Int.J.Nano Dim. 2(4): 261-267, Spring 2012
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage: *www.IJND.ir*

Synthesis of ZrO_2 nanoparticle by combination of sol-gel auto-combustion method- irradiation technique, and preparation of Al-ZrO_2 metal matrix composites

S. A. Khorramie[1,*]
M. A. Baghchesara[2]
R. Lotfi[1]
Sh. Moradi Dehagi[1]

[1]Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran
[2]Department of Metallurgy & Materials Engineering, Masjed Soleyman Branch, Islamic Azad University, Masjed Soleyman, Iran.

Received: 04 March 2011
Accepted: 25 May 2011

ABSTRACT

Nanocrystalline ZrO_2 with particle size of about 38 nm was directly synthesized by sol-gel auto-combustion method. The overall process involved three steps: formation of homogeneous sol at 50-55°C; formation of dried gel at 110°C, and combustion of the dried gel at 400°C. Experiments revealed that ZrO_2 dried gel derived from glycine (Fuel) and nitrate sol exhibited self propagating combustion at 400°C that it was ignited in air. The auto-combustion was considered as a heat-induced exothermic oxidation-reduction reaction between nitrate ions and carboxyl group. After auto-combustion, products were calcined at 650°C. ZrO_2 nano particle were incorporated into the A356 aluminum alloy by a mechanical stirred at 850°C and after that, cylindrical specimens were cast. After preparing the samples, mechanical properties were measured. The results of microstructure, compression and hardness tests indicated that addition of ZrO_2 nano particulates to aluminum matrix composites improved the mechanical properties. Also, Based on experiments, it was revealed that the presence of ZrO_2 reinforcement led to significant improvement in hardness and compressive strength.

Keywords: *ZrO_2; Nanostructure; Mechanical properties; Sol-Gel; Auto-Combustion; Ultrasonic.*

INTRODUCTION

Zirconium oxide (ZrO_2) has attracted considerable attention because of its diverse practical applications in fuel-cell technology [1], as a catalyst or catalyst support [2], oxygen sensor [3], protective coating for optical mirrors and filters [4], nanoelectronic devices, thermal–barrier coating [5], ceramic biomaterial [6], and thermo luminescence UV dosimeter [7]. ZrO_2 nanostructures are of significant current interest in preparing piezoelectric, electro optic, dielectric, and nanocomposite materials [8-10].

* Corresponding author:
Saeid Abedini Khorramie
North Tehran Branch, Islamic Azad University, Tehran, Iran.
Tel +98 21 22262561
Fax +98 21 22977853
Email sakhorramie@iau-tnb.ac.ir

ZrO_2 is classified as a wide band gap semiconductor and tends to become more conductive with increasing temperatures.

The crystal structure of ZrO_2 significantly influences its physical properties. Pure ZrO_2 exists in three polymorphic phases at different temperatures: monoclinic, tetragonal, and cubic. At very high temperature (>2370°C) the material has a cubic structure. From temperature 1150°C to 2370°C, ZrO_2 has a tetragonal structure. At low temperature (below 1150°C) the material transforms to the monoclinic structure which is a thermodynamically stable phase [11].

ZrO_2 powders with nanostructured particles have been synthesized by various techniques [12-15]. Hydrothermal route is one of the most extensively employed techniques in the synthesis of metal oxide nanostructures [16].

Aluminum matrix composites possess many advantages such as low specific density, high strength and good wear resistance with the development of some non-continuous reinforcement materials, whisker, fibers or particles. In particular, the aluminum matrix composites reinforced with particles, not only has good mechanical and wear properties, but also are economically viable [17-20].

There are many methods for fabrication of metal matrix composites (MMCs) such as powder metallurgy [21], squeeze casting [22-25], and compocasting [26-29]. For the metal matrix composites, molten metal mixing is a cost effective method while powder metallurgy is costly, and squeeze casting provides good infiltration quality of chopped performs [30, 31].

In this paper, we study the synthesis of ZrO_2 nanostructure by combination of sol-gel auto-combustion method and irradiation technique using zirconium (IV) nitrate as a precursor. Then, ZrO_2 nanopowder was stirred into the molten A356 aluminum alloy with a graphite stirrer at 850°C.

