Vol. 37, No. 4 (2015) 413-420

Tribology in Industry

www.tribology.fink.rs

RESEARCH

Nanoindentation of Za-27 Alloy Based Nanocomposites Reinforced with Al_2O_3 Particles

D. Džunić[a], S. Mitrović[a], M. Babić[a], I. Bobić[b], M. Pantić[a], D. Adamović[a], B. Nedeljković[c]

[a]*Faculty of Engineering, University of Kragujevac, Kragujevac, Serbia,*
[b]*"Vinča" Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia,*
[c]*Metrology Laboratory, BSS-LAB D.O.O., Kragujevac, Serbia.*

Keywords:

ZA-27
Nanocomposites
Nanoindentation
Hardness
Elastic modulus

Corresponding author:

Dragan Džunić
Faculty of Engineering,
University of Kragujevac,
Kragujevac, Serbia
E-mail: dzuna@kg.ac.rs

A B S T R A C T

Nanoindentation has been widely used for material mechanical characterization. In this study, nanocompozite of ZA-27 alloy matrix reinforced with different volume fractions of nanometric Al_2O_3 ceramic particles ranging from 0 to 5 %, were produces using compocasting technique. Nanoindentation tests were performed using Berkovich three sided diamond pyramid, with maximum load of 100 mN and maximum load holding time of 15 s. Indentation imprints were investigated using optical and atomic force microscopy (AFM). Average particle size was 20-30 nm. Nanoindentation tests showed that nanocomposites have higher values of hardness and lower values of elastic modulus in comparison to the ZA-27 matrix alloy. Obtained results have different values in comparison to the theoretical investigations.

1. INTRODUCTION

Zinc based alloys has been widely used in industry, and it has a good combination of hardness, strength and toughness. Because of their bearing capabilities they are often used for bearings. Zinc alloys have a good bearing capabilities, tribological properties, low casting temperatures and they are cost effective [1-3]. Zn-Al alloy contain a small amount of Cu and because of that it could be very cost effective replacement for a great number of metals, due to better wear resistance [3]. ZA alloy is very important for bearings that work in high loads and low sliding speeds contact conditions [4]. Because of good tribo-mechanical properties low mass, good foundry castability and fluidity, good machinability, high strength and hardness in as cast condition, good corrosion resistance [5,6], low initial expenses, energy efficient casting, safe for human environment, equal or even better bearing capabilities, ZA alloys (mostly ZA-12 and ZA-27) are capable to replace aluminium and bearing bronze [4]. Important aspect is reducing of production costs 25 to 50 % and 40 to 75 % in comparison to aluminium and casting bronze, respectively [7-9].

However, the most restricting property of those alloys is their inferiority on elevated temperatures, above 100 °C [3,10]. ZA-27 alloy belong to the family of ZA alloys, and it has a great strength and it is widely used for bearings and sleeves, as a replacement for bearing bronze [11-13] due to low production costs equal and even better properties. Besides that, because they are used for thin walled castings and components for electric, automotive, industrial and agricultural machines and devices, make them very popular alloy for bearings, wear resistance components, valves, pulleys and etc. [14].

Among various techniques for producing composites reinforced with particles, stir casting is generally accepted as most promising technique [15]. Stir casting advantages refer to the simplicity, flexibility and mass production applicability. Also, stir casting is the most economic composite producing technique of all actual techniques [14]. Within this technique, reinforcement particles are infiltrated in molten metal, with intensive mixing in order to achieve vortex movement on the surface of the molten metal. Reinforcement particles were added to the molten metal on the edge of the vortex. Vortex movement proved to be very useful in particle distribution process, due to mismatches among internal and external pressure of the molten metal, which pulls in reinforcement particles deep into the molten metal [16].

Great number of information's about mechanical properties of the material could be obtained using indentation technique. The most important mechanical properties are hardness and Young's modulus, and beside these properties about induced stresses, work hardening, residual thermal stresses could be measured. Indentation technique could be applied both at homogeneous and heterogeneous materials [17-20]. Indentation technique is widely used for determination of material mechanical properties due to simplicity and time effectiveness methodology. During past decade's indentation investigations are descended on the nano level.

