Association of Metallurgical Engineers of Serbia
AMES

Scientific paper
UDC: 669.13.018.9:661.862

THE ANALYSIS OF THE TRIBOLOGICAL PROPERTIES OF MULTIPLE STRENGTHENED NANOCOMPOSITE OF THE Cu-Al_2O_3 SYSTEM

Marija Korać[1*], Željko Kamberović[2], Zoran Anđić[3], Miloš Tasić[3], Aleksandar Vujović[3]

[1]*Innovation center of the Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia*
[1]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*
[3]*Scientific Research Center, Veliki park 1, Užice, Serbia*

This paper was previously presented at
4th International Conference Processing and Structure of Materials
held on Palic, Serbia May 27- 29, 2010

Abstract

This paper presents the results of examined tribological properties of the multiple strengthened nanocomposite Cu-Al_2O_3 system. Cu-Al_2O_3 composite powder was obtained by combination of the thermo-chemical procedure and mechanical alloying, which is a completely new approach to synthesis of these materials. The synthesized powders were cold pressed with 940MPa and sintered in hydrogen atmosphere in temperature range of 725-925^{o}C during 15-120 minutes. The samples were thermo-mechanically treated in two stages after sintering: cold rolling with the final reduction degree of 30% and annealing at 800^{o}C for 1h in hydrogen atmosphere. Characterization of the sintered, rolled and annealed samples included the microstructural examination by scanning electron microscopy (SEM), the quantitative analysis of the SEM microphotographs and the examination on tribological properties. Tribological examinations have shown that the best wear resistance have the samples after heat treatment. The significant influence on the tribological properties has the effect of multiple strengthening mechanisms. These mechanisms include strengthening of copper matrix achieved by dispersion of fine particles of Al_2O_3, strengthening by the grain boundaries due of the appearance of nanosized Al_2O_3 particles and the $Cu_xAl_yO_z$ phase, as well as by deformation strengthening and strengthening by annealing. Based on the results of the quantitative analysis and tribological examinations, it can be concluded that apart from these strengthening effects porosity also has a significant influence on

* Corresponding author: Marija Korać, marijakorac@tmf.bg.ac.rs

the tribological properties, i.e. reduction of the volume share in porosity improves tribological properties.
Key words: copper, Al_2O_3, multiple strengthening, tribological properties

Introduction

In recent years the term "nanotechnology" is increasingly used to describe the technological processes and analytical techniques used in the synthesis of materials in ultra-fine range of the value order of the millionth part of a millimeter. Since these new technologies will have a significant role in XXI century they may be considered as the flywheel of the forthcoming industrial revolution.

The synthesis of nanoparticles can be generally divided into the methods of "from the bottom - to the top" approach ("bottom-up approach"), such as the deposition from the gas phase, or from the liquid phase, the thermal decomposition (evaporation-condensation), and the methods with "from the top-to bottom approach ("top-down approach"), wherein mechanical grinding processes are distinctive. At the approach "from the bottom - to the top" nanoparticles are formed atom by atom or molecule by molecule, while at the approach "from the top - to bottom", large volumes are gradually reduced in proportion to reach the nanometer dimensions [1].

Recently dispersive strengthening has arisen the great interest both in theoretical and practical terms. It is known that by introduction of fine dispersed particles in the metal matrix the significant effect of hardening may be achieved. This type of hardening results in the retention of improved mechanical properties during operations at high temperature along with keeping these properties at room temperature after high temperature exposure. The improvement in mechanical properties is achieved without significant loss in electrical and heat conductivity [2-4]. Ultra-fine and nanoparticles of oxides proved to be very suitable in achieving high degrees of hardening of metal matrix. This is the way how metal matrix composites could be obtained. Considering their hardness, stability and insolubility in the metal base nanoparticles of oxides represent very good barriers to movement of dislocation at room and elevated temperatures. The significant strengthening effects are achieved by complex activities of different mechanisms [5, 6]. Finely dispersed particles and their homogeneous distribution in the matrix of the base metal cause the stabilization of dislocation substructures formed during the deformation. In addition to dispersion strengthening of the matrix, in some systems such as $Cu-Al_2O_3$ strengthening of the grain boundaries may also occur, due to the appearance of $Cu_xAl_yO_z$ phase at the interface of Cu-Al [7-10]. If further plastic deformation is carried out combined with the subsequent heat treatment, deformation strengthening and strengthening by annealing appear as the strengthening mechanisms [11].