EXPERIMENTAL

Zirconium (IV) nitrate ($Zr(NO_3)_4.3H_2O$, Merck), glycine (Merck), NH_4OH (Merck) and Al powder (Merck) were used as raw materials. All the reagents were used without further purification. Deionized water was used for all experiments. Aluminum (A356) was obtained from Kian Alloy Company, in Kashan of Iran as metal matrix of composites. The chemical analysis of Al alloy is given in Table1.

Table1. Chemical analyses of A356.

Element	Mass Percent
Al	91.73
Mn	0.02
Cu	0.18
Fe	0.32
Si	7.23
Mg	0.38
Zn	0.05
Ni	0.02
Ti	0.01

Nanoparticles of ZrO_2 are prepared by sol-gel auto-combustion method. Appropriate amounts of analytical grade $Zr(NO_3)_4.3H_2O$ are taken and mixed with glycine. The ratio of the nitrate to glycine is equal to 1:3. The mixture is then dissolved in deionized water. The addition of glycine helps the homogenous distribution and segregation of the metal ions. A small amount of ammonium hydroxide is added carefully to the solution to change the pH value to 7. The solution is continuously stirred using a magnetic stirrer. The resultant sol is poured in a platinum crucible and heated at 400°C.

The reinforced phases used to improve strength of ZrO_2 ceramics matrix in this research were aluminum alloy A356. The ZrO_2 powders were synthesized particle size of about 38nm. The structure of the ZrO_2 nano particle was monoclinic structure. Therefore, cast treatable alloy A356 was selected. The ZrO_2 powders were mixed homogeneously with 0.75 and 1.5 Vol. % and Al powder at room temperature. The mixture was then placed in a stainless steel mold and 20 MPa of pressure was used to form the ZrO_2 performs.

X-ray diffractometer (Model: XPERT-MPD, Phylips) using Cu Kα radiation (λ=1.05406Å) with operated at 40 Kv and current of 40mA. The shapes and morphologies of nano powder and Al/ZrO_2 composites were analyzed by Scanning Electron Microscopy (SEM- Philips XL30). The HF-Frequent 35 KHz, 240W/ Made in Germany was used as ultrasonic bath at room temperature.

For casting Al/ZrO_2 Composite, a resistance furnace equipped with a stirring system was used. After smelting the aluminum ingots, an amount given of keryolite was added to the molten Al alloy and the stirring was established for a few min. ZrO_2 nanopowder with 0.75 and 1.5 Vol. % were wrapped into the aluminum foils and added to the melt Al alloy to produce Al-ZrO_2 composite. The processing temperature have been chosen at 850°C. Stirring was continued for another 10 min for homogeneous dispersion and to prevent agglomeration of particulates. A metallic mold is used for casting.

The morphology of the composites were analyzed by scanning electron microscope (SEM, Oxford CAMSCAN-MV2300), equipped with X-ray mapping system and Specimens were polished and etched using Keller solution. The compression test was conducted in air at room temperature (Instron Universal Testing Machine-1195 machine) according to ASTM-E9. At least five specimens were tested for each casting conditions. After grinding and polishing, composite samples were tested using the Brinell method (The hard meter system DVRB-M model made by Eseway Company-England) with a load of 306.56 N.

RESULTS AND DISCUSSION

The XRD patherns of the ZrO_2 nano particle is shown in Figure 1**.** The particle size of the samples has been calculated employing the Scherres equation:

$$D=K\lambda/\beta Cos\theta \qquad (1)$$

Where θ is the angle between the incident and diffracted beams (degree), β, the full with half maximum (rad.), D, the particle size of the sample (nm) and λ is the wavelength of the X-ray. The results of XRD show at lower temperature the diffraction lines have confirmed the formation of single phase of monoclinic ZrO_2 nanostructure. The grain size of the prepared ZrO_2 is found to be about 38nm.

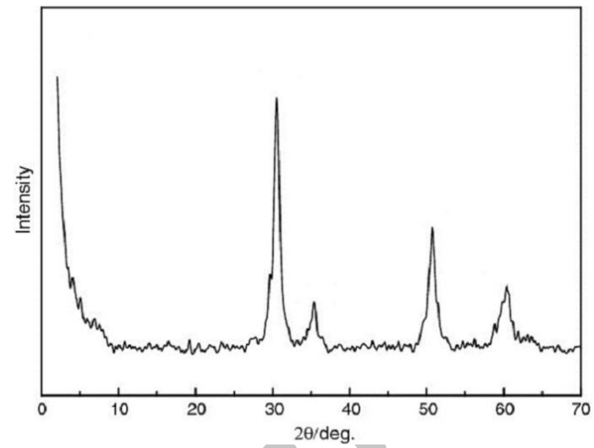

Fig. 1. The XRD pattern for ZrO_2 nano particles.