In the present study mechanical properties of nanocomposites based on ZA-27 alloy, using nanoindentation technique, were investigated. ZA-27 is reinforced with 1, 3 and 5 vol. % of Al_2O_3 nanoparticles, with average size 20-30 nm. All obtained results for nanocomposites were compared to the results obtained for base ZA-27 alloy. Also, influence of volume fraction on mechanical properties of nanocomposites was investigated.

2. EXPERIMENTAL DETAILS

2.1 Material

Produced nanocomposites are based on ZA-27 alloy. Chemical composition of ZA-27 alloy is presented in Table 1.

Table 1. Chemical composition of ZA-27 alloy.

Label	Chemical composition (wt. %)			
	Al	Cu	Mg	Zn
ZA-27	25-27	2-2,5	0,015-0,02	Balance

The nanocomposite specimens were obtained by the compocasting procedure, which was executed by mixing in the isothermal regime. The apparatus and detailed description of the compocasting procedure can be found elsewhere [4].

Tested specimens are previously milled to the specified dimension, after that they were grounded with sand papers with differennt grit sizes and finaly polished. During these processes it was taken into account that the surface temperature of the specimens does not exceed 100°C, which would result in degradation of mechanical properties of the ZA-27 based materials [3,10].

2.1 Nanoindentation

Nanoindentation was performed with Berkovich three sided diamond pyramid. Diamond is indenters most often used material due to high hardness and elastic modulus that minimalize influence of indenter on measured values [21]. For nano scale, hardness and elastic modulus measurement, Berkovich indenter stands out, among four sided Vickers and Knoops pyramids, because it is much easier to achieve sharp tip on three sided pyramid.

Nanoindentation investigations were conducted on CSM Nanoindenter, under 100 mN normal load, 15 s maximum load holding time, 200 mN/min loading and unloading speed. The mechanical responses of the tested specimens were assessed as the average behaviour of 9 indentations, organized in a 3x3 array. Distance between centres of imprints was 50 μm, it was taking into account that imprints are not too close to each other to avoid influence of work hardening on mechanical properties of tested material. Also, matrix type of measurement is selected in order to facilitate the perception of indentation imprints on AFM (Atomic Force Microscope). Indentation imprints analysing and precise dimensions determination was done using AFM.

3. RESULTS AND DISCUSION

Table 2 presents measured nanoidentation values, HIT instrumented hardness (calculated from the projected area of indentation imprint), HV hardness expressed in Vickers units, E elastic modulus, h_m maximum indentation depths, h_c contact depths (representing real contact depth of indenter with material). Values presented in table are mean values of all nine measurements.

From the presented curves it could be seen that hardness is going bigger with the increase of volume fraction of reinforcement. Main reason for that is the presence of nanoparticles of reinforcement in base alloy, due to restricting dislocations movement that are produced during indentation process. Nanocomposites have a lover value of elastic modulus in comparison to the base alloy, which is expected because the elastic modulus of Al_2O_3 is lower than base alloy, 150 GPa [23]. Rule of mixtures can be applied to calculate hardness and elastic modulus [24]:

$$H_c = H_m F_m + H_r F_r \tag{1}$$

$$E_c = E_m F_m + E_r F_r \tag{2}$$

Table 2. Mean values of indentation process performed on ZA-27 alloy and nanocomposites reinforced with 1, 3 and 5 vol. % of Al_2O_3.

	H_{IT} MPa	H_V Vikers	E GPa	h_m nm	h_c nm
ZA-27	1214.118	112.441	182.702	1881.312	1841.065
ZA-27+1% Al_2O_3	1310.206	121.339	117.307	1844.096	1780.6
ZA-27+3% Al_2O_3	1358.473	125.809	132.637	1814.467	1763.698
ZA-27+5% Al_2O_3	1428.913	132.333	126.557	1777.173	1719.016

