni}}$  composites

Temperature (°C)	2 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (g/cm <sup>3</sup> )	10 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (g/cm <sup>3</sup> )
1200	13,51	13,35
1400	13,36	13,27

**Compression Strength and Hardness Tests**

**Table 3.** Temperature dependent changes in the compression strength of  $(\text{WC})_{\text{Ni}}$  composites

Temperature (°C)	2 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (MPa)	10 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (MPa)
1200	574,45	547,58
1400	532,32	501,16

The temperature dependent changes in the compression strengths of 2 and 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  are given in Table 3. The temperature

dependent compression strengths of the composites with two different powder sizes were determined by taking the highest failure point. The compression strength of the sample with a powder size of 10  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite was measured to be lower than those of 2  $\mu\text{m}$   $(\text{WC})_{\text{Ni}}$  composite at both sintering temperatures. Zhang et al., 2007 proposed that when micro and nano sized WC powders are used the physical and mechanical properties of cemented carbides are improved. This study indicated that as the sizes of the WC powders decreased, the strength of the composites increased regardless of sintering temperature. In addition to the size of particles used in the production of composite, some compounds may also be responsible for the mechanical properties. Li et al., 2006, suggested that the mechanical properties of WC-Ni composites are known to be affected by compounds such as  $\text{W}_2\text{C}$  phase, which is stable during cooling following the sintering. However, XRD study suggests that this phase did not form in our specimens but  $\text{Ni}_4\text{WC}$  compound appears to have formed instead. At temperature nearly to the melting point of Ni, i.e. 1400  $^\circ\text{C}$ , the liquifying of Ni may be responsible for the lowering of strength by forming Ni rich regions within the matrix. A similar trend was also observed with hardness values of  $(\text{WC})_{\text{Ni}}$  composite with respect to their sintering temperature. Temperature dependent hardness values of the ceramic-metal composites sintered in a microwave oven were measured by the Brinell test (Table 4). In the  $(\text{WC})_{\text{Ni}}$  system, the Brinell hardness values of the samples with powder sizes of 2  $\mu\text{m}$  and 10  $\mu\text{m}$  were poorly dependent on the sintering temperature, causing a decrease in the hardness with increasing sintering temperature.

**Table 4** Temperature dependent changes in hardness values of  $(\text{WC})_{\text{Ni}}$  composites

Temperature ( $^\circ\text{C}$ )	2 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (Brinell)	10 $\mu\text{m}$ $(\text{WC})_{\text{Ni}}$ (Brinell)
1200	470,92	452,78
1400	440,40	434,24

#### 4. Conclusions

Electroless Ni coated 2 and 10  $\mu\text{m}$  WC powders were successfully microwave sintered at 1200 $^\circ\text{C}$  and 1400  $^\circ\text{C}$  temperatures. It is proposed that fine powder sizes with electroless Ni coating method produced a better bonding compared to coarse sized particles. It was observed in the XRD peak analysis that Ni, W, WC and  $\text{Ni}_4\text{WC}$  phases formed during the sintering with varying amounts. As the specimens sintering temperature increases, the density values, hardness and mechanical properties are negatively affected due possibly to sintering temperature being close to melting point of Ni. On the contrary to temperature effect, the size of particles has good effect on all properties measured in this study.

#### 5. References

- Clark, D., Sutton W.H., 1996. Microwave processing of materials, *Annu Rev Mater Sci*, **26**, 299–331.
- Xiong, Y., Lau, K., Zhou, X., Schoenung, J. M., 2008. A Streamlined Life Cycle Assessment On The Fabrication Of WC-Co Cermets, *Journal Of Cleaner Production*, **16**, 1118-1126.
- Dinesh, DK, 1998. Microwave Processing of Ceramics, *Current Opinion in Solid State and Materials Science*, (3), 5, 480–485.

- Diger, Ro. K., Dreyer, K., Gerdes, T., Willert-Porada, 1998, M. Microwave sintering of hardmetals, *International Journal of Refractory Metals and Hard Materials*, **(16)** 4, 409–416.
- Ban, Z.G., Shaw, L. L., 2002. Synthesis and processing of nanostructured WC-Co materials, *Journal Of Materials Science*, **(37)**, 3397 – 3403
- Upadhyaya G.S., Bhaumik S.K., 1988. Sintering of submicron WC-10wt.%Co Hard Metals Containing Nickel And Iron *Material Science And Engineering-A*, Volume:249, 105–106, 1988.
- Taegong R., Sohn H. Y., Han G., Hwang K. S., Mena M., Fang Z. Z., 2008. Nanograined WC-Co Composite Powders By Chemical Vapor Synthesis, *Metallurgical And Materials Transactions B*, **39(B)**, 1007-1012.
- Ban Z. G., Shaw L. L., 2002. Synthesis And Processing Of Nanostructured WC-Co Materials”, *Journal Of Materials Science*, **37**, 3397-3403.
- Breval, E., Cheng, J.P., Agrawal, D.K., Gigl P., Dennis, M., Roy, R., Papworth, A.J., 2005. Comparison between microwave and conventional sintering of WC/Co composites, *Materials Science and Engineering A* **391** 285–295
- Demirskyi, D., Borodianska, H., Agrawal, D., Ragulya, A., Sakka, Y. Vasykiv, O. 2012. Peculiarities of the neck growth process during initial stage of spark-plasma, microwave and conventional sintering of WC spheres, *Journal of Alloys and Compounds*, **523**, 1–10
- Chang, S.H., Chen, S.L., 2014. Characterization and properties of sintered WC–Co and WC–Ni–Fe hard metal alloys, *Journal of Alloys and Compounds*, **585**, 407–413.
- Wittmann, B., Schubert, W.D., Lux B., 2002. WC grain growth and grain growth inhibition in nickel and iron binder hardmetals, *Int. J. Refract. Met. Hard Mater.*, **20**, 51–60.
- Guilemany, J.M., Sanchiz, I., Mellor, B.G., Llorca, N., Miguel, J.R., 1993-1994. Mechanical-Property Relationships of Co/WC and Co-Ni-Fe/WC hard metal alloys, *Int. J. Refract. Met. Hard Mater.*, **12**, 199–206
- Taheri-Nassaj E., Mirhosseini, S.H., 2003. An In Situ WC–Ni Composite Fabricated By The SHS Method, *Journal Of Materials Processing Technology*, **142**, 422–426.
- Yönetken A., Erol, A., 2010. The Effect of Microwave Sintering on the Properties of Electroless Ni Plated WC-Fe-Ni Composites, *Science And Engineering Of Composite Materials*, **(17)** 3, 191-198.
- Singleton, M., Nash P., 1989. The C-Ni (Carbon Nickel) System, *Bulletin of Alloy Phase Diagrams*, **(10)** 2,121-126.
- Okamoto, H., 1991. Ni-W (Nickel-Tungsten), *Journal of Phase Equilibria*, **(12)** 6, 706.
- Agrawal, D., Cheng, J., Lackner, A., Ferstl, W., 1999. Microwave sintering of commercial WC/Co based hard metal tools, *Proceedings of the Euro PM'99 Conference* 175–182
- Zhang W. Z., Gao H. Y., Cao S. H., 2007. Fabrication Of Nanocrystalline WC-6C0 Composite Powder, *Journal Of Central South University*, **(38)**5, 837-842.
- L1 T., L1 Q., Fuha J.Y.H., Yu P. C., Wu C.C., 2006. Effects Of Lower Cobalt Binder Concentrations In Sintering Of Tungsten Carbide, *Materials Science and Engineering A*, **(430)**, 113–119.