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THE PROCESSING AND PROPERTIES OF Ag-W-TiO₂ COMPOSITES

Silver-based composites can be divided into two types: type 1 uses a pure element or carbide as the dispersed phase; type 2 uses oxides as the dispersed phase. In this work was shown the combined effect of small additions of oxides with tungsten. Attempts have been made to describe the influence of production process parameters on the microstructure and properties of Ag-W-TiO₂ composites. The compositions of the powder mixtures are $Ag + 10\% W + 1\% TiO_2$, $Ag + 20\% W + 1\% TiO_2$, $Ag + 30\% W + 1\% TiO_2$. The powder mixtures were prepared by tumbling in a Turbula type mixer. The mixtures were then subjected to a double-press/double-sinter process. The studies show that a nearly fully-dense material made of silver, tungsten and TiO₂ powders cannot be achieved by double pressing and double sintering. The relative density near 90% of the composites was achieved. The electrical conductivity and bending strength of Ag-W-TiO₂ materials decrease with tungsten content, but the hardness of Ag-W-TiO₂ materials increase with the amount of tungsten. The $Ag + 10\% W + 1\% TiO_2$ and $Ag + 20\% W + 1\% TiO_2$ materials studied in this work also show relatively homogenous distribution of the tungsten and TiO₂ additions.

Keywords: tungsten, titanium dioxides, silver, sintering, electrical contacts

WYTWARZANIE I WŁASNOŚCI KOMPOZYTÓW Ag-W-TiO₂

Kompozyty na osnowie srebra można podzielić na dwa typy materiałów: te umacniane dodatkiem czystych pierwiastków lub węglików oraz te umacniane dodatkiem tlenków. Praca niniejsza przedstawia materiał, w którym połączono niewielki dodatek tlenku z dodatkiem wolframu. Badania obejmowały wytwarzanie kompozytów Ag-W-TiO₂ oraz ich własności i mikrostruktury. Do badań stosowano mieszanki proszków $Ag + 10\% W + 1\% TiO_2$, $Ag + 20\% W + 1\% TiO_2$, $Ag + 30\% W + 1\% TiO_2$. Mieszanki proszków przygotowano w mieszalniku typu Turbula. Kształtki dwukrotnie prasowano pod ciśnieniem 600 MPa i dwukrotnie spiekano w temperaturze 900°C w atmosferze wodoru przez 1 godzinę. Uzyskano kompozyty o gęstości zbliżonej do 90% gęstości teoretycznej. Twardość kompozytów oraz ich wytrzymałość na zginanie zależy od udziału wolframu. Przewodność elektryczna kompozytów maleje ze wzrostem zawartości wolframu. Mikrostruktura kompozytów charakteryzuje się dość dobrym rozmieszczeniem wolframu oraz tlenku tytanu w osnowie srebra, zwłaszcza w kompozytach $Ag + 10\% W + 1\% TiO_2$ i $Ag + 20\% W + 1\% TiO_2$.

Słowa kluczowe: wolfram, dwutlenek tytanu, srebro, spiekanie, styki elektryczne

INTRODUCTION

Electrical contacts are metal devices that make and break electrical circuits. Contacts are made of elemental metals, composites, or alloys that are made by the melt-cast method or manufactured by powder metallurgy (P/M) processes [1-14]. Powder metallurgy facilitates combinations of metals which ordinarily cannot be achieved by alloying. A majority of contact applications in the electrical industry utilize silver-type contacts, which include pure metal, alloys, and powder metal combinations. Silver, which has the highest electrical and thermal conductivity of all metals, is also plated, brazed, or mechanically bonded onto other contact materials - notably, copper and copper-based materials [1-5]. Other types of contacts used include the platinum group metals, tungsten, molybdenum, copper, copper alloys, and mercury. Aluminum is generally a poor contact material because it oxidizes readily, but is used in some contact applications because of its good electrical and mechanical properties and its availability and cost. The desirable properties of electrical contact materials include such characteristics as high electrical conductivity to minimize the heat generated during the passage of current; high thermal conductivity to dissipate both resistive and arcing developed heat; high resistance to chemical reactions in all application environments so as to avoid the formation of insulating oxides, sulfides, and other compounds; and immunity to arcing damage on the making and breaking of electrical contact. The melting point of electrical contact materials should also be high enough to limit arc erosion, metal transfer, and welding or sticking, but low enough to increase resistance to reignition in switching. When the melting point is high, contacts continue to heat gas in the contact gap after the current drops to zero, thus