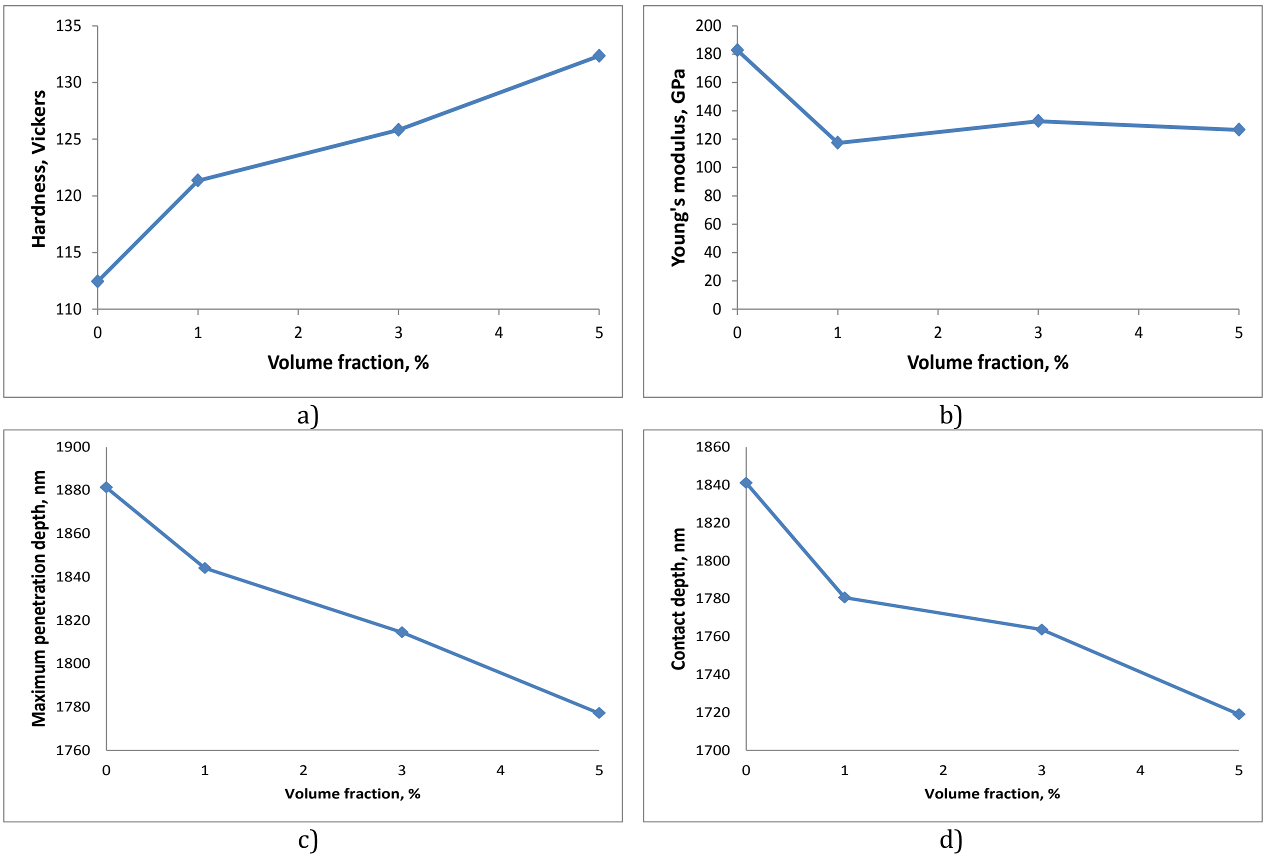

Fig. 1. Nanocomposites nanoindentation values: a) hardness, b) elastic modulus, c) maximum indentation depth and d) contact depth, in comparison to the volume fracture of reinforcement.

