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COMPOSITES THEORY AND PRACTICE

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PROBLEMS FABRICATING CAST MAGNESIUM MATRIX COMPOSITES WITH ALUMINOSILICATE CENOSPHERES

The problems with fabricating magnesium matrix composites with aluminosilicate cenospheres were demonstrated. Two casting methods, typical stir-casting and vacuum casting processes were chosen to obtain AZ91 magnesium matrix composites with hollow cenospheres 63÷125 μm in diameter. In both methods, violent reactions between the components precluded the fabrication of the desired composites with undestroyed cenospheres. The main reaction products were oxides and an Mg_2Si compound. The creation of a Ni-P coating on aluminosilicate cenospheres (by electroless plating method) in connection with the application of the vacuum casting process allowed the authors to obtain composites with cenospheres not filled by the matrix alloy. The proposed solution contributed to the fabrication of composites characterized by about 60 vol.% uniformly distributed cenospheres and a final material density equal to about 1.16 g/cm^3.

Keywords: **magnesium matrix composites, aluminosilicate cenospheres, fabrication processes, microstructure**

PROBLEMY WYTWARZANIA ODLEWANYCH KOMPOZYTÓW MAGNEZOWYCH Z MIKROSFERAMI GLINOKRZEMIANOWYMI

Przedstawiono problem z wytwarzaniem kompozytów magnezowych z mikrosferami glinokrzemianowymi. Zastosowano dwie metody odlewnicze, tj. mechanicznego mieszania oraz infiltracji podciśnieniowej, do otrzymania kompozytów na osnowie stopu magnezu AZ91 z pustymi wewnętrznie mikrosferami o średnicy 63÷125 μm. W obu metodach gwałtowne reakcje pomiędzy komponentami uniemożliwiały wytworzenie pożądanych kompozytów z nieuszkodzonymi mikrosferami. Głównymi produktami reakcji były tlenki oraz związek Mg_2Si. Wytworzenie warstwy Ni-P na mikrosferach glinokrzemianowych (metodą bezprądowego osadzania) w połączeniu z metodą infiltracji podciśnieniowej pozwoliło na otrzymanie kompozytów z mikrosferami niewypełnionymi stopem osnowy. Proponowane rozwiązanie pozwoliło na wytworzenie kompozytów charakteryzujących się równomiernym rozmieszeniem 60% obj. mikrosfer i końcową gęstością materiału równą około 1,16 g/cm^3

Słowa kluczowe: **kompozyty magnezowe, mikrosfery glinokrzemianowe, proces wytwarzana, mikrostruktura**

INTRODUCTION

Cenospheres in fly ashes (FAs) from coal-fired thermo-electric powder stations are hollow thin-walled spheres of a size from several tens of microns to 500 μm. According to their chemical composition, these light materials belong to a multicomponent system with an $SiO_2 + Al_2O_3 + Fe_2O_3$ content of approximately 90 wt.%. The remaining 10% belongs to the CaO-MgO-Na_2O-K_2O-TiO_2 system. In their mineral phase composition, cenospheres belong to glass-ceramic materials based on aluminosilicate glass, mullite, quartz, calcite, Fe oxides, as well as Ca silicates and sulphates. Cenospheres are spherical in shape (sphericity is close to 100%) and have a true density of 0.4÷0.6 g/cm^3. Because of their specific porous structure and metallic nature, they posses several functional properties like sound absorption, vibration reduction or fire proofing [1-4]. In recent years, cenospheres have started to be used as reinforcement in metal matrix composites in order to reduce the cost and weight of these materials. In this case, aluminium or magnesium alloys are chosen as the matrix [5-13]. Dowund et al. [9] prepare the composites on the base of the ZC63 magnesium alloy with cenospheres by the casting method. Zhi-giu et al. [12] prepared by the stir-casting method a composite on the base of the AZ91D magnesium alloy. On the other hand Rohatgi et al. [10] proposed incorporating fly ash cenospheres in die cast the AZ91D magnesium alloy. The main problem during the production of these composites is the violent reaction between the liquid matrix alloy and the cenospheres or fractured cenospheres during the composite production process. Finally, the microstructures of the obtained composites were characterised very often by cenospheres filled with the matrix alloy. The different results proved that cenospheres may also fracture as a result of the stresses during composite handing and processing. One of the possibilities to reduce the reaction between the components during fabricating cast metal matrix composites is the creation of cenosphere coatings. Electroless plating is a favourite method for several deposition technologies, such as physical and chemical vapour deposition or sputtering plating [14-16]. In this paper, composites based on the AZ91 magnesium matrix alloy with uncoated and Ni-P coated cenospheres fabricated by two casting methods were presented.