facilitating reignition. In an electric make-break switching device, there are two different types of contacts: arcing contacts and sliding contacts. Arcing contact points, which usually consist of a pair of thin shaped slabs, perform the actual duty of making, carrying, and breaking the current. Arcing contacts differ from sliding contacts in that the moving member of the switching device travels perpendicular to the contact surfaces. As a result, arcs generated during opening and closing actions always strike and consequently damage the conducting surfaces.

Silver-base composites can be divided into two types [8-11]: type 1 uses a pure element or carbide as the dispersed phase; type 2 uses oxides as the dispersed phase. In many cases, the desired combination of properties can be realized only by utilizing highly refractory metals (tungsten, molybdenum, etc.), either alone or in combination with high conductivity metals such as silver or copper. Metals such as tungsten, molybdenum etc. are highly valued as contact materials since they have high resistance to heavy current without sticking, welding or arcing. Silver tungsten contact materials have similar characteristics to copper-tungsten combinations, however, the high oxidation resistance of silver makes silver-tungsten materials useful in air as well as in oil operations. In silver composites, the second phase (for example TiO_2) forms discrete particles that are dispersed in the silver matrix. First, it increases the hardness of the composite material in a manner similar to dispersion hardening. Second, in the region where two mating contacts touch upon closure, the second phase particles reduce the surface area of silver-to-silver contact. This greatly reduces the tendency to stick or weld. In cases where the contacts do weld, the second-phase oxide particles (which are weaker and more brittle than silver) behave as slag inclusions and reduce the strength of the weld, allowing the device a contact-separating force to pull the contacts apart.

Attempts have been made to describe the influence of production process parameters on the microstructure and properties of Ag-W-TiO_2 composites. Pure silver can be used as contact material only where relatively low mechanical and electrical loads being used. Tungsten and TiO_2 were added to increase the mechanical properties of silver.

EXPERIMENTAL PROCEDURE

The starting powders are shown in Figure 1. Selected physical properties of the starting powders are given in Table 1.

The powder mixtures were prepared by tumbling the powders for 30 minutes in a Turbula-type mixer. The mixtures were then subjected to a double-press/double-sinter process. The cold pressing operations were performed in a rigid die on a double action press at 600 MPa. Both sintering cycles included a one hour hold at 900°C in hydrogen.

The composite specimens were subsequently tested for density, Brinell hardness, bending strength and resistance to wear, and subjected to microstructural examinations by means of both light microscopy (LM) and scanning electron microscopy (SEM).

The electrical conductivity of the contact materials was carried out on an electrical conductivity measurement device (Fig. 2).
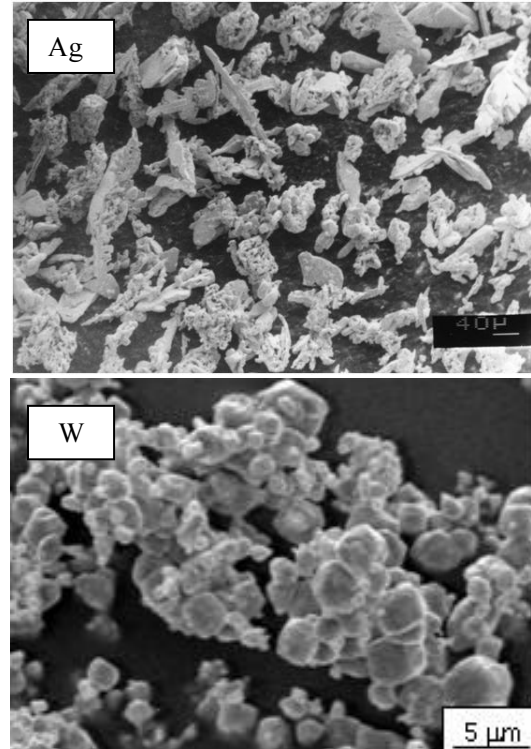