In comparison to conventional materials, metal matrix composites have significant advantages: a higher strength-density ratio, higher stiffness-density relationship, the greater resistance to material fatigue, better properties at high temperatures (higher strength, lower level of creep), lower coefficient of thermal expansion, better resistance to wear [12-14]. Economic consequences of the material wear due to the neglecting the effect of mechanical interactions between different surfaces have a very high price. In this sense, the extensive research is carried out in the field of tribology, for the purpose of maximum reducing and removing the losses occurring due to friction and wear. Basic understanding of the nature and consequences of the interactions between the materials at the atomic level leads to the rational shaping of materials for suitable application [15].

The aim of this paper was to study tribological properties of the multiple strengthened nanocomposite $Cu-Al_2O_3$ system which was obtained by combination of the thermo-chemical procedure and mechanical alloying.

Experimental

The synthesis of nanocomposite powder based on copper and Al_2O_3 was performed by a combination of the thermo-chemical procedure and the procedure of mechanical alloying. The powder that was used for strengthening the copper base by mechanical alloying is nanocomposite powder based on $Cu-Al_2O_3$, obtained by thermo-chemical procedure. The starting raw-material for synthesis of this powder was a water solution of soluble salts of copper and aluminum nitrates in ratio which allows the required composition (with 50wt.%) of nanocomposite $Cu-Al_2O_3$ powder Al_2O_3 to be obtained. Thus, the nanocomposite $Cu-Al_2O_3$ powder with 50wt.% Al_2O_3 and a commercial copper powder (99,8% <45μm) obtained by water atomization process were used as the starting powders for mechanical alloying in the ceramic mill with corundum balls of purity ≥ 99% Al_2O_3. The previous work [16] showed the detailed procedure of the synthesis as well as the characterization of nanocomposite $Cu-Al_2O_3$ powder, obtained by combination of thermo-chemical procedure and mechanical alloying.

The sintering of the obtained mixture of powders was performed by the conventional methods of pressing and sintering. Pressing of powders mixture was performed applying the pressure on both sides (two-sided pressing), in the tool with dimensions at the base 8□32mm and 2mm at the height. The sintering pressure was 940MPa. The sintering of $Cu-Al_2O_3$ samples was carried out in the hydrogen atmosphere in the temperature range 725-925^oC within 15-120 minutes.

After sintering the compacted samples were uniaxially compressed by cold rolling with the reduction degree of 30%. In order to determine the stability at higher temperatures the rolled samples were annealed at 800^oC for one hour in the hydrogen atmosphere. The characterization of the sintered, rolled and annealed samples included the examinations by SEM analysis, quantitative analysis of the obtained SEM photographs and examinations of the tribological properties.

Wear testing was performed by the method of Taber in accordance to ASTM standard MNL 56-Guide for testing by friction, wear and erosion (Guide to friction, wear and erosion testing [17]) of 2007. Basic information on test conditions are:

- the diameter of the grinding plate - 640mm,
- the diameter of the grinding path - 265mm,
- the calculated speed of the grinding path - 832.5mm
- the granulation of Corundum Al_2O_3 Ø100μ m.

Results and discussion

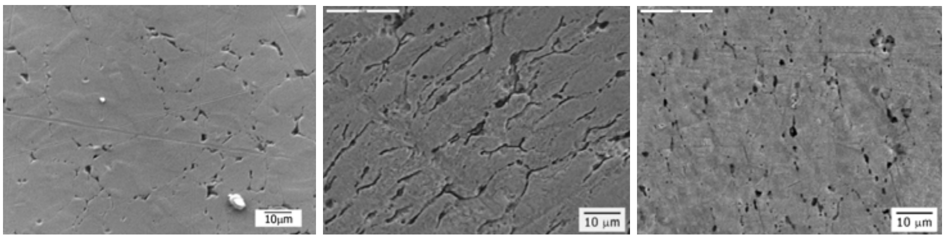
The procedure of the synthesis nanocomposite Cu-Al_2O_3 powder, the combination of the thermo-chemical procedure and mechanical alloying was described in previous works [12, 16]. Characterization of the obtained powders showed that the size of individual particles was rather small, i.e. approximately 30nm. Due to their small size and high surface energy these single particles formed agglomerates sized approximately 150nm.

Considering results [12] suggesting that the best combination of mechanical and electrical properties was achieved in the systems with 1wt.% Al_2O_3 sintered at 875^{o}C/1h, further experimental results will be aimed only to these processing parameters.

The properties of metallic materials depend both on the composition and microstructure. From geometric point of view, the microstructure is characterized by size, shape and orientation of grains. In addition to this, the pores have a large impact on the behavior of materials. Due to the high sensitivity of properties of the materials in the presence of pores, the evaluation of size, shape, distribution and volume share of pores is a necessary task.

Quantitative analysis of the SEM microphotographs SEM (Figure 1a-c) is performed and Table 1 presents the statistical data of the examinations of porosity of the sintered, rolled and annealed Cu-1wt.% Al_2O_3 sample.