MATERIALS AND EXPERIMENTAL PROCEDURES

The as-received hollow cenospheres were supplied by the Opole electric power station, Poland, with the chemical composition presented in Table 1. The particle size distribution varies from 63÷125 μm. The Ni-P coating on the cenospheres was performed by the electroless plating method described in [17]. The obtained Ni-P layers on the cenospheres was equal to about 0.4 μm. Figures 1a and b present the SEM images of uncoated and Ni-P coated cenospheres, respectively. In order to confirm the presence of the Ni-P layer on the cenospheres, XRD analyses were conducted (Brucker D8 Advance diffractometer; $Cu_{K\alpha}$ radiation). A comparison of the X-ray diffraction patterns obtained from uncoated and coated cenospheres is presented in Figure 2. The commercial AZ91 magnesium alloy with the chemical composition given in Table 2 was used as the matrix alloy. The composites were fabricated by the stir-casting and vacuum casting methods. The parameters of both processes were chosen experimentally for each composite material. Microstructure examinations were performed by light and scanning electron microscopes (JOEL JSM-6610LV and JSM-5400). The Raman spectroscopy method was used to identify some structural constituents (spectrometer ENWAVE, EZRaman-L, laser source: 50 mW, wavelength: 785 mm, laser spot size: about 3 μm). The density of the fabricated composites was investigated by the pycnometer method in ethyl alcohol.

TABLE 1. **Chemical composition of used cenospheres**
TABELA 1. **Skład chemiczny zastosowanych mikrosfer**

Chemical composition [mas.%]						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O+Na_2O	TiO_2
53÷63	21÷31	4.4÷5.6	1.5÷2.5	0.3÷0.7	0.8÷1.6	0.1÷0.7

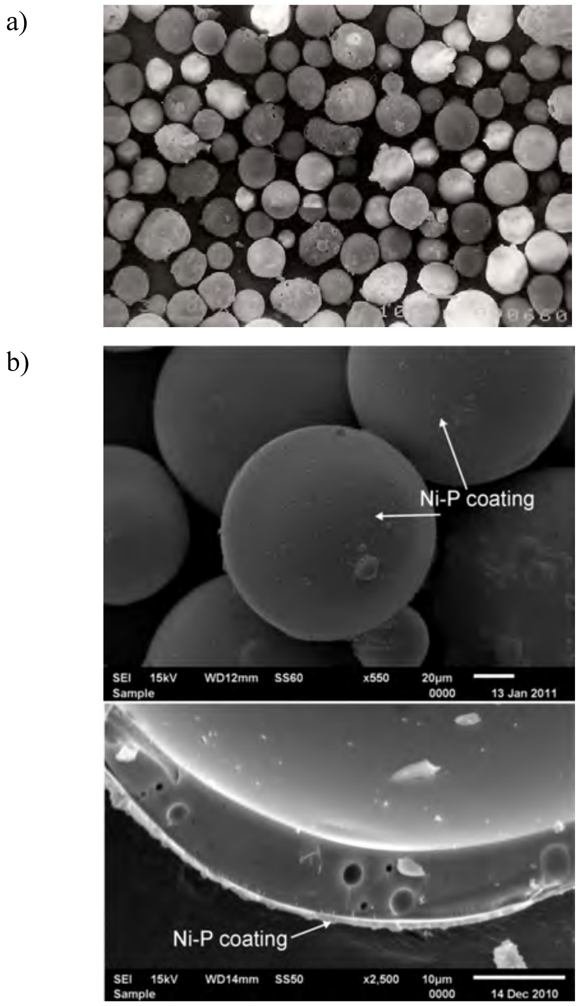


Fig. 1. SEM images of used aluminosilicate cenospheres: a) uncoated, b) Ni-P coated

Rys. 1. Obrazy SEM użytych mikrosfer glinokrzemianowych: a) niepokrytych, b) pokrytych warstwą Ni-P

