



The 4th International Conference
"Advanced Composite Materials Engineering"
COMAT 2012
18- 20 October 2012, Brasov, Romania

MICROSTRUCTURAL CHARACTERIZATION OF AlSi7Mg/AlN AND AlSi12Mg/SiC COMPOSITES OBTAINED BY REACTIVE GAS INJECTION METHOD

D. Mitrica¹, V. Soare¹, I. Constantin¹, F. Stoiciu¹, G. Popescu²

¹ National R&D Institute for Nonferrous and Rare Metals, Pantelimon, ROMANIA, dmitrica@imnr.ro, vivisoare@imnr.ro, iconstantin@imnr.ro, fstoiciu@imnr.ro

² University "POLITEHNICA" of Bucharest, Bucharest, ROMANIA, gabriela81us@yahoo.com

Abstract: The paper studies the microstructural and chemical characterization of in-situ AlSi7Mg/AlN and AlSi12Mg/SiC composites obtained by the injection of reactive gases (CH₄ and N₂) in aluminum alloy melt. The samples were characterized using optical microscopy, X-ray diffraction and SEM. The chemical composition was determined by inductive coupled plasma spectrometry. Samples taken from different parts of the product revealed uneven compositional distribution of reinforcements and primary silicon in the alloy matrix. In the upper side of the products was found a significant enrichment of the reinforcing particles, for both composite systems, caused by the small dimensions of the particles and the upward movement of the injected gas, during the bubbling process. Optical micrographs revealed SiC and AlN particles of irregular shapes and small sizes (<10µm).

Keywords: composites, in-situ, SiC, AlN

1. INTRODUCTION

Composite materials possess remarkable mechanical properties (yield strength, stiffness, hardness and resilience), high temperature stability and a reduced specific weight. The special properties of composite materials make them attractive for applications as structural and functional materials, if conventional materials do not reach the specific demands.

Particle reinforced aluminum metal matrix composites are known for their high strength to weight ratio. Examples of applications for these products range from expensive satellites and aerospace structures to sports products. Further development in manufacturing particle reinforced aluminum metal matrix composites created the possibility to obtain large concentrations exceeding 10% by volume of reinforcement (SiC, AlN, Al₂O₃, etc.). The improvement of the strength and wear resistance at elevated temperatures of the composites, made them appropriate for the use in automotive applications, such as the pistons, rotors, disc brakes, and propeller shafts [1]. But, in order to benefit from the advantages of the composite materials a reasonable production cost – performance relationship must be obtained [2]. Recent innovations in the manufacturing of aluminum-based metal matrix composites provided material quality improvements but no feasible solutions for lowering the present high price of the final product.

One solution that can produce new stable composites for advanced structural and wear applications is represented by the in-situ methods for manufacturing of metal-matrix composites (MMCs) [3]. In this type of process a part of the starting metal or alloy is used as a reactive element for the obtaining of secondary phase particles by the interaction with highly reactive gases or solids. Thermodynamically stable reinforcing particles are obtained by in situ processing and the interface incompatibilities are eliminated. A fundamental characteristic of the in situ methods is that the nucleation and growth of the reinforcing particles occur in the matrix. Depending on the nature of the base alloy a wide range of oxides, nitrides, carbides, borides and silicides can be obtained [4].

Various trials, with successful, have been performed for producing in-situ MMC by different methods (SHS, DIMOX, XD, PRIMEX, RD, Mixalloy, Osprey, Direct nitridation, Mixed Salt Reaction, [4,5,6]), reactive plasma synthesis in [7], casting [8], rapid solidification [9,10], DERP [11,12], magnetochemistry reaction [13], reactive gas injection (RGI) [14,15,16,17], etc..

The synthesis of aluminium metal matrix composites (AIMMC) by reactive gas injection (RGI) was first proposed by Kocsak and Kumar [14]. This is a relatively simple method where the reinforcing particles are obtained in-situ from the reaction of the injected gas with the molten matrix alloy. Various systems have been investigated in the past, with CH_4 , N_2 , NH_3 , or a mixture of these as the reactive gas and the molten alloy was composed of Al, Si, Ti, Ta, etc. Wu and Reddy [15] studied the synthesis of Al-Si/SiC composites by RGI method. The research results indicated the presence of a large quantity of reinforcement (30 wt.%) in a solidified foam composite collected in a tray under the crucible, composite obtained by overflowing of the melt during the bubbling process. The SiC reinforcing particles were agglomerated around the primary silicon formations, had irregular shapes and were of small sizes (5-10 μm). Q. Zheng and R. G. Reddy [16] investigated the in situ processing of AlN particle reinforced aluminum composites by bubbling nitrogen gas in a pure molten aluminum matrix. The obtained in situ AlN particles were small in size (<5 μm) and were present in the top part of the product formed in the crucible. They concluded that nitrogen gas injection did not lead to the formation of significant AlN due to the deleterious effect of the trace oxygen impurities in the bubbling gas.

