

PRODUCTION OF MATRICES WITH MOLYBDENUM AS AN ALTERNATIVE TO MATRICES WITH COBALT IN DIAMOND CUTTING TOOLS

IZDELAVA SEGMENTOV Z MOLIBDENOM KOT NADOMESTILO ZA SEGMENTE S KOBALTOM PRI REZALNIH ORODJIH Z DIAMANTI

Ertuğrul Çelik¹, Serkan Islak², Cumali İlkılıç³

¹Tunceli University, Faculty of Engineering, Department of Mechanical Engineering, Tunceli, Turkey

²Kastamonu University, Faculty of Engineering and Architecture, Department of Materials Science and Nanotechnology Engineering, Kastamonu, Turkey

³Firat University, Technology Faculty, Automotive Engineering Department, Elazığ, Turkey
serkan@kastamonu.edu.tr

Prejem rokopisa – received: 2013-11-05; sprejem za objavo – accepted for publication: 2013-12-16

This study is about the production of new matrices that are an alternative to cobalt matrices in diamond cutting tools. Thus, Fe, Cu, Al₂O₃ and Mo were used as the matrix components. The mass fractions of 1 %, 2 % and 3 % Mo were added to the matrix. The production of matrices was performed in a fully automatic hot-pressing machine under 35 MPa of pressure, at a sintering temperature of 850 °C, with a dwell period 4 min. The microstructures and phase compositions of the matrices were established with a scanning electron microscope (SEM-EDS) and an X-ray diffractometer (XRD). The hardness and bending strength of the segments were determined. The transverse rupture strength (*TRS*) of the segments was determined using the three-point bending test. The results revealed that Mo increased the bending strength and hardness of the segments.

Keywords: molybdenum, diamond cutting tool, microstructure, mechanical properties

Ta raziskava se nanaša na pripravo novih segmentov, namesto segmentov s kobaltom, pri rezalnih orodjih z diamanti. V ta namen je bila uporabljena osnova z Fe, Cu, Al₂O₃ in Mo. Masni delež Mo, ki je bil dodan osnovi, je bil 1 %, 2 % in 3 %. Sinteza segmenta je bila izvršena na avtomatski vroči stiskalnici s pritiskom 35 MPa pri temperaturi sintranja 850 °C s 4-minutnim zadržanjem. Pregled mikrostrukture in analiza sestave faz sta bila izvršena z vrstičnim elektronskim mikroskopom (SEM-EDS) in z rentgensko difrakcijo (XRD). Izmerjeni sta bili trdota in upogibna trdnost segmentov. Prečna trdnost segmentov (*TRS*) je bila izvršena s tritočkovnim upogibnim preizkusom. Rezultati so pokazali, da Mo povečuje upogibno trdnost in trdoto segmentov.

Ključne besede: molibden, rezalno orodje z diamanti, mikrostruktura, mehanske lastnosti

1 INTRODUCTION

Diamond cutting tools are used in natural stone-cutting processes. Day by day, the usage of such tools has been increasing. In order to attain a high bonding strength between a bonding matrix and diamond grits without causing any deterioration of diamond grits, the composition of the bonding matrix must be designed in such a way that a low hot-pressing temperature can be applied, no catalytically deteriorating elements, such as Fe, Co, and Ni, exist in the bonding matrix, an interfacial transient layer can be developed, and a relative abundance of a strong but brittle bonding matrix that can lead to a self-dressing capability can be tailored.¹ Cobalt is an important binding element used in cutting tools. Thus, cobalt powders are widely used in the production of the metal matrices of diamond cutting tools that are designed to drill and cut hard rocks and concretes.² With the gradually increasing usage of diamond cutting tools in natural-stone cutting, the consumption of Co used in the production of cutting tools has also rapidly increased. As a result of the above, Co prices continually increase as well. The increases in the raw-material prices cause the production of diamond cutting tools to be more expen-

sive. Thus, other alternative cheap metals are required to be used in diamond cutting tools instead of Co as the matrix additive metals.³ In addition, it is partially dangerous to be exposed to metal powders during the cutting process due to the toxic property of cobalt.⁴ In order to eliminate this danger, the only thing to do is to find a new metal matrix that has no toxic risk.⁵⁻⁷

Some researchers studied the production of a new matrix that has its properties similar to the ones of the matrix with Co and such examinations are still being continued. New matrices with molybdenum (Mo) with perfect mechanical properties and exhibiting the same performance as the matrix with Co were produced during this study. The microstructures and mechanical properties of these matrices were experimentally investigated.