Fig. 1. SEM micrographs of silver and tungsten powders

Rys. 1. Morfologia cząstek proszków srebra i wolframu, SEM

TABLE 1. **Powder particle physical properties**
TABELA 1. **Własności proszków**

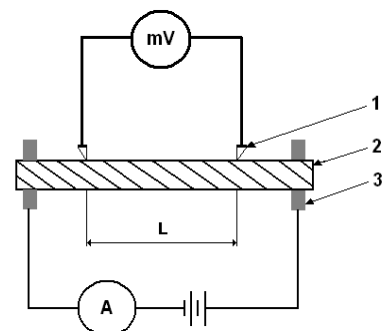| Starting powders	Particle size [μm]	Average particle size (Fisher) [μm]	Tap density [g/cm³]	Flow [s/50 g]	Densification at 600 MPa [g/cm³]	Theoretical density [g/cm³]
W	0÷10	3.1	2.82	-	12.54	19.39
Ag	0÷63	32.8	1.53	60	9.76	10.5
TiO₂	0÷63	24.3	0.98	-	-	4.26

Fig. 2. Diagram of electrical conductivity measurement device: 1 - electric resistance tester, 2 - sample, 3 - grip spring

Rys. 2. Schemat urządzenia do badania przewodności elektrycznej: 1 - miernik oporności, 2 - próbka, 3 - uchwyt sprężynowy

The conductivity of annealed copper is 5.8 x 10^7 S/m and copper is defined to be 100% IACS at 20°C. All the other conductivities are compared to annealed copper and expressed in relative values.

RESULTS AND DISCUSSION

The combined effects of the powder mix composition and its processing route on the relative densities of the composites are shown in Figure 3.
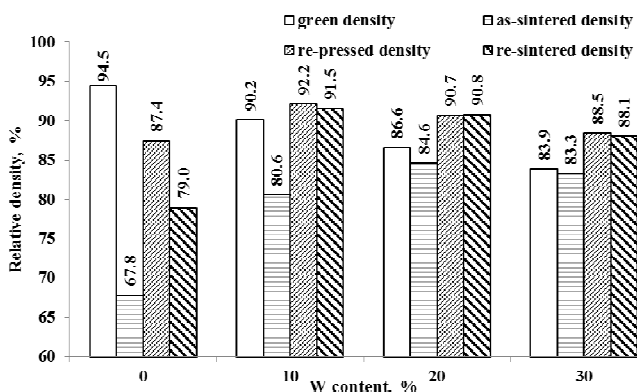

Fig. 3. Relative densities as a function of powder processing route and W content

Rys. 3. Gęstość względna w zależności od etapu produkcji i udziału wolframu

The green and as sintered densities were measured by the gravity method. The nearly fully-dense material made of silver, tungsten and TiO₂ powders cannot be achieved by double pressing and double sintering at the temperature of 900°C. The sintering was carried out in solid state. Figure 3 shows that the Ag-W-TiO₂ composites fully densified at 900°C, and that the re-sintered density is approximately equal to the green density after repressing. Figure 4 shows the volume changes during the production of composites, where − means that the volume grew during analyzed process, + means that the volume of the samples decreased during the analyzed process.
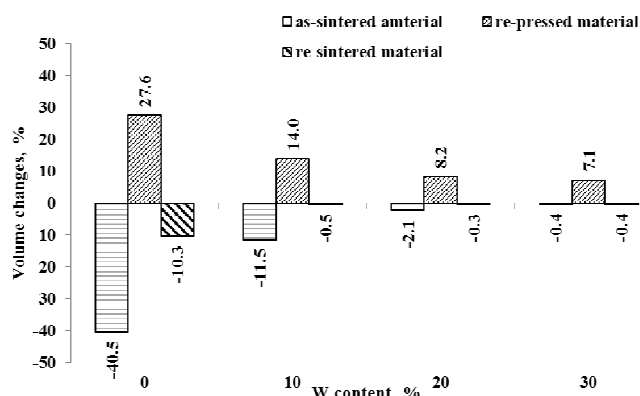