C. Borgonovo and D. Apelian [17] also obtained AlN reinforced composites, in an aluminum melt with high magnesium additions. They observed that magnesium acted as an oxygen getter diminishing the content of oxygen in the melt by MgO formation and thus enhancing the nitridation reaction. The size of the particle embedded in the matrix varied from 1- 3 μm to sub-micron scale.

Present paper studies the chemical and microstructural characterization of AlSi7Mg/AlN and AlSi12Mg/SiC composites obtained in situ by injection of reactive gases (CH_4 and N_2) in the alloy melt. The research work is intended to produce in-situ composites without overflowing in a foam state (for SiC synthesis) and using purified nitrogen as precursor gas in conjunction with the addition of a small quantity of magnesium in the initial alloy (for AlN synthesis). The research work investigates the structural particularities of the samples for the two types of MMC systems.

2. EXPERIMENTAL

The schematic diagram of the experimental installation is given in figure 1. A vertical Carbolite resistance furnace with a working temperature of up to 1200°C was used in the experiments. The experiments took place in a sealed reaction chamber which was introduced in the furnace. The reaction chamber was provided with a water cooled lid, protective atmosphere, a thermocouple to record the process temperature, a pressure gauge and a gas flowmeter. An eye hole was provided on the top of the reaction chamber for observing and monitoring the process.

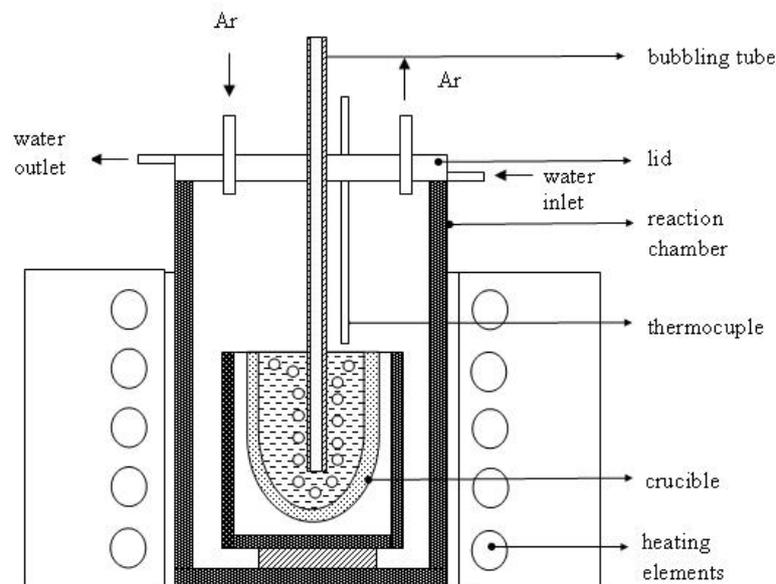


Figure 1. Experimental installation for the in-situ synthesis of AlSi7Mg/AlN and AlSi12Mg/SiC composites

The starting aluminum alloy Al-Si-Mg (300 grams, 7÷12% Si) was placed in a crucible, in the reaction chamber. Before the experiments, the system was evacuated and purged with argon for 30 minutes and was maintained at 0.1 bar during the whole process.

The alloy was melted and maintained at the process temperature (900 - 1200°C) for 30 minutes, before the beginning of the bubbling process. The bubbling tube (high density graphite, 30 cm long) was submersed into the melt close to the bottom of the crucible. The reactive gas was injected in the alloy melt at a constant flow rate, through four nozzles situated at the bottom of the bubbling tube. The entire process was monitored through the eye hole placed on the lid of the reaction chamber. The duration of the bubbling process was estimated from the stoichiometric relationship between initial materials and expected reinforcement percentage. At the end of the bubbling process, the resulting material was left in the furnace to cool at room temperature. The obtained material was then prepared for chemical and microstructural characterization.

The chemical analysis was performed using an optical emission plasma spectrometer – DCP, Spectraspan V-Beckman – Germany. The SiC and AlN quantity was determined by the investigation of the carbon and nitrogen content with a Leybold Heraeus CS 5003 gas analyzer and calculated from the stoichiometry of the SiC and AlN formation reactions.

The metallographic characterization of the samples was effectuated with a Zeiss Axio Scope A1m Imager microscope, with bright field, dark field, DIC and polarization capabilities, and high-contrast EC Epiplan 10X/50X/100X lenses. The micrographs were captured with a polarised camera provided with the equipment.

The SEM-EDAX analyses were performed using a FEI Quanta Inspect F scanning electron microscope, provided with field emission and a dispersive energy analysis system (EDS).

The X-ray diffraction characterization of the samples was performed using a BRUKER D8 DISCOVER X-ray diffractometer. The obtained data was processed using the FPM (Full Pattern Matching) module from the DIFFRACplus BASIC (Bruker AXS) program package and the ICDD PDF-2 Release 2006 database.

3. RESULTS AND DISCUSSIONS

Tables 1 and 2 represent the chemical composition of the two composite samples. The analyses performed on samples taken from the top part of the composites revealed significant concentrations of AlN and SiC. The variation of the magnesium contents with the height of the crucible is due to the bubbling process.