2 EXPERIMENTAL STUDIES

In this study, matrices with molybdenum that are an alternative to matrices with cobalt were produced using the powder-metallurgy (PM) method. Fe, Cu, Al₂O₃ and Mo metal powders were used for the matrices. **Table 1** illustrates some of the properties of these powders.

Table 1: Metal powders used for the matrix**Tabela 1:** Kovinski prahovi, uporabljeni za osnovo

Metal	Powder size (μm)	Pureness (%)
Fe	40	99.9
Cu	< 63	99.9
Al_2O_3	< 10	99.9
Mo	40	99.9

Of the elements in **Table 1**, Fe and Cu had the largest fractions of the matrix composition. Al_2O_3 , used in addition to the other elements, was included in the matrix in order to prevent grain coarsening during the sintering, fill up the pores that might have occurred in the matrix and increase the wear resistance of the matrix. Various amounts of molybdenum were added to this matrix to improve the microstructure and mechanical properties of the matrix. **Table 2** shows the design of the new matrix formed by mixing these elements together at specific ratios. Metal powders were prepared by being weighed with a precision electronic scale forming the amounts shown in **Table 2** and then they were placed in a mixer and mixed homogeneously for 30 min. No Mo was added to the A0 sample included in **Table 2** and used as a reference sample.

Table 2: Matrix design and sintering parameters**Tabela 2:** Oblikovanje osnove in parametri sintranja

Sample number	Composition (w/%)	Sintering temperature ($^{\circ}\text{C}$)	Sintering time (min)
A0	Fe-10Cu-1 Al_2O_3	850	4
A1	Fe-10Cu-1 Al_2O_3 -1Mo		
A2	Fe-10Cu-1 Al_2O_3 -2Mo		
A3	Fe-10Cu-1 Al_2O_3 -3Mo		

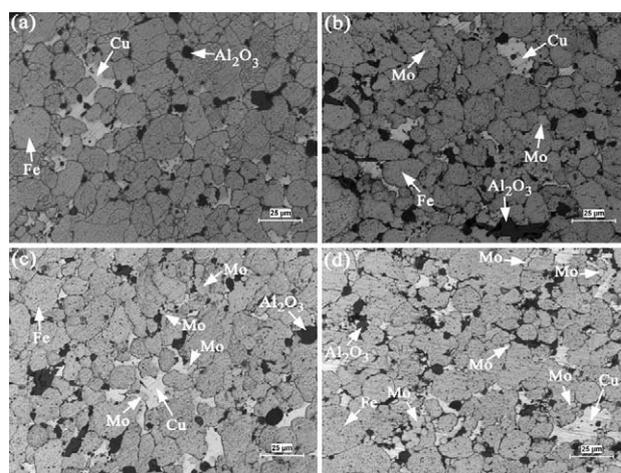
In this study, no diamond grains were added to the powder mixture because only the matrix design was considered. In order to press the powder mixture prepared, the computer-aided and laboratory-type hot press, which can be controlled with a computer programme, and graphite moulds were used. Before the powder mixture was placed in a graphite mould, it was not subjected to any cold-pressing process. The powder mixture was placed directly in the graphite mould. After the mixture filled the graphite mould, it was placed in a sintering oven as a single block. The sintering process was performed under an argon atmosphere. At the beginning of the sintering process, the pressure and temperature were applied to the mixture via the graphite mould. This application continued up to a temperature of 700°C and a pressure of 35 MPa, taking 6 min. As of this moment, every group sample was kept at 850°C and under 35 MPa of pressure for 4 min. When the sintering process was completed, the heating unit was deactivated and the samples were kept inside the moulds to cool down to room temperature in order to prevent oxidation.

The hardness measurements of hot-pressed samples were performed using a Brinell scale with a ball with a diameter of 2.5 mm and a load of 62.5 kg. In order to

determine the transverse rupture strength (TRS) of the segments, three-point bending tests were performed using a Schimatzu universal testing machine at a loading rate of 1 mm/min at room temperature according to ASTM B 528-83a standard. The microstructures of the sintered samples were observed with scanning electron microscopy (SEM). A quantitative surface analysis was performed with energy dispersion spectroscopy (EDS). The crystallographic structures of the materials were investigated with an X-ray diffraction analysis (XRD – X'Pert Philips Diffractometer).