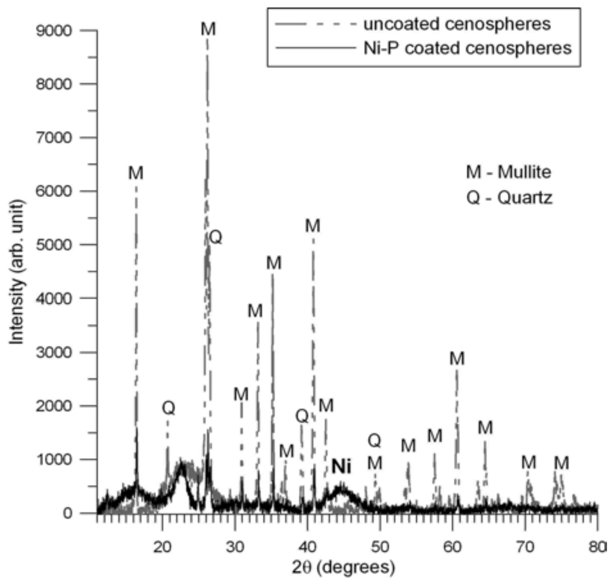


Fig. 2. X-ray diffraction patterns obtained from uncoated and Ni-P coated cenospheres

Rys. 2. Dyfraktogramy rentgenowskie otrzymane dla niepokrytych oraz pokrytych warstwą Ni-P mikrosfer

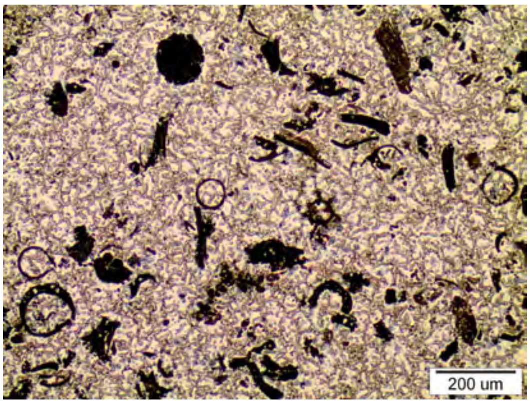
TABLE 2. **Chemical composition of AZ91 matrix alloy (according to ASTM B93-94)**
TABELA 2. **Skład chemiczny stopu osnowy AZ91 (zgodnie z ASTM B93-94)**

Chemical composition [mas.%]*						
Al	Zn	Mn	Si	Fe	Cu	Ni
8.5÷9.5	0.45÷0.9	0.17÷0.04	max. 0.005	max. 0.005	max. 0.003	max. 0.002
* Mg rest						

RESULTS AND DISCUSSION

The microstructures of the AZ91 magnesium matrix composites with uncoated aluminosilicate cenospheres fabricated by the stir-casting and vacuum casting methods are presented in Figures. 3a and b, respectively. Figure 3 shows that in both cases, a large percentage of cenospheres are cracked and filled with the matrix alloy during fabrication.

a)



b)

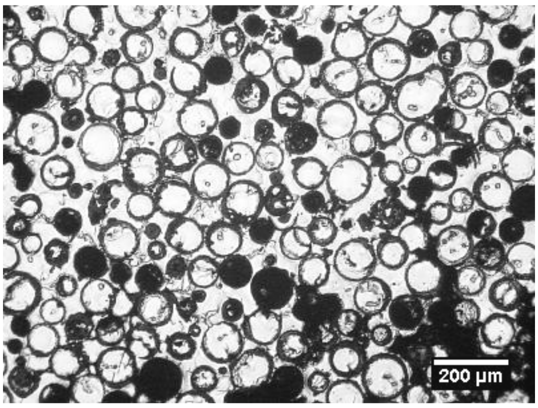
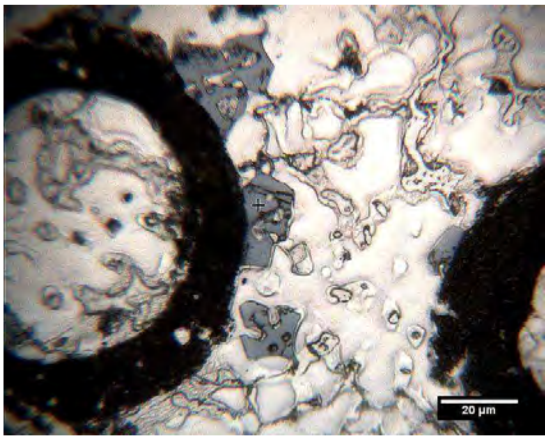


Fig. 3. Microstructures of composites with uncoated aluminosilicate cenospheres fabricated by stir-casting method (a) and vacuum casting method (b)

Rys. 3. Mikrostruktura kompozytów z niepokrytymi mikrosferami glinokrzemianowymi wytwarzanych metodą mechanicznego mieszania (a) i infiltracji podciśnieniowej (b)