Fig. 4. Volume changes as function of powder processing route and W content

Rys. 4. Zmiany objętości w zależności od etapu produkcji i udziału wolframu

From Figure 4, it is evident that the shrinkage of compacts containing 10, 20 and 30 vol.% W after sintering at 900°C is negligible; whereas repressing at 600 MPa results in a marked increase in the density of the material. An addition of 10, 20 and 30% tungsten powders decreases the green and re-pressed density presumably due to tungsten particles hardness. If the silver amounts are higher and in pure silver, the relative density after the first sintering cycles gradually decreases and also volume growth is high, mostly in the pure silver samples. According to the literature data, the following reasons could be considered responsible for the decrease in the sinter density [1-3, 8, 11-14]: oxidation of a sintered composite diffusion of the composite components expanding action of gases.

The oxidation of composite components is always accompanied by changes in the mass and in the sinters' external appearance. In the specimens under consideration, neither the external appearance nor the mass change. Thus, oxidation can be excluded as a cause of swelling of - sintered products containing higher silver amounts. Summing up the above information and data, a hypothesis can be suggested that specimen samples containing adequately high concentrations swell owing to the expansion of gas remaining in the profile pores. Hence, those samples should be compressed for a second time in order to obtain- a more compact material. The re-sintering operation has a negligible effect on the final density of the composites.

The other properties of double pressed and double sintered composites are given in Figures 5-7.
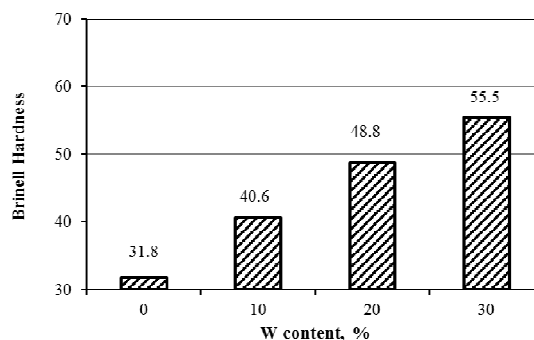

Fig. 5. Brinell hardness as function of W content

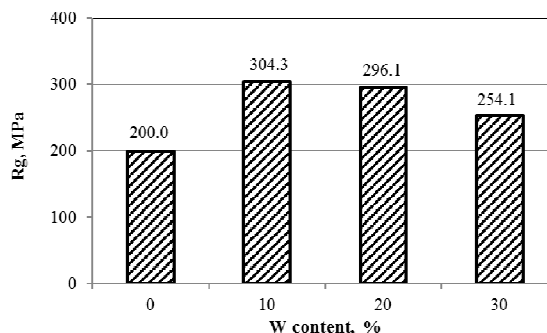Rys. 5. Twardość badanych kompozytów w zależności od zawartości wolframu

Fig. 6. Bending strength *Rg* as function of W content

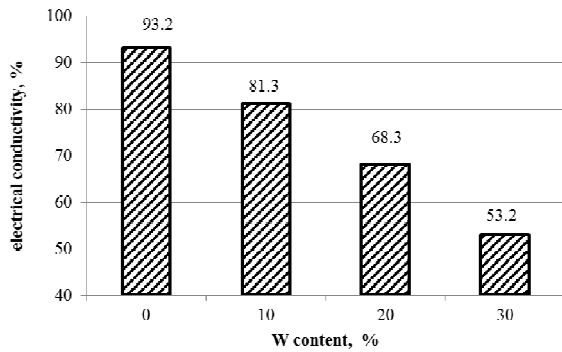Rys. 6. Wytrzymałość na zginanie badanych kompozytów w zależności od zawartości wolframu

Figures 5-7 show that the properties of the investigated composites are a complex function of the manufacturing route and tungsten content. The Brinell hardness of the Ag-W-TiO$_2$ composites increases with an increased content of tungsten, whereas the bending strength seems to be adversely affected by the addition of the tungsten powder. Silver imparts conductivity while tungsten and molybdenum strengthen the composites. The electrical conductivity of both Ag-W-TiO$_2$ composites strongly depends on the silver volume fraction because there is practically no mutual solubility of the components.