3 RESULTS AND DISCUSSION

The segment matrices with or without molybdenum were produced successfully via hot pressing under 35 MPa of pressure, at a sintering temperature of 850°C , with a dwell period 4 min. **Figure 1** illustrates the microstructure images of the samples with and without molybdenum. In the micrograph on **Figure 1a**, light brownish areas show Fe, dark brownish and cornered shapes show Al_2O_3 , and reddish areas show Cu. In the microstructure images on **Figures 1b** to **1d**, it is observed that the molybdenum added to the segment matrix was included between the iron and copper particles. The Mo particles, homogeneously distributed in the segment matrix, generally surrounded the Cu and Fe particles. It was observed that the copper (Cu) in the sample without Mo distributed regularly between the Fe particles and aluminium oxide (Al_2O_3) was placed in the spaces between the Fe particles. It can be understood from the images that the copper which remained among the Fe particles could not be evenly spread among the particles but remained in rather large lumps. The reason for this was a lower liquidity of the copper due to the non-performance of the liquid-phase sintering. It is understood from the microstructure image that although the sintering temperature was not so low, no sufficient strong bond was formed

**Figure 1:** Light micrographs of the alloys sintered at 850°C : a) $w(\text{Mo}) = 0\%$, b) $w(\text{Mo}) = 1\%$, c) $w(\text{Mo}) = 2\%$ and d) $w(\text{Mo}) = 3\%$ **Slika 1:** Svetlobni posnetki mikrostrukture segmentov, sintranih pri 850°C : a) $w(\text{Mo}) = 0\%$, b) $w(\text{Mo}) = 1\%$, c) $w(\text{Mo}) = 2\%$ in d) $w(\text{Mo}) = 3\%$

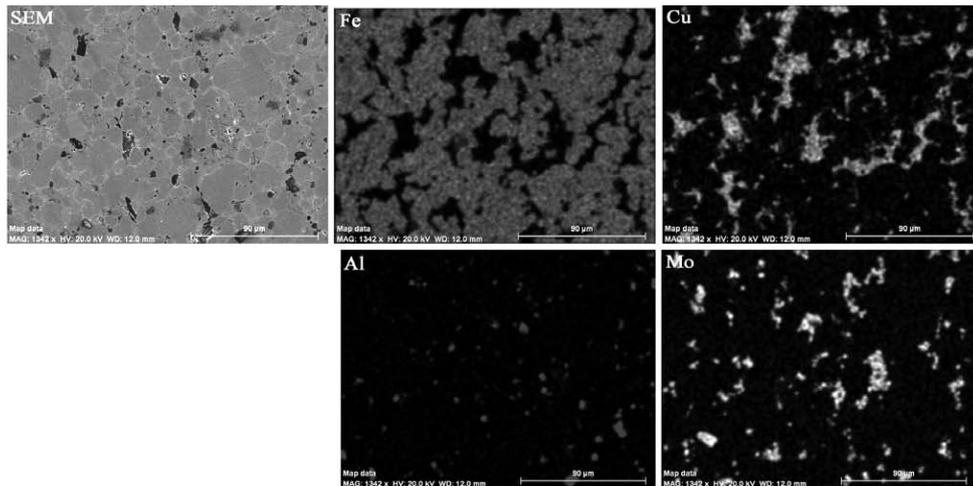


Figure 2: SEM-MAP analysis showing a uniform phase distribution of Fe, Cu, Al and Mo elements for Fe-10Cu-1Al₂O₃-3Mo
Slika 2: SEM-MAP-analiza izkazuje enakomerno porazdelitev elementov Fe, Cu, Al in Mo v Fe-10Cu-1Al₂O₃-3Mo

between the metal-powder particles due to the short sintering period (4 minutes). The formation of this bond became harder with the addition of molybdenum.

It is very important to obtain other homogeneous components in the matrix in order to enhance the mechanical properties of the materials. **Figure 2** shows the images of the SEM-MAP analysis of the sintered Fe-10Cu-1Al₂O₃-3Mo. The SEM image illustrates a fairly homogeneous distribution of Cu, Al₂O₃ and Mo in Fe. The EDS images show the main spectrums of Fe, Cu, Al and Mo elements at all locations. The level of Fe was considerably higher compared to Cu, Al₂O₃ and Mo. Aluminium spectrums represent the presence of Al₂O₃.