The structural morphology of the nano particles was investigated using SEM. Figure 2 shows the SEM images of ZrO_2 nano particles.

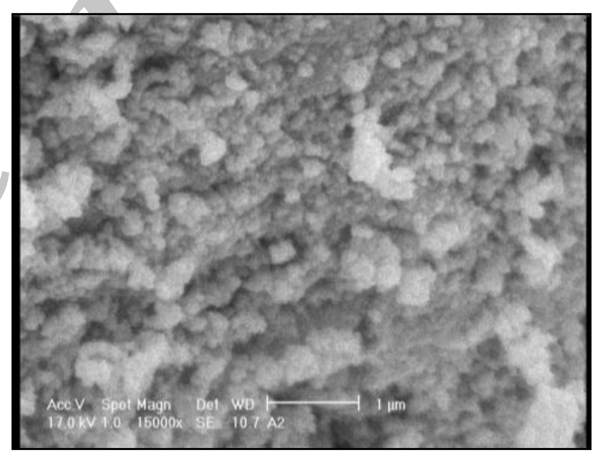

Fig. 2. SEM images of ZrO_2 nanoparticles.

The phase analyses of the A356/ZrO_2 composites were performed using X-ray diffraction pattern. The results of phase analyses of A356/ZrO_2 are shown in Figure 3.

Also, Figure 3 shows the XRD peck of A356/ZrO_2 at 850°C. The composite had only monoclinic ZrO_2 peck with 0.75 Vol. %. Because of the stability of monoclinic ZrO_2 structure, casting with molten aluminum alloys with very short process, no other reaction product in the compositions was found.

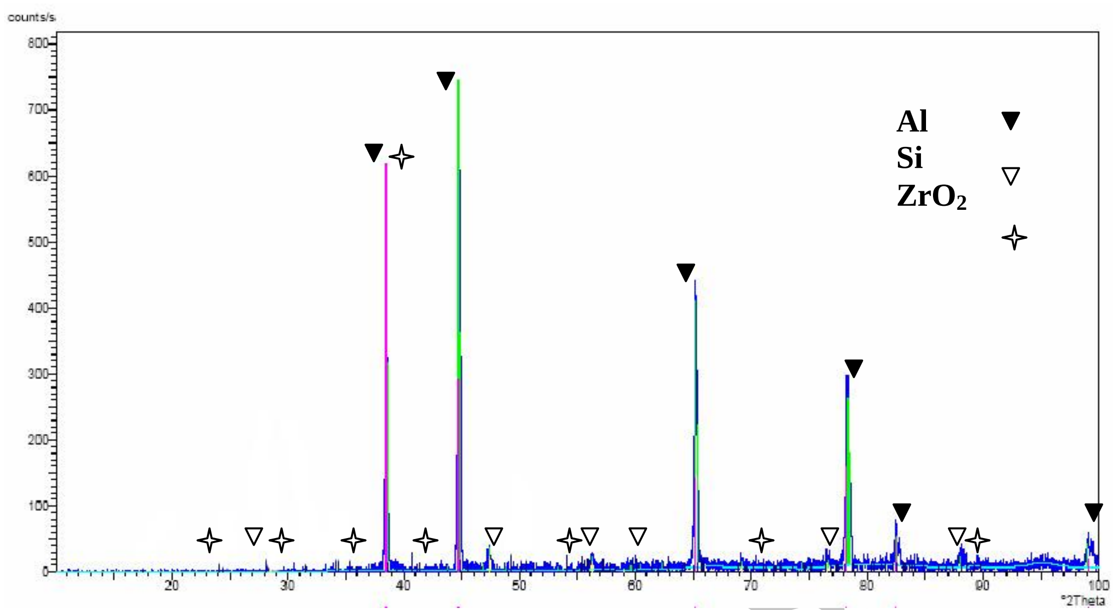

Fig. 3. X-ray diffraction pattern of A356/ZrO_2 composite at 850°C.

The morphology of the A356/ZrO_2 is shown in Figures 4 and 5. The black matrix is aluminum and the white spots represent ZrO_2 nano particles. And the grey part is porous base materials. The phases are indicated by arrows on images. It should be noted that nano-sized ZrO_2 particles were well dispersed in the matrix of aluminum and just a partial agglomeration in composites with 0.75 and 1.5% content of ZrO_2 could be detected in Figures 4 and 5.