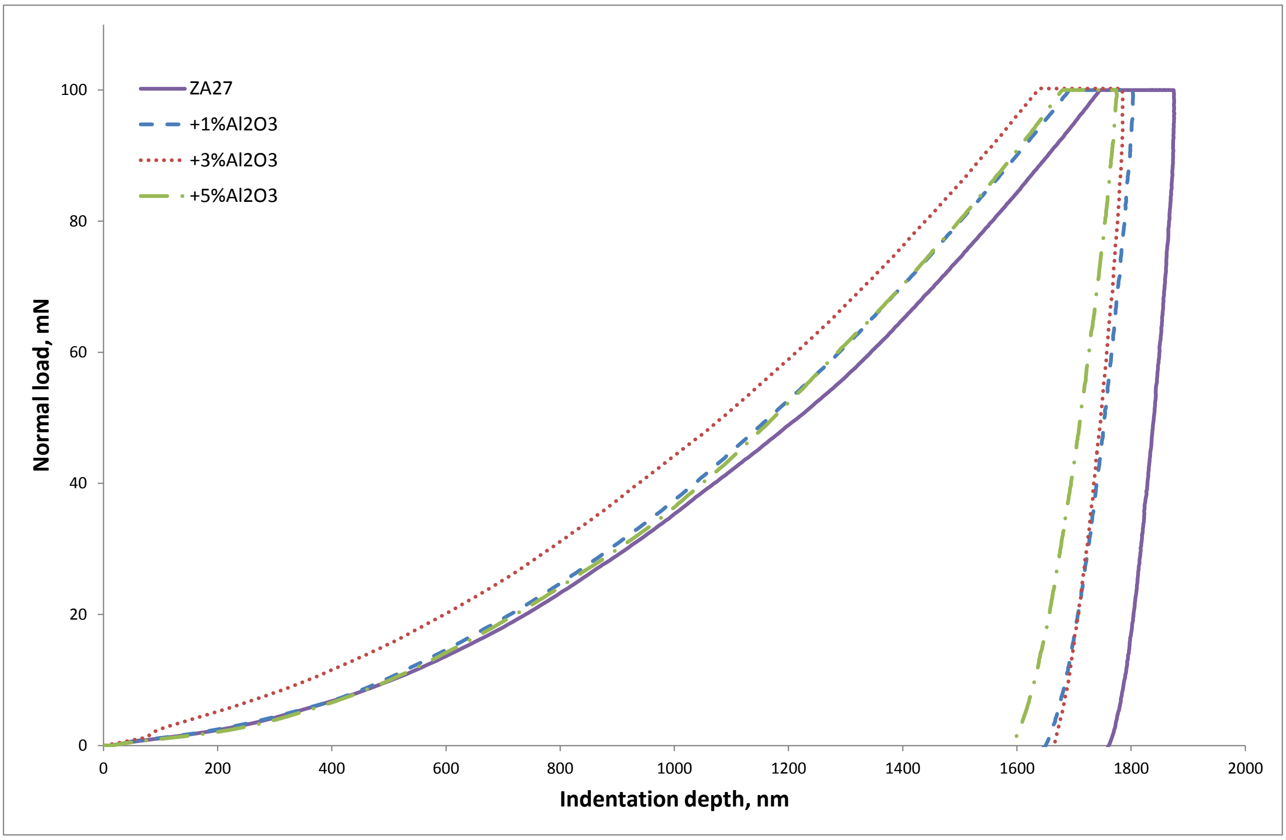

Fig. 2 – Nanoindentation curves for ZA-27 alloy and tested nanocomposites reinforced with 1, 3 and 5 vol. % of Al_2O_3.

H_c, H_m and H_r, show the hardness of the composite, matrix and reinforcement, respectively. E_c, E_m and E_r show the elastic modulus of the composite, matrix and reinforcement, respectively. F_m and F_r are fractional volumes of matrix and reinforcement. From equations (1) and (2) it could be concluded that hardness and elastic modulus depends on volume fraction of reinforcement.

Based on equation (1) and the fact that hardness of Al_2O_3 is ~880 HV [23], it could be said that with each volume fraction of reinforcement hardness of nanocomposites should raise for ~7, and with 5 % of reinforcement hardness of the nanocomposites should be ~150 Vickers. Comparing this value with the value of hardness presented in Tabel 1, it can be seen that there is a difference, and that measured value is lower, probably due to porosity and agglomeration of nanoparticles. Same case is with elastic modulus, decrease in value of elastic modulus shouldn't be much lower in comparison to the elastic modulus of base alloy. From Fig. 1b it could be seen that with volume fraction increase of reinforcement, value of elastic modulus remain almost constant.