Figure 3 illustrates the X-ray graphs for all the samples that were sintered for four minutes at 850 °C. From the results, it was understood that numerous phases developed. The phases seen in the matrix without Mo were Fe, Cu, Al₂O₃, Cu₄₀Fe₆₀, Cu₃Al₂, Al₇Cu₂Fe, Fe₃Al, CuO, Fe₂O₃ and Fe₃O₄. The Fe₂O₃ phase (111) in the structure had a sliding plane and the Fe₃O₄ phase (200) also had a sliding plane. As a result of the Mo addition to

the reference sample, along with the above mentioned phases, some other phases occurred in the alloy such as Mo, Fe₃Mo and Mo₄O₁₁. It was believed that the Fe₃Mo phase, developed between Fe and Mo, formed due to the micro-alloying at the contact points of the particles. According to the XRD graph, the Al₂O₃ peaks showed lower intensity values compared to Fe and Cu. This may be attributed to the fact that extremely small Al₂O₃ particles were embedded in the matrix.

The hardness values of the segments were determined by taking the mean of five different measurements for each sample. **Figure 4** illustrates the hardness graph of the segment matrices. The hardness of the segments increased with the increasing Mo amount. While the hardness value for the segment without Mo was 75 HB, its values for the segments with (1, 2 and 3) % Mo were measured to be (97, 99 and 105) HB, respectively. A small difference between the hardness values of the segments with 1 % and 3 % Mo can be explained with their similar addition amounts. The complex phases and oxides formed in the microstructure caused an increase in the hardness of the segments. Thus, such phases in the structure contributed to an increase in the hardness by

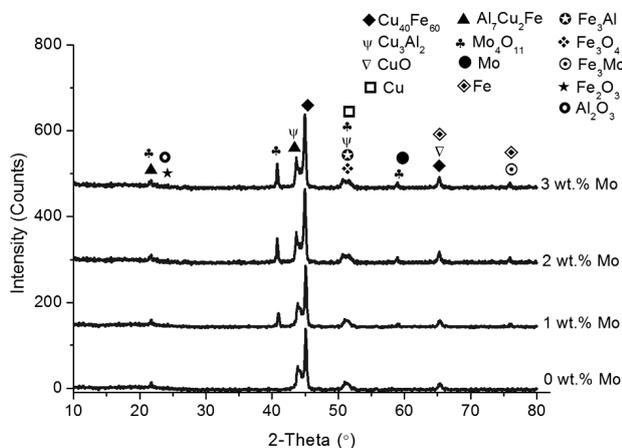


Figure 3: XRD diffraction patterns of the segment matrices
Slika 3: XRD-posnetki osnove segmenta

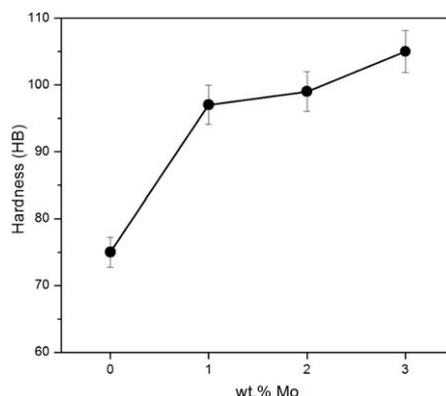


Figure 4: Hardness of the segments
Slika 4: Trdota segmentov

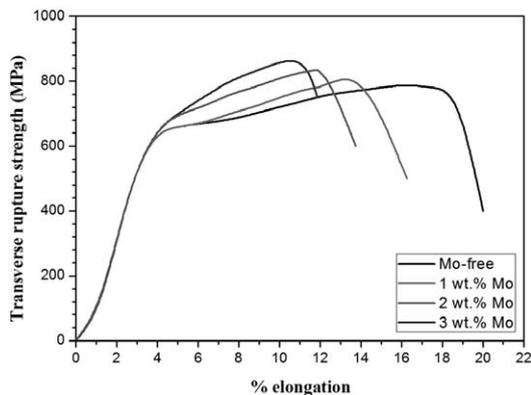


Figure 5: TRS graph of the segment matrices sintered at 850 °C
Slika 5: Upogibna trdnost (TRS) osnove segmentov, sintranih pri 850 °C

acting as a reinforcement.⁸ Weber and Weiss⁹ investigated the some properties of Fe-based matrices with cobalt. They reported that the hardness of the matrices with $w(\text{Co}) = 15\text{--}20$ was measured as the average of 80–95 HRB (≈ 140 HB). However, in our study, a maximum of $w(\text{Mo}) = 3\%$ was added to the Fe-based matrix.