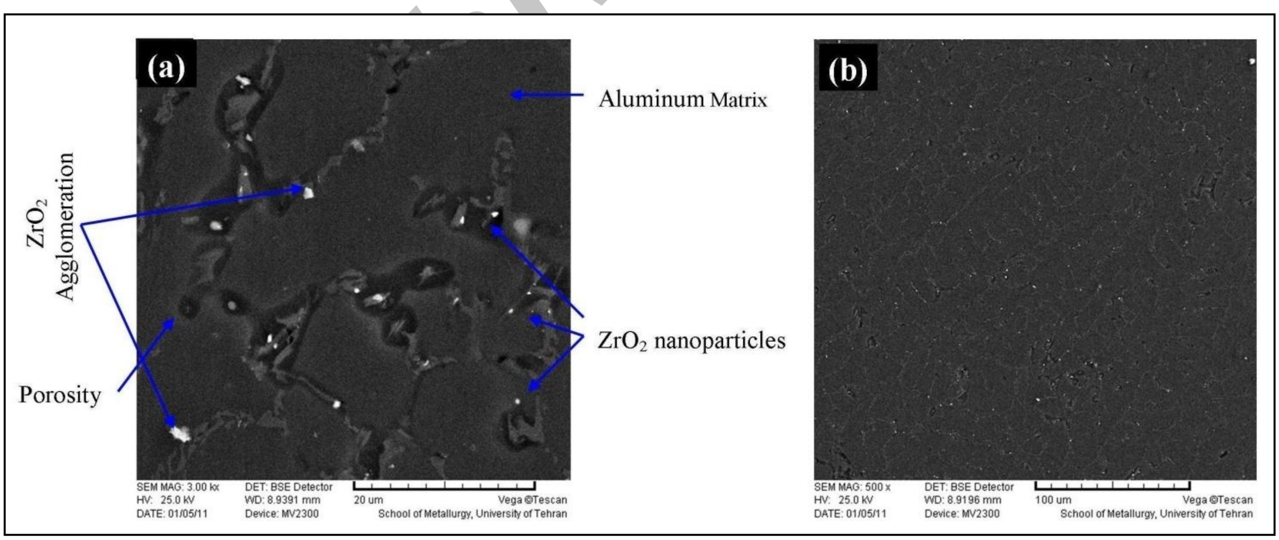

Fig. 4. SEM micrographs of Al356/ZrO_2 composite specimens with 0.75 vol. % ZrO_2 and prepared at 850°C at different magnifications: a) 3.00kX and b) 500X.