Maximum indentation depth and contact depth decrease with increase of volume fraction of reinforcement and it is in correlation value of hardness, shown on Fig. 1a.

It must be said that presented equations do not take in consideration particle dispersion in matrix alloy, and possible existence of porosity and agglomeration, that have a great influence on mechanical properties of composite material.

Indentation curves (indentation depth dependence on normal load) are shown on Fig. 2. From those curves it is clearly that maximum load holding time is properly selected, and there is no irregularities (a "nose" in the load–displacement data in the unloading segment appears) caused by short holding time [25]. Thus, it can be concluded that a sufficient hold time is necessary to avoid errors in unloading data due to viscoplasticity during the unloading process.

There are no major differences in indentation curves for all tested materials. Also it is no possible to notice three different phases in loading process, as Fale [26] did. On presented curves two phases can be noticed in loading process. First on is a result of elastic deformation of tested material and piling up of dislocations in front of indenter. This phase ends up with indentation depth ~400 nm. After that, there are no significant changes in the loading curves trends.

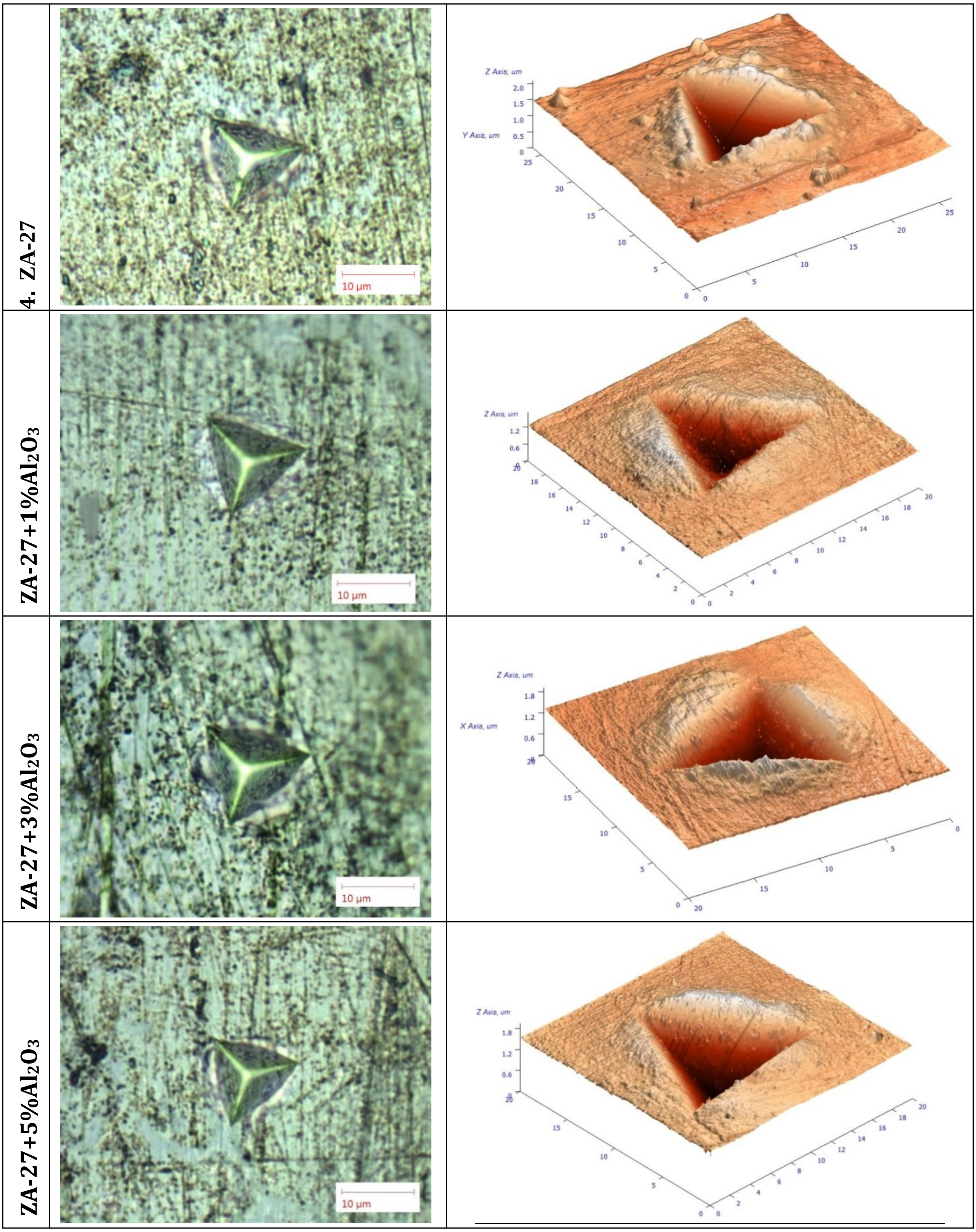

Fig. 3. Indentation imprints analysed by optical and atomic force microscopy.

Figure 3 shows indentation imprints examined by optical and atomic force microscopy. Indentation imprints shown on a Fig. 3 are those which hardness values are close to the values shown in tab 2. Around all shown imprints it can be noticed brighter zones on optical and atomic force microscopy; and they are result of material plastic deformation [27].

Hosseini [28] and Sameezadeh [29] have shown that hardness of nanocomposites rise with increasing volume fraction of reinforcements, up to 3 %, with further increasing of volume fraction, up to 5 %, hardness of nanocomposites decreases. Kang and Chan [30] concluded that if the volume fraction of reinforcement exceeds critical level, effect of mechanical properties improvement diminishes. This behaviour is a result of saturation of grain boundaries with nanoparticles that prevents more grain refining function and also aggregation of particles results in brittleness and weakness of the boundaries. Also, depending on grain size after addition of certain amount of reinforcement, nanoparticles can easily agglomerate and form clusters. In that case inter particle distance become larger than the expected distance, therefore, effect of Orowan strengthening mechanism decreases.