The analogical results were obtained by fabricating different metal matrix composites with cenospheres [5-13]. It should be noted that very violet reactions between the components proceeded during both fabrication processes. The molten magnesium matrix reacted with the oxides present in the cenosphere walls, which result in strong exothermic reactions and cenosphere cracking. As was concluded from the investigations, the main reaction products were oxides and the Mg_2Si compound. The presence of this phase in the fabricated composites was confirmed by Raman spectroscopy (Fig. 4), on the basis of [18-20] data. This structural constituent was also observed in magnesium matrix composites with fly ashes fabricated by different authors, [12, 13]. Additionally, during the stir-casting method of composite fabrication, cenosphere cracking is possible due to the mechanical mixing of the composite suspension.

a)



b)

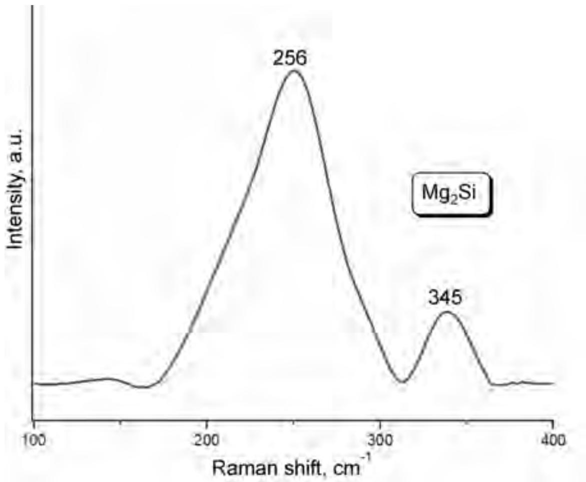
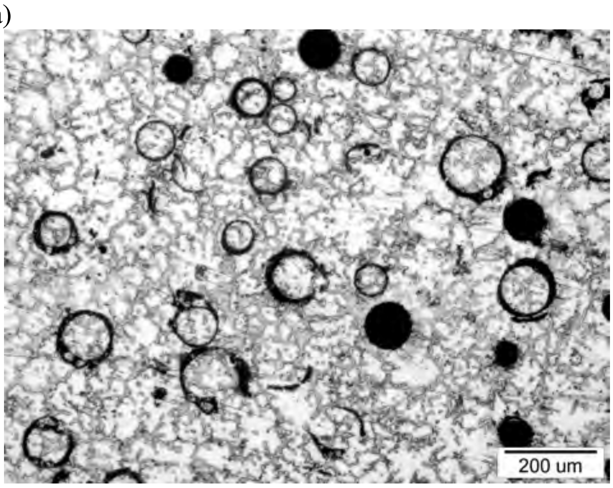


Fig. 4. Microstructure of composites with uncoated aluminosilicate cenospheres fabricated by stir-casting method (a), Raman spectra for observed structural constituent (b)

Rys. 4. Mikrostruktura kompozytów z niepokrytymi mikrosferami glinokrzemianowymi wytwarzanych metodą mechanicznego mieszania (a), widmo Ramana dla obserwowanego składnika struktury (b)

Figures 5a and b show the photomicrographs of AZ91 matrix composites with Ni-P coated aluminosilicate cenospheres fabricated by the stir-casting and vacuum casting methods, respectively. In the case of composites fabricated by the stir-casting method, a large part of cenospheres was still infiltrated by the matrix alloy. It should be noted that the application of Ni-P coated cenospheres negligibly improved the obtained composites microstructure. The desired composite microstructure was obtained by the vacuum casting method.

a)



b)

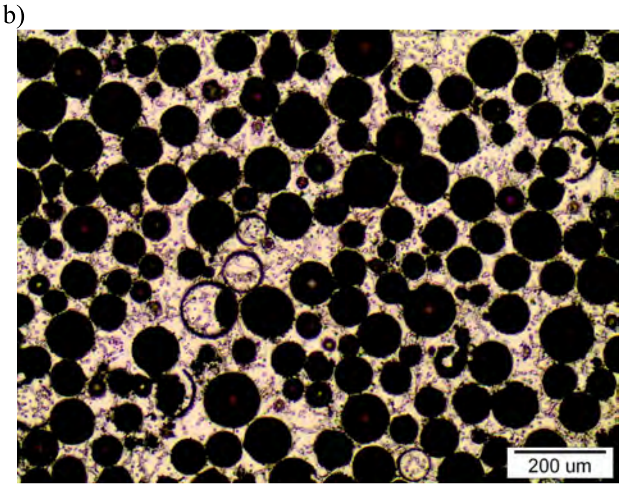
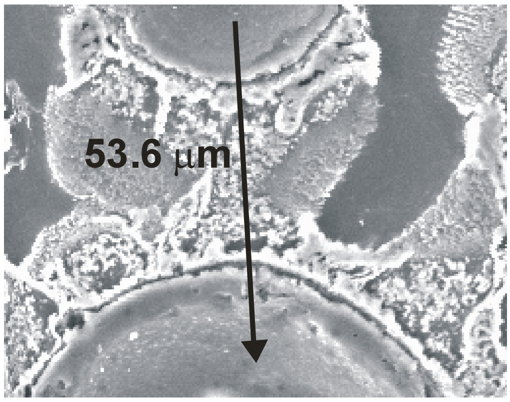