The wear test results of the composites double pressed/double sintered at 900°C are given in Figure 8.
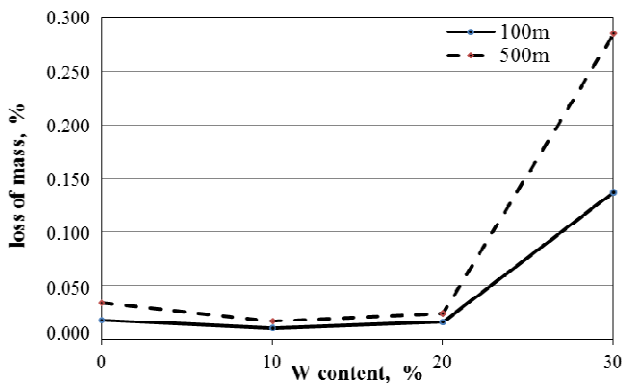

Fig. 8. Composite mass loss as function of sliding distance and W content
Fig. 8. Ubytek masy w funkcji drogi tarcia i zawartości wolframu

It has been found that the tribological behavior of the investigated composites depends on the chemical composition of the material, and the wear resistance was higher for the Ag + 10% W + 1% TiO$_2$ and Ag + 20% W + 1% TiO$_2$ materials. Moreover, the wear loss of the composites increases with increasing sliding distance. Interestingly, the highest loss of mass was observed in the Ag + 30% W + 1% TiO$_2$ composites. This may be attributed to the presence of easily spalling tungsten. The additions of tungsten powder particles are detached in this type of composites.

Characteristic surface topographies after the wear test are presented in Figure 9.
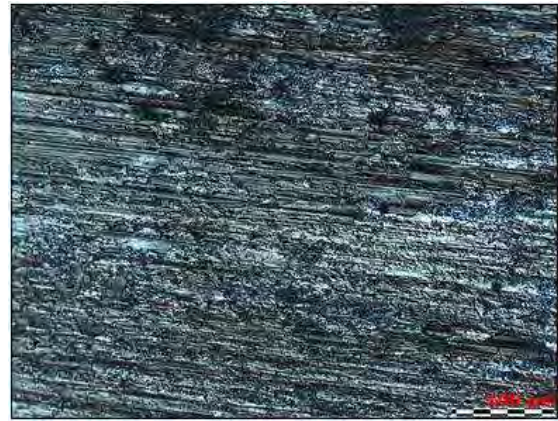
Ag+20%W +1% TiO$_2$
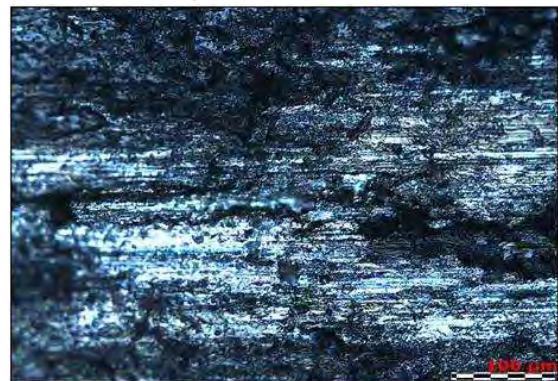
Ag+30%W +1% TiO$_2$

Fig. 9.   Surface topographies of selected composites after wear test on sliding distance 500 m (LM - Nomarsky contrast)
Rys. 9. Powierzchnia po teście odporności na ścieranie na dystansie 500 m (kontrast Nomarskiego)