Improvement in compressive strength due to reducing of composite grain size, load transfer from matrix material to the reinforcement particles and due to increased dislocation density, is shown by Akbarpour [31]. Increased dislocation density is result of residual compressive stresses induced by mismatch in thermal expansion coefficients between matrix and reinforcement. Increase in volume fraction of reinforcement results in finer grain size of matrix material which come closer to the size of nanoparticles of the reinforcement. In that case most of nanoparticles would be found not in the grains but on the grain boundaries. Thermal mismatch between matrix and the reinforcement results in generation of dislocations, which leads to increase in dislocation density in the nanocomposite material [32]. Higher dislocation density leads to higher level of internal stress and higher resistance to external forces i.e. improved mechanical properties of nanocomposites in comparison to the matrix material. Values of thermal expansion coefficient for ZA-27 alloy and Al_2O_3 reinforcement are 23.3 – 26.0 μm/°C and 8.1 μm/°C, respectively [33]. Based on those values and on literature conclusions it can be said that combination of ZA-27 alloy and Al_2O_3 reinforcement is suitable for producing nanocomposites with high dislocation density.

5. CONCLUSION

Based on results and literature review it can be concluded that presence of reinforcement particles in matrix material should restrict dislocation movement or lead in increase of dislocation density generated as result of thermal mismatch between matrix material and reinforcement, induced by penetrating of indenter in the surface of nanocomposites.

Presence of agglomeration and porosity reduces mechanical properties improvement with adding reinforcement particles to the matrix material. During indentation process, material in front of indenter will be pushed toward the zones with minimal internal stresses i.e. trapped gas bubbles. In that case reinforcement particles are unable to restrict dislocation movement, but moves pushed by dislocation to zones with lower internal stresses.

Acknowledgement

Research presented in this paper was supported by Ministry of Education, Science and Technology Development of Republic of Serbia, Grant TR-35021.