The porosity in the structure of the examined *sintered sample* is relatively evenly distributed. Pores are arbitrarily oriented, and their shape is irregular. Their size, based on relative distribution of porosity and the obtained the statistical data, varies in the range from 210nm to 2.38 μm with average diameter of 1.24 μm. The volume share of porosity is 7.638%. The pores are closed indicating the final stage of the process of sintering when the process of structural stabilization is completed.



a) b) c)

Figure 1. SEM of the sample Cu-1wt.% Al_2O_3: a) sintered at 875^{o}C/1h; b) rolled by the reduction degree of 30%; c) annealed at 800^{o}C/1h in the hydrogen atmosphere

Table 1. Statistical data of testing the porosity of sintered, rolled and annealed Cu-1wt.% Al_2O_3

Sample	Min [μm]	Max. [μm]	Av. [μm]	Std Error	Std Dev.	Vv [%]
sintered	0.21	2.38	1.24	0.06	0.42	7.638
rolled	0.20	2.20	0.82	0.05	0.40	6.311
annealed	0.16	1.56	0.55	0.03	0.29	4.507

In the structure of the samples subjected to *cold plastic deformation* porosity is also relatively evenly distributed, with a clearly visible pores oriented in one direction. The size of pores, based on relative distribution of porosity and the obtained statistical results, varies in the range from 200nm to 2.20 μm with average diameter of 0.82 μm. The pores are closed, and their volume share is 6.311%.

The comparative analysis of the porosity results of the samples subjected to cold plastic deformation by rolling and the sintered samples indicates the significant porosity in the sintered samples both from the aspect of the pore size, and also from the aspect of their volume share. The accumulation of the pores is clearly noticeable at grain boundaries in the cold deformed samples, indicating that the pores in the moment of contact with the moving grain boundaries were too large to be absorbed by the boundary. As a result the grain boundary movement was impeded as well as its growth.

Rolling can change the distribution and the size of secondary phase, as well as to reduce the number of pores. After rolling, the particles of Al_2O_3 become more dispersive, while the relative density increases [18].

The porosity in the structure of the samples subjected to heat treatment after cold plastic deformation is relatively evenly distributed. The pores are arbitrarily oriented, and their shape is irregular. Based on relative distribution of porosity and statistical data, the size of pores is in the range from 160nm to 1.56 μm with average diameter of 550nm. The volume share of porosity is 4.5%.

The comparative analysis of the results of the porosity of the sintered samples, the samples subjected to cold plastic deformation and the annealed samples points to significant porosity of the sintered samples and the samples subjected to cold plastic deformation in relation to the annealed samples not only from the aspect of the pore size, but also from their volume share. In order to evaluate the stability of structure during previously described processes, the examinations on tribological properties were performed.

The reduced rate of erosive wear is a consequence of an increase in the index of the deformation hardening. Increasing the index of the deformation hardening affects increase of the critical voltage required to start the localize deformation during the process of wear [19].

Tribological tests have shown that the best resistance to wear exhibit samples after heat treatment (Figure 2), which can be explained by the fact that after annealing recrystalization and grain growth do not occur due to the blocking effect of homogeneously distributed of nanosized Al_2O_3 particles and formation of the $Cu_xAl_yO_z$ phase, identified in [7-10,12].

Based on the results of quantitative analysis and tribological examinations, it can be concluded that apart from these strengthening effects the role of porosity has a significant influence on the tribological properties, i.e. as the volume share of porosity is reduced the tribological properties are improved.

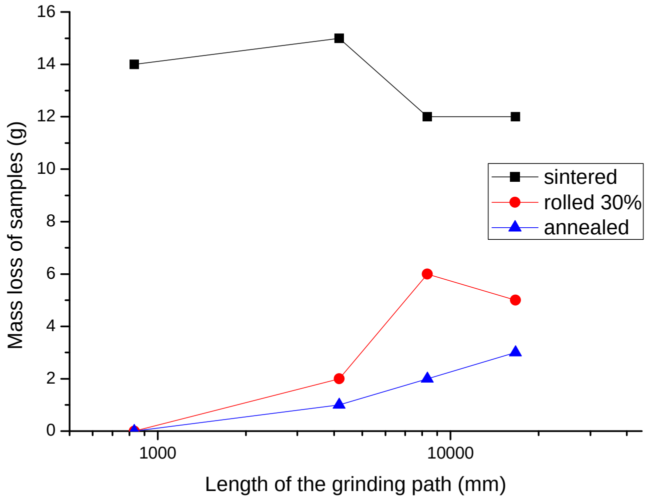


Figure 2. Wear resistance of the sintered (875°C/60min), rolled and annealed samples

Different strengthening mechanisms impose the significant influence on the tribological properties. Strengthening the copper matrix is achieved by dispersion strengthening, due to the dispersion of fine Al_2O_3 particles, strengthening by the grain boundaries by nanosized Al_2O_3 particles and $Cu_xAl_yO_z$ phase, as well as the deformation strengthening and strengthening by annealing play important roles in the increasing strength of this system. During mechanical alloying the coating of copper particle powders with the particles of Cu- Al_2O_3 nanocomposite occurs.