Fig. 5. Microstructure of composites with Ni-P coated aluminosilicate cenospheres fabricated by stir-casting method (a) and vacuum casting method (b)

Rys. 5. Mikrostruktura kompozytów z pokrytymi warstwą Ni-P mikrosferami glinokrzemianowymi wytwarzanych metodą mechanicznego mieszania (a) i infiltracji podciśnieniowej (b)

The application of Ni-P coated cenospheres and this fabrication process allowed us to obtain a microstructure with non-filled (hollow) cenospheres, uniformly distributed in the magnesium matrix alloy. Figure 6 shows the linear distribution of the main elements in the composite microstructures. The Ni-P coating prevented reactions between the cenospheres and molten matrix alloy. The short time of contact between the cenospheres and the melted matrix alloy during the vacuum casting process guaranteed a stable interface between the components. The application this technique (and Ni-P coated component), allowed us to obtain composites with about 60 vol.% cenospheres (Fig. 5b). The mean density of this material was equal to about 1.16 g/cm^{-3}.

a)



b)

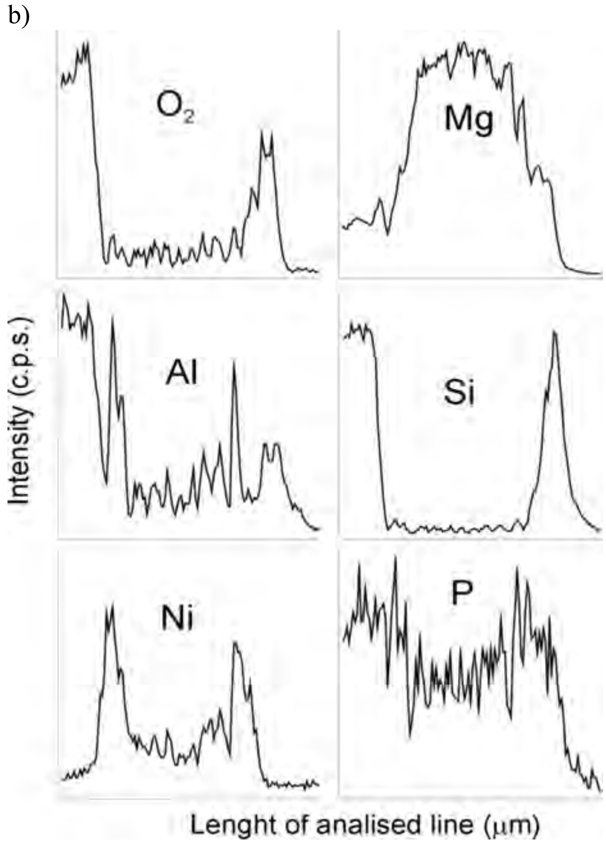


Fig. 6. SEM image of composite with Ni-P coated aluminosilicate cenospheres fabricated by vacuum casting method (a) and linear distribution of main elements SEM+EDX (b)

Rys. 6. Obraz SEM kompozytu z pokrytymi warstwą Ni-P mikrosferami glinokrzemianowymi wywarzonego metodą infiltracji podciśnieniowej (a) wraz z rozkładem liniowym głównych pierwiastków SEM+EDX (b)

CONCLUSIONS

1. Obtaining magnesium matrix composites with a high volume fraction of non-filled (non-fractured) aluminoslilicate cenospheres by casting methods is practically impossible due to violent reactions between the molten matrix alloy and oxides present in the cenosphere walls.
2. The application of Ni-P coated cenospheres in connection with the vacuum casting process allowed us to obtain composites with a high volume fraction (about 60 vol.%) of hollow cenosperes.