REFERENCES

[1] M. Babić and R. Ninković: *Tribološki potencijal ZnAl legura*. Kragujevac: Faculty of Mechanical Engineering, Serbia, 2007. (on Serbian)

[2] M. Babić and S. Mitrović, *Tribološke karakteristike kompozita na bazi ZnAl legura*, Kragujevac: Faculty of Mechanical Engineering, Serbia, 2007. (on Serbian)

[3] S. Tjong and F. Chen, 'Wear behavior of As-cast ZnAl27/SiC particulate metal-matrix composites under lubricated sliding condition', *Metall and Mat Trans A*, vol. 28, no. 9, pp. 1951-1955, 1997.

[4] M. Babic, M. Slobodan, D. Džunic, B. Jeremic and B. Ilija, 'Tribological Behavior of Composites

Based on ZA-27 Alloy Reinforced with Graphite Particles', *Tribology Letters*, vol. 37, no. 2, pp. 401-410, 2010.

[5] B. Bobic, J. Bajat, Z. Acimovic-Pavlovic, M. Rakin and I. Bobic, 'The effect of T4 heat treatment on the microstructure and corrosion behaviour of Zn27Al1.5Cu0.02Mg alloy', *Corrosion Science*, vol. 53, no. 1, pp. 409-417, 2011.

[6] B. Bobić, J. Bajat, Z. Aćimovic-Pavlović, I. Bobić and B. Jegdić, 'Corrosion behaviour of thixoformed and heat-treated ZA27 alloys in NaCl solution', *Transactions of Nonferrous Metals Society of China*, vol. 23, no. 4, pp. 931-941, 2013.

[7] I. Bobić, M. Jovanović and N. Ilić, 'Microstructure and strength of ZA-27-based composites reinforced with Al_2O_3 particles', *Materials Letters*, vol. 57, no. 11, pp. 1683-1688, 2003.

[8] A. Türk, M. Durman and E. Kayali, 'The effect of manganese on the microstructure and mechanical properties of zinc–aluminium based ZA-8 alloy', *Journal of Materials Science*, vol. 42, no. 19, pp. 8298-8305, 2007.

[9] C. Dominguez, M. V. Morenolopez and D. Rios-jara, 'The influence of manganese on the microstructure and the strength of a ZA-27 alloy', *Journal of Materials Science*, vol. 37, pp. 5123–5127, 2002.

[10] T. Chen, C. Yuan, M. Fu, Y. Ma, Y. Li and Y. Hao, 'In situ silicon particle reinforced ZA27 composites: Part 1 – Microstructures and tensile properties', *Materials Science and Technology*, vol. 24, no. 11, pp. 1321-1332, 2008.

[11] G. Ranganath, S. A, M. Krishna and M. Muruli, 'A Study of Mechanical Properties and Fractography of ZA-27/Titanium-Dioxide Metal Matrix Composites', *Journal of Materials Engineering and Performance*, vol. 11, no. 4, pp. 408-413, 2002.

[12] S. Sharma, B. Girish, R. Kamath and B. Satish, 'Graphite particles reinforced ZA-27 alloy composite materials for journal bearing applications', *Wear*, vol. 219, no. 2, pp. 162-168, 1998.

[13] T. Savaşkan, G. Pürçek and S. Murphy, 'Sliding wear of cast zinc-based alloy bearings under static and dynamic loading conditions', *Wear*, vol. 252, no. 9-10, pp. 693-703, 2002.

[14] Y. Li, T. Ngai, W. Xia and W. Zhang, 'Effects of Mn content on the tribological behaviors of Zn-27% Al-2% Cu alloy', *Wear*, vol. 198, no. 1-2, pp. 129-135, 1996.

[15] J. Hashim, L. Looney and M. Hashmi, 'Metal matrix composites: production by the stir casting method', *Journal of Materials Processing Technology*, vol. 92-93, pp. 1-7, 1999.

[16] F. Girot, L. Albingre, J. Quenisset and R. Naslain, 'Rheocasting Al Matrix Composites', *JOM*, vol. 39, no. 11, pp. 18-21, 1987.

[17] J. Bucaille, S. Stauss, E. Felder and J. Michler, 'Determination of plastic properties of metals by instrumented indentation using different sharp indenters', *Acta Materialia*, vol. 51, no. 6, pp. 1663-1678, 2003.