Conclusion

Synthesis of nanocomposite Cu-Al_2O_3 powder suitable for obtaining multiple strengthened systems could be successfully performed by combination of the thermo-chemical procedure and the mechanical alloying. The combination of thermo-chemical procedures and the procedure of mechanical alloying is a completely new approach to the synthesis of powders. Thus obtained powders allow obtaining the final product with high degree of strengthening.

Tribological examinations of the sintered, rolled and annealed Cu-Al_2O_3 samples clearly indicate that the best resistance to wear is demonstrated by samples after heat treatment. The significant influence on the tribological properties has the multiple strengthening of this system. Namely, strengthening of the copper is achieved by dispersion strengthening, due to the dispersion of fine Al_2O_3 particles, by grain boundaries strengthening due to the formation of nanosized Al_2O_3 particles and $Cu_xAl_yO_z$ phase, as well as by the deformation strengthening and the strengthening by annealing.

The comparative analysis of the results of the porosity of examined samples, i.e. sintered samples, samples subjected to cold plastic deformation by rolling and the annealed samples points out the significant presence of porosity in the sintered samples and the samples subjected to cold plastic deformation by rolling compared to the annealed samples as from the aspect of the pore size and their volume share. Based on the results of quantitative analysis and tribological examinations, it can be concluded that apart from these multiple strengthening mechanisms the porosity also has a significant influence on the tribological properties, i.e. with the reduction in the volume share of porosity tribological properties are improved.

References

[1] M. Hosokawa, K. Nogi, M. Naito and T. Yokoyama: Nanoparticle Technology Handbook, (2007) 385-417.

[2] J. Naser, H. Ferkel and W. Riehemann: Mater. Sci. Eng. A, 234-236 (1997) 470-473.

[3] Z. Trojanová, H. Ferkel, P. Luká, J. Naser and W. Riehemann: Scr. Mater., 40 (1999) 1063-1069.

[4] B. Trian, P. Liua, K. Songa, Y. Lia, Y. Liua, F. Rena, J. Sua: Mater. Sci. Eng. A, 435-436 (2006) 705-710

[5] G. Plascencia and T. A. Utigard: Corros. Sci., 47 (2005) 1149-1163.

[6] S. Lianga, Z. Fana, l. Xua and L. Fangb: Composites Part A, 35 (2004) 1441-1446.

[7] P. K. Jena, E. A. Brocchi, I. G. Solórzano and M. S. Motta: Materials Science and Engineering, A317 (2004) 72-78.

[8] P. K. Jena, E. A. Brocchi and M. S. Motta: Materials Science and Engineering, A313 (2001) 180-186.

[9] D. W. Lee and B. K. Kim: Materials Letters, 58 (2004) 378-383.

[10] Z. Anđić PhD. Thesis: TMF, University of Belgrade, 2007 (in Serbian)

[11] S. Nestorović, I. Rangelov and D. Marković: Protection of materials 49 (2008) 31-36.

[12] M. Korać: D. Sc. Thesis, TMF, University of Belgrade, 2009 (in Serbian)

[13] M. Korać, Z. Anđić, M. Tasić, Ž. Kamberović: J. Serb. Chem. Soc. 72 (2007) 1115-25.

[14] Z. Anđić, M. Korać, Ž. Kamberović, A. Vujović and M. Tasić: Science of Sintering, 39 (2007) 145-152.

[15] V. Kovačević, D. Vrsaljko and W. Brostow: Polimers, 30(2009) 76-82.

[16] M. Korać, Ž. Kamberović, Z. Anđić, M. Filipović: Science of Sintering, 39 (2007) 145-152.

[17] ASTM standard MNL 56 - Guide to friction, wear and erosion testing, 2007

[18] M. Korać, Ž. Kamberović, M. Tasić and M. Gavrilovski: Chemical Industry & Chemical Engineering Quarterly 14(4) (2008) 215-218

[19] X-B. Liu, C-C Jia, X-H. Chen, G-s. Gai: Microstructures and properties of 1.0%Al_2O_3/Cu composite treated by rolling, The Transactions of Nonferrous Metals Society of China 17, Special issuse International Conference of Nonferrous Materials (ICNFM) Part IIB, (2007) 626-629.

[20] K. H. Zum Gahr: Microstructure and Wear of Materials, Chapter 8: Erosive wear of metals, Elsevier, Amsterdam, 1987