In order to determine the transverse rupture strength (TRS) of the segments, three-point bending tests were performed using the Schimatzu universal testing machine at a loading rate of 1 mm/min at room temperature. **Figure 5** shows the tension-percentage elongation graphs obtained as a result of the three-point bending test for all the samples. In the graphs, it can be seen that the highest elongation and lowest bending strength belonged to the A0 sample without Mo and that with the increasing Mo addition, the elongation values of the samples decreased and their bending strengths slightly increased. While the TRS value of the segment without an addition of Mo was measured as 750 MPa, the TRS values of the segments with (1, 2 and 3) % Mo additions were measured as (800, 830 and 860) MPa, respectively. These results were expected. The sintering temperature of the diamond cutting tool was 850 °C and the sintering period was as short as 4 min. Within this short period, Mo could not develop a sufficiently strong bonding with the other elements. Furthermore, we also maintain that the reason why molybdenum could not have a perfect bonding with the matrix was the fact that the Mo_4O_{11} phase developed with the oxidation of molybdenum adversely affected the cohesive strength between the particles.¹⁰ Thus, this caused the matrix to be brittle and also resulted in a slight increase in the hardness and a slight decrease in the toughness. Significant differences occurred in the amounts of elongation as well. While the elongation was approximately 18 % in the segment without an addition of Mo, it was between 9–13 % in the segments containing Mo.

4 CONCLUSIONS

The segments with and without molybdenum were produced successfully with the hot-pressing technique at

35 MPa of pressure, at a sintering temperature of 850 °C for a sintering period 4 min, and the microstructure, hardness and bending-strength properties of these segments were experimentally examined. The results are as follows:

From both the light photographs and the SEM-MAP analyses, it is seen that the molybdenum added to the segment matrix was distributed between the Fe and Cu particles. The Mo particles, distributed homogeneously in the segment matrix, generally surrounded the Cu and Fe particles.

According to the XRD analysis results, the molybdenum added to the segments caused the formations of new phases in the matrix. During micro-alloying, some phases formed between the metallic powders added to the matrix due to the effect of the temperature and pressure.

The addition of molybdenum caused a slight increase in the hardness values of the segments. The complex phases and oxides that formed between the metals forming the matrix also provided an extra contribution to this hardness increase.

With the three-point bending tests, it was found that the elongation values of the samples with Mo decreased but an increase occurred in the bending strengths.

Acknowledgments

The study was supported by the Firat University Scientific Research Projects Unit (Project no: FÜBAP-1604).

5 REFERENCES

- C. S. Lin, Y. L. Yang, S. T. Lin, Performances of metal-bond diamond tools in grinding alumina, *Journal of Materials Processing Technology*, 201 (2008), 612–617
- J. D. Dwan, Impact properties of diamond impregnated metal matrices, *Industrial Diamond Review*, 2 (2003), 50–56
- D. Lison, Human toxicity of cobalt-containing dust and experimental studies on the mechanism of interstitial lung disease (hard metal disease), *Critical Reviews in Toxicology*, 26 (1996), 585–616
- R. G. Ojeda, M. Del Villar, P. Muro, I. Iturriza, F. Castro, Densification of diamond tools with Co, Ni and Fe based metallic binders, *Proceedings of Powder Metals World Congress*, 4 (1998), 481–486
- Y. Z. Hsieh, S. T. Lin, Diamond tool bits with iron alloys as the binding matrices, *Materials Chemistry and Physics*, 72 (2001), 121–125
- M. del Villar, P. Muro, J. M. Sanchez, I. Iturriza, F. Castro, Consolidation of diamond tools using Cu–Co–Fe based alloys as metallic binders, *Powder Metallurgy*, 44 (2001), 82–90
- S. Spriano, Q. Chen, L. Settineri, S. Bugliosi, Low content and free cobalt matrixes for diamond tools, *Wear*, 259 (2005), 1190–1196
- E. Çelik, Alternative binders of diamond cutting tools, PhD thesis, Firat University, Turkey, 2009
- G. Weber, C. Weiss, Diamix – a family of bonds based on diabase – V21, *Industrial Diamond Review*, (2005) 2, 28–32
- S. Usmani, S. Sampath, Time-dependent friction response of plasma-sprayed molybdenum, *Wear*, 225–229 (1999), 1131–1140