[18] A. Gouldstone, N. Chollacoop, M. Dao, J. Li, A. Minor and Y. Shen, 'Indentation across size scales and disciplines: Recent developments in experimentation and modeling', *Acta Materialia*, vol. 55, no. 12, pp. 4015-4039, 2007.

[19] M. Dao, N. Chollacoop, K. Van Vliet, T. Venkatesh and S. Suresh, 'Computational modeling of the forward and reverse problems in instrumented sharp indentation', *Acta Materialia*, vol. 49, no. 19, pp. 3899-3918, 2001.

[20] J.G. Swadener, E.P. George and G.M. Pharr, 'The correlation of the indentation size effect measured with indenters of various shapes', *Journal of the Mechanics and Physics of Solids*, vol. 50, no. 4, pp 681-694, 2002.

[21] B. Bhushan, *Handbook of micro/nanotribology, 2nd ed*. Boca Raton (FL): CRC Press, 1999.

[22] X. Li and B. Bhushan, 'A review of nanoindentation continuous stiffness measurement technique and its applications', *Materials Characterization*, vol. 48, pp. 11 – 36, 2002.

[23] T. C. Chou, T. G. Nieh, S. D. McAdams, G. M. Pharr and W.C. Oliver, 'Mechanical Properties and Microstructures of Metal/Ceramic Microlaminates: Part II. A Mo/Al2O3 System', *Journal of Materials Research*, vol. 7, no. 10, pp. 2774-2784, 1992.

[24] G. Dieter, *Mechanical metallurgy. 2.ed*. New York, N.Y.: McGraw-Hill, 1976.

[25] D. Singh, N. Chawla, G. Tang and Y. Shen, 'Anomalous viscoplasticity during nanoindentation of Al/SiC nanolaminated composites', *Materials Science and Engineering: A*, vol. 528, no. 13-14, pp. 4608-4614, 2011.

[26] Sandeep Fale, Ajay Likhite and Jatin Bhatt, 'Nanoindentation studies of ex situ AlN/Al metal matrix nanocomposites', *Journal of Alloys and Compounds*, vol. 615, pp. S392–S396, 2014.

[27] J. Roa, E. Jiménez-Piqué, J. Tarragó, M. Zivcec, C. Broeckmann and L. Llanesm, 'Berkovich nanoindentation and deformation mechanisms in a hardmetal binder-like cobalt alloy', *Materials Science and Engineering: A*, vol. 621, pp. 128-132, 2015.

[28] N. Hosseini, F. Karimzadeh, M.H. Abbasi and M.H. Enayati, 'A comparative study on the wear properties of coarse-grained Al6061 alloy and nanostructured Al6061–Al2O3 composites', *Tribology International*, vol. 54, pp. 58–67, 2012.

[29] M. Sameezadeh, M. Emamy and H. Farhangi, 'Effects of particulate reinforcement and heat treatment on the hardness and wear properties of AA 2024-MoSi2 nanocomposites', *Materials & Design*, vol. 32, no. 4, pp. 2157-2164, 2011.

[30] Y.-C. Kang and S.L.-I. Chan, 'Tensile properties of nanometric Al2O3 particulate-reinforced aluminum matrix composites', *Materials Chemistry and Physics*, vol. 85, pp. 438–443, 2004.

[31] M. Akbarpour, E. Salahi, F. Alikhani Hesari, H. Kim and A. Simchi, 'Effect of nanoparticle content on the microstructural and mechanical properties of nano-SiC dispersed bulk ultrafine-grained Cu matrix composites', *Materials & Design*, vol. 52, pp. 881-887, 2013.

[32] M. Akbarpour, E. Salahi, F. Alikhani Hesari, A. Simchi and H. Kim, 'Fabrication, characterization and mechanical properties of hybrid composites of copper using the nanoparticulates of SiC and carbon nanotubes', *Materials Science and Engineering: A*, vol. 572, pp. 83-90, 2013.

[33] Thermal expansion coefficient available at: http://accuratus.com/index.htm, accessed: 11.02.2012.