3. The fabricated AZ1 magnesium matrix composites with aluminosilicate cenospheres are characterized by uniformly distributed components and a density equal to about 1.16 g/cm^{-3}.

REFERENCES

[1] Vassilev A.V., Menedez R., Alvarez D., Diaz-Somoano M., Martinez-Tarazona M.R., Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 1. Characterization of feed coals and fly ashes, Fuel 2003, 82, 1793-1811.

[2] Vassilev A.V., Menedez R., Alvarez D., Diaz-Somoano M., Martinez-Tarazona M.R., Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 1. Characterization of ceramic cenosphere and salt concentrates, Fuel 2004, 83, 585-603.

[3] Pichór W., Mars K., Godlewska E., Mania R., Mechanical Properties of metal-coated cenospheres, Kompozyty (Composites) 2010, 10(1), 149-153.

[4] Pichór W., Properties of electroless Cu coated fly-ash cenospheres particles for smart cement-based composites, Kompozyty (Composites) 2009, 9(2), 164-169.

[5] Deqing W., Ziyan S., Hong G., Lopez H.F., Synthesis of lead-fly-ash composites by squeeze infiltration Journal of Materials Synthesis and Processing 2001, 9, 247-251.

[6] Roghtai P.K., Guo R.Q., Iksan H., Borchelt E.J., Asthana R., Pressure infiltration technique for synthesis of aluminum-fly ash particulate composite, Materials Science and Engineering 1998, 244A, 22-30.

[7] Długosz P., Darłak P., Purgert M.R., Sobczak J., Synthesis of light composites reinforced with cenospheres, Kompozyty (Composites) 2011, 11(4), 288-293.

[8] Zahi S., Daud A.R., Fly ash characterization and application in Mg-based Mg alloys, Materials and Design 2011, 32, 1337-1346.

[9] Daoud A., About El-khair M.T., Abdel-Aziz M., Rohatgi P., Fabrication, microstructure and compressive behavior of ZC63 Mg-microballoon foam composites, Composites Science and Technology 2007, 67, 1842-1853.

[10] Roghati P.K., Daoud A., Schultz B.F., Puri T., Microstructure and mechanical behavior of die casting AZ91D-Fly ash cenosphere composite, Composites: Part A, 2009, 40, 883-896.

[11] Rohatgi P.K., Kim J.K., Guo R.Q., Robertson D.P., Gajdardzinska-Jasifovska M., Age-hardening characteristics of aluminum alloy-hollow fly ash composites, Metallurgical and Materials Transaction A 2002, 33A, 1541-1547.

[12] Zhi-giu H., Si-rong Y., Mu-gin L., Microstructure and compressive properties of AZ91D/fly-ash cenospheres composites, Transactions of Nonferrous Metals Socitey of China 2010, 20, 458-462.

[13] Liu J.A., Yu S.R., Huang Z., Ma G., Liu Y., Microstructure and compressive property of in situ Mg_2Si reinforced Mg-microballoon composites, Journal of Alloys and Compounds 2012, 537, 12-18.

[14] Aixiang Z., Weihao X., Jian X., Electroless Ni-P coating of cenospheres using silver nitrate activatior, Surface and Coating Technology 2005, 197, 142-147.

[15] Zhang Q., Wu M., Zhao, Electroless nickel plating on hollow glass microspheres, Surface and Coating Technology 2005, 19, 213-219.

[16] Meng X., Li D., Shen X., Liu W., Preparation and magnetic properties of nano-Ni coated cenosphere composites, Applied Surface Science 2010, 156, 3753-3756.

[17] Kamieniak J., AZ91 magnesium matrix composites with aluminosilicate cenospheres, Doctoral Thesis, Czestochowa University of Technology, Czestochowa 2012.

[18] Zlateva G., Atanssov A., Baleva M., Nicolova L., Raman scattering characterization of ion-beam synthesized Mg_2Si, On the orientation growth of Mg_2Si phase in (001) and (111) Si substrates, Plasma Processes and Polymers 2005, 3, 224-228.

[19] Zlateva G., Atanssov A., Baleva M., Nicolova L., Abrashev M.V., Polarized micro-Raman scattering characterization of Mg_2Si nanolayers in (001) Si matrix, Journal of Physics and Biophysics 2007, 19, 210-220.

[20] Atanssov A., Zlateva G., Baleva M., Goranova E., Amov B., Raman scattering characterization of ion-beam synthesis Mg_2Si, Influence of the technological conditions on the formation of the Mg_2Si in (100) Si matrix, Plasma Processes and Polymers 2006, 3, 219-223.