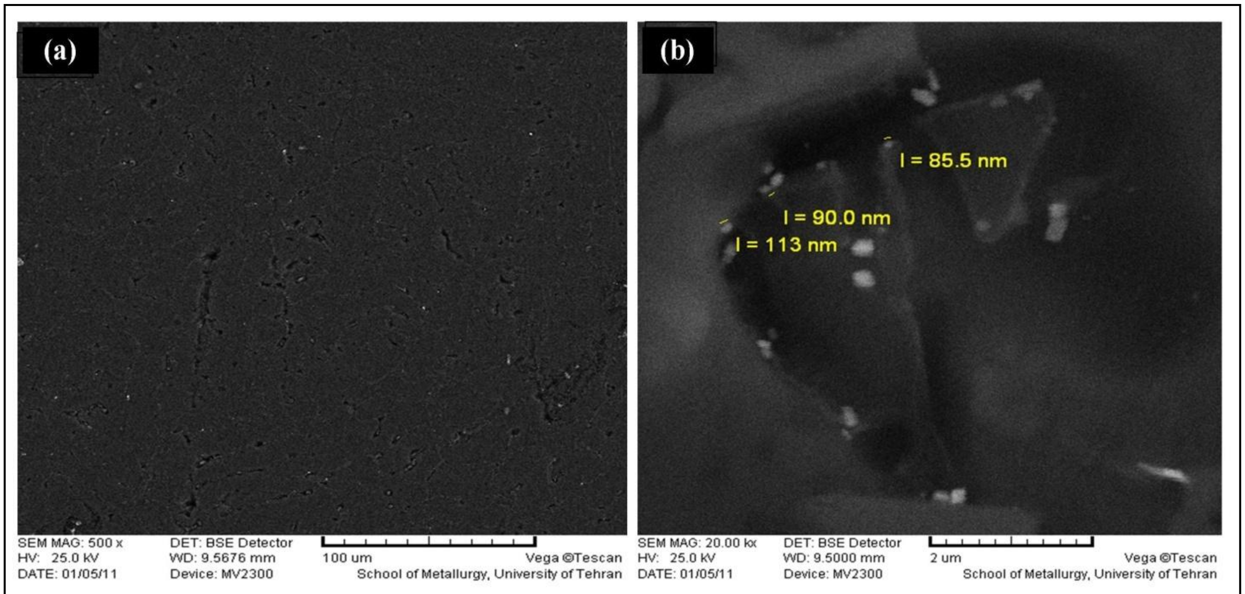

Fig.5. SEM micrographs of Al356/ZrO_2 composite specimens with 1.5 vol. % ZrO_2 and prepared at 850^{o}C at different magnifications: a) 500X and b) 20.00kX.

Presence of ZrO_2 nano particles in Al356 alloy resulted in enhancement of mechanical properties such as hardness and compressive strength values. Considering that the hardness values of the ZrO_2 (for composites samples with 0.75 and 1.5 Vol. % of ZrO_2 are 58 and 50 BHN, respectively) is higher than the matrix alloy (45 BHN), improvement in hardness properties of composites would occur by presence of ZrO_2 nano particles. Also, with increasing the volume percent of ZrO_2 reinforcement particles, the values of the compressive strength (for composites samples with 0.75 and 1.5 Vol. % of ZrO_2 are 736 and 810 MPa, respectively) compared with unreinforced matrix alloy (700 MPa), increased. This enhancement seems to be related to work-hardening behavior. This could be because of elastic properties effects of ceramic particles and inhibition response of plastic deformation of matrix.

CONCLUSION

A nitrate-glycine gel was prepared from metal nitrates and fuel by a sol-gel auto-combustion process in order to synthesize ZrO_2. The well-crystalline ZrO_2 was produced when pH=7. So, it was necessary to adjust appropriate pH to produce pure ZrO_2. The grain sizes of the prepared nano particles were found to be about 38 nm. The particles have been calcined at 650°C for 4 h. Then the product was placed in ultrasonic bath of n-propanol for 15 min. SEM results showed that the grains were regular sphere-shaped nano particles. The XRD data shows ZrO_2 nano powders have monoclinic structure.

Also aluminum alloy was successfully reinforced with monoclinic ZrO_2 nano powders having the grain size of about 38 nm, and A356/ZrO_2 composite were produced at 850°C. High hardness of ZrO_2 increases the hardness of Al-ZrO_2 composite. Also, the compressive strength of Al-ZrO_2 composite was increased comparing with unreinforced Al matrix.

REFERENCES

[1] Park S., Vohs J. M., Gorte R. J., (2000), Direct oxidation of hydrocarbon in a solidoxide fuel cell, *Nature* (404): 265-269.

[2] Li. Y. W., He D. H. Chang Z. X., Su C. L., Li J. R., Zhu M. J., (2001), Effect of calcium salts on isosynthesis over ZrO_2 catalysts, *Mol. Catal. A* (175): 267-271.

[3] Subbarao E. C., Maiti H. S., (1988), Science and technology of zirconia, *Adv. Ceram*., (24): 731-737.

[4] Zhang Q., Shen J., Wang J., Wu G., Chen L., (2000), Sol-gel derived ZrO_2-SiO_2 highly reflective coatings, *Int. J. Inorg. Mater*. (2): 319-322.

[5] Wright P. K., Evans A. G., (1999), Mechanisms govering the performance of thermal barrier coating, *Curr. Opin. Solid State Mater. Sci*, (4): 25-30.

[6] Piconi C., Maccauro G., (1991), Zirconia as a ceramic biomaterial, *Biomaterials*, (20): 1-6.

[7] Salas P., Roza-Cruz E. D., Diaz-Torres L. A., Castano V. M., Melendrez R., Barboza-Flores M., (2003), Monoclinic, ZrO_2 as a broad spectral response thermoluminescence UV desmeter, Radiat. *Meas*. (37): 187-193.

[8] Somiya S., Yamamato N., Yanagina H., Science and Technology of Zirconia(III), American Ceramic Society, vol. 24A and 24B, 1988, *Westerville*.