Observation of the wear tracks indicates an abrasive wear mechanism in all the materials. The surface topographies of the Ag + 20% W + 1% TiO$_2$ and Ag + + 30% W + 1% TiO$_2$ specimens after a 500 m sliding distance give evidence of massive micro-ploughing by W particles pulled out of the matrix to act as abrasives, higher in the Ag + 30% W + 1% TiO$_2$ materials. Tungsten forms large size agglomerates of small particles, which are detached when abraded and spread across the wear track. At first, these particles act as abrasives, promoting three-body wear behaviour. However, when the amount of tungsten decreases, the particles are encrusted in the silver matrix, protecting it; the tungsten particles have more cohesion. This has two effects: on one hand, fewer particles are detached from the tungsten clusters, and on the other hand, these particles are not encrusted in the matrix, producing three-body abrasion in Ag + 10% W + 1% TiO$_2$ and Ag + 20% W + 1% TiO$_2$ compositions. Figure 9 also shows the smearing of silver over the surface of the Ag + 30% W + 1% TiO$_2$ composites which implies a marked contribution of adhesive wear. In general, significant improvements in wear, compared with the base material (pure sintered silver), are only found in Ag + 10% W + 1% TiO$_2$ and Ag + 20% W + 1% TiO$_2$ compositions.

Typical microstructures of double pressed and double sintered composites are shown in Figures 10-12.

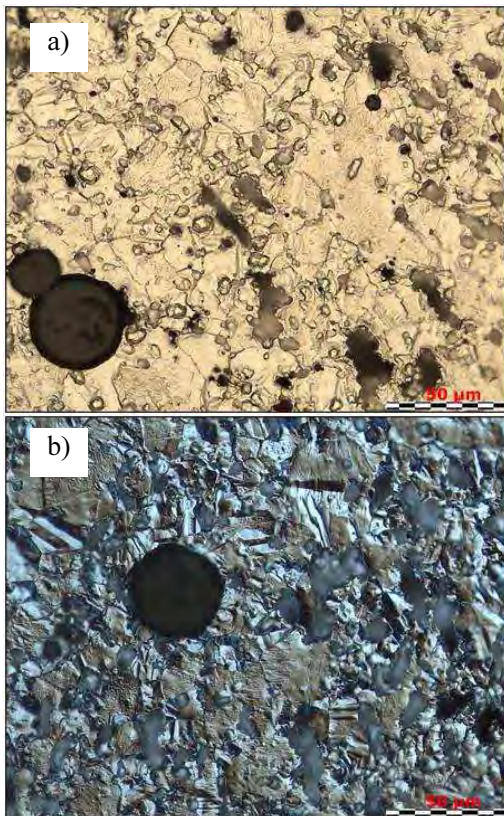The photos were made using light microscopy using the bright field a) (BF) and phase contrast b) (PC).

Fig. 10. Microstructures of as sintered Ag + 10% W + 1% TiO₂
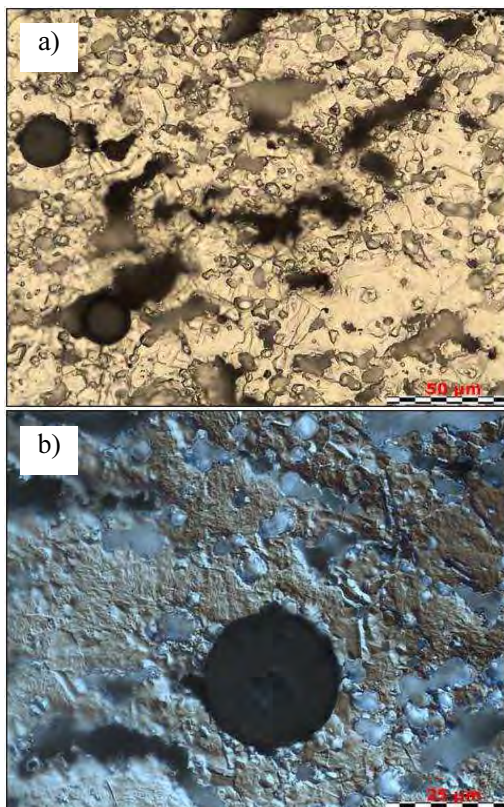Rys. 10. Mikrostruktura kompozytu Ag + 10% W + 1% TiO₂