[9] Li G., Li W., Zhang M., Tao K., (2004), Characterization and catalytic application of homogenous nano-composite oxides ZrO_2-Al_2O_3, *Catal. Today* (93): 595-603.

[10] Tuan W. H., Chen J. R., Ho C. J., (2008), Critical zirconia amount to enhance the strength of alumina, *Ceram. Int*. (34): 2129-2133.

[11] Gao P., Meng L. J., Dos Santos M. P., Teixeira V., Andritschky, (2000), Study of ZrO_2-Y_2O_3 films prepared by rf magnetron reactive sputtering, *Thin Solid Film* (377): 32-35.

[12] Mc Cormick P. G., Tsuzuki T., Robinson J. S., Ding J., (2001), Nanopowders synthesized by mechanochemical processing, *Adv. Mater*. (13): 1008-1112.

[13] Gole J. L., Prokes S. M., Stout J. D., Glembocki O. J. Yang R., (2006), Unique properties of selectively formed zirconia nano structures, *Adv. Mater*. (18): 644-649.

[14] Kumari L., Du G. H., Li W. Z., Selva Vennila R., Saxena S. K., Wang D. Z., (2009), Synthesis, microstructure and optical characterization of zirconium oxide nano structures, *Ceramics International* (35): 2401-2408.

[15] Pradeep A., Priyadharsini P., Chandrasekaran G., (2008), Production of single phase nano size $NiFe_2O_4$ particles using sol-gel auto combustion route by optimizing the preparation conditions, *Materials Chemistry and Physics* (112): 572-576.

[16] Somiya S., Akiba T., (1999), Hydrothermal zirconia powders: a bibliography, *J. Eur. Ceram. Soc*., (19): 81-85.

[17] Kocazac M. J., Khatri S. C., Allison J. E., Bader M. G., MMCs for ground vehicle, aerospace and industrial applications. In: Suresh, et al, editor. Fundementals of metal matrix composites. *Grildford, UK: Butterworth*, 1993,. 297-303.

[18] Rohatgi P. K., (1991) Cast aluminium matrix composites for automotive applications, *J. Mrt.* 43 (4): 10-15.

[19] Chadwich G. A., Heath P. J., (1990), Machining of metal matrix composites, *Met. Mater*. (2-6): 73-76.

[20] Sahin Y., (1998), The effect of sliding speed and microstructure on the dry wear properties of metal-matrix composites, *Wear* (214): 98-106.

[21] Zamzam M., Ros D., Grosch J., (1993), Fabrication of P/M in situ fibre composite materials part-I: formation of fibrous structure, *Key. Eng. Mater*. (79-80): 235-246.

[22] Mortensen A., Michaud V. J., Flemings M. C., (1993), Pressure infiltration processing of reinforced aluminium, *J. Met*. 45 (1): 36-43.

[23] Cooke P. S., Werner P. S., (1991), Pressure infiltration casting of metal matrix composites, *Mater. Sci. Eng. A* (44): 189-193.

[24] Kok M., (1999), Ph. D. Thesis, The Istitute of Science and Technology of Elazig University, Turkey.

[25] Cornie A., Moon H. K., Fleminges M. C., (1990), A review of semi-solid slurry processing of Al matrix composites, International Conference on fabrication of particle reinforced MMCs, Montreal, Canada, September 17-20: 63-78.

[26] Chong Y., Atkins H. V., Jones H., (1993), Effect of ceramic particle size, melt superheat, impurities and alloy conditions on threshold pressure for infiltration of SiC powder compacts by al-based melts, *J. Mater. Sci. Eng A* (173): 232-237.

[27] Fukunaga H., Goda K., (1984), Fabrication of fibre-reinforced metal by squeeze casting, Bull. *JSME* 27 (228): 1245-1250.

[28] Bardal A., (1992), Wethability and interface reaction producing in the AlSiMg surface oxidized SiC system, *J. Mater. Sci. Eng. A* (159): 119-123.
[29] Lyod D. J., (1994), Particle-reinforced aluminium and magnesium matrix composites, *Int. Mater. Rev*. 39 (1): 1-23.
[30] Mansur L. J., Mortensen A., Cornic J. A., Flemings M. C., (1998), Infiltration of fibrous performs by a pure metal, part(II)-experiment, *Metall. Trans 20 (A)*: 2547-2553.
[31] Zhang Z., Long S., Flower H. M., (1994), Light alloy composite production by liquid metal infiltration, *Composites* 25 (5): 380-392.