Fig. 11. Microstructures of as sintered Ag + 20% W + 1% TiO₂
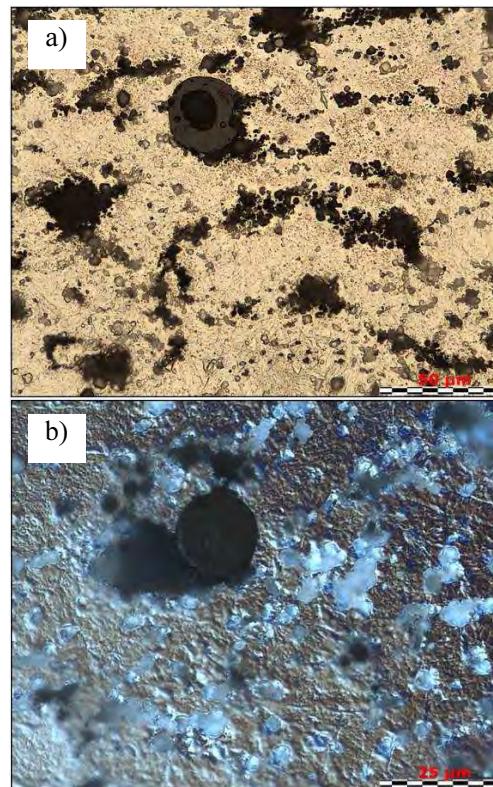Rys. 11. Mikrostruktura kompozytu Ag + 20% W + 1% TiO₂

Fig. 12. Microstructures of as sintered Ag + 30% W + 1% TiO₂
Rys. 12. Mikrostruktura kompozytu Ag + 30% W + 1% TiO₂

The microstructures of the double pressed and double sintered Ag-W-TiO₂ materials in Figures 10-12 illustrate uniform distribution of tungsten (dark), silver (gray), titanium dioxide (circular gray) and small residual porosity, although it seems that the tungsten powder particles a show tendency to form agglomerates with an increased content of tungsten. In the -W-TiO₂ materials, higher amounts of tungsten particles increase the number of its agglomerates, thus compound cohesion with the matrix and less homogeneous structures. Therefore tungsten particles are better linked to the silver matrix in the Ag + 10% W + 1% TiO₂ and Ag + 20% W + 1% TiO₂ compositions. The TiO₂ particles seem to have good cohesion to the silver matrix. It is well known that sintering composite powders is more effective than conventionally prepared powders [8-10]. During milling, the original tungsten particles are crushed and became much smaller, but during mixing not all the tungsten agglomerates are broken up. The growth of tungsten grains is possible by sintering and coalescence of the tungsten particles inside the agglomerates. Both elements (silver and tungsten) are mutually insoluble, even at temperatures above 900°C. The tungsten particles inside the sample are very small and are already surrounded by silver. During sintering of the composites at the temperature of 900°C, the silver particles should sinter together, building up a network. The diffusion of silver from the bulk of the particles to build neck is energetically favourable because the silver-silver interface area increases due to the silver neck growth. One author [11] stated that the copper phase is

the main agent responsible for the densification of the W-Cu system and in order to obtain the highest densification in solid state sintering, the copper phase should be very fine and well dispersed. Probably the same situation is in the Ag-W system, but there is also the expanding action of gases during sintering, which result in a decrease in the sinters' density.

CONCLUSIONS

Double pressing and double sintering of Ag-W-TiO$_2$ materials has proved to be a suitable technique whereby nearly fully-dense electrical contact materials are produced at low cost.

The electrical conductivity of Ag-W-TiO$_2$ materials decreases with tungsten content.

The hardness of Ag-W-TiO$_2$ materials increase with the amount of tungsten but the wear increases only in the Ag + 10% W + 1% TiO$_2$ and Ag + 20% W + 1% TiO$_2$ compositions.

The Ag + 10% W + 1% TiO$_2$ and Ag + 20% W + 1% TiO$_2$ materials studied in this work show a relatively homogenous distribution of tungsten and TiO$_2$.

Acknowledgements

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