The obtained AlN and SiC quantities were calculated using the values obtained after the nitrogen and carbon determinations in the samples and the molecular ratios of the atomic masses. The analyses performed on samples taken from the top part of the composite products revealed higher concentrations of AlN, SiC, Mg and Si. This is explained by the low surface tension of these substances with the gas bubble, determining their entrainment in the gas flow in the liquid alloy.

Table 1. Chemical composition (%) from different parts of the in-situ AlSi7Mg/AlN product

Level	Si	Mg	AlN	Fe	Cu	Mn	Ti	Al
top	6.87	0.40	4.47	0.10	<0.1	<0.01	<0.001	base
middle	6.27	0.12	2.73	0.12	<0.1	<0.01	<0.001	base
bottom	6.22	0.04	0.71	0.12	<0.1	<0.01	<0.001	base

Table 2. Chemical composition (%) from different parts of the in-situ AlSi12Mg/SiC product

Level	Si	Mg	SiC	Fe	Cu	Mn	Ti	Al
top	12.61	0.59	7.60	0.091	<0.1	<0.01	<0.001	base
middle	12.03	0.36	3.57	0.093	<0.1	<0.01	<0.001	base
bottom	11.40	0.29	0.86	0.061	<0.1	<0.01	<0.001	base

The optical micrographs captured from the upper side of the AlSi7Mg/AlN composite samples (figure 2) indicated the presence of light color Al_{ss} dendrites, black pores generated by the gas, grey Al-Si interdendritic eutectic and AlN particle agglomerations. The reinforcement particles presented irregular shapes, small dimensions and were grouped as clusters and strings at the grain boundaries and in the areas with increased porosity.

In the samples taken from the upper side of the AlSi12Mg/SiC composite products (figure 3), the typical structure of the AlSi12 alloy can be observed (dark grey primary Si and Al-Si eutectic lamellae embedded in α -AlSi) and the presence of in-situ formed SiC particles, separated from the matrix by dark boundaries. The ceramic reinforcing particles were of small sizes (<10 μ m) and with angular contour.

The different distribution of the particles in the two composite systems is explained by the particle/matrix compatibility and the differences in the sizes of the particles.

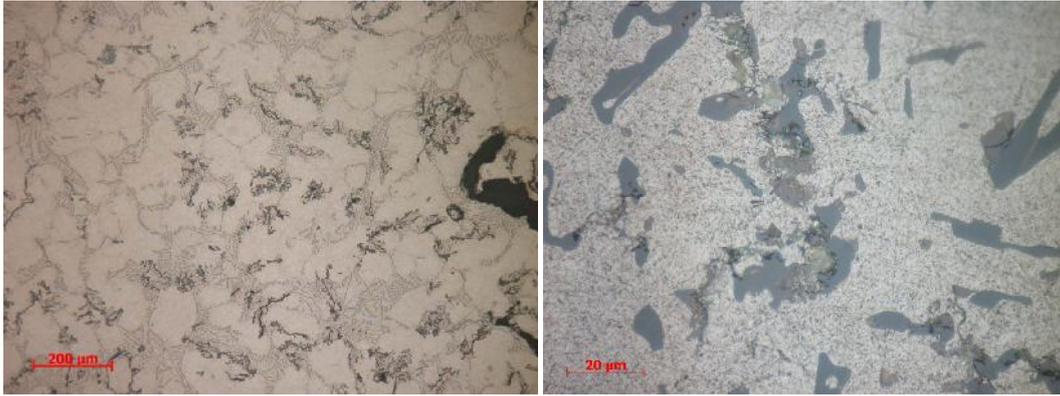


Figure 2. Micrographs of the top part of the AlSi7Mg/AlN composite sample

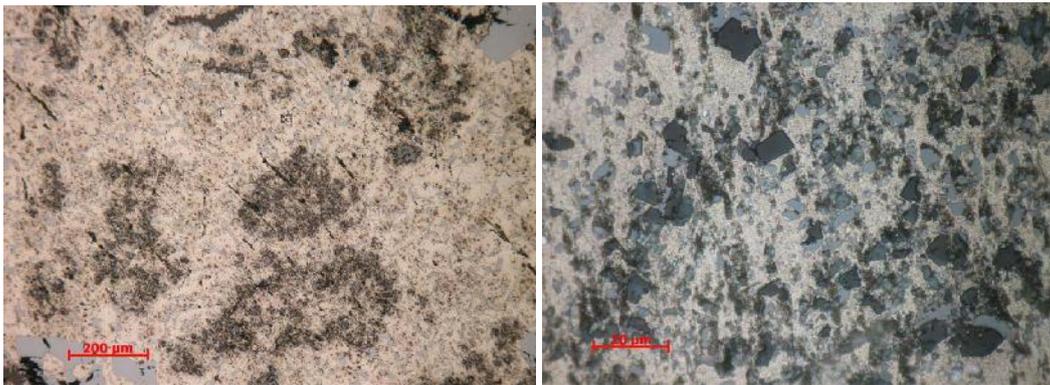


Figure 3. Micrographs of the top part of the AlSi12Mg/SiC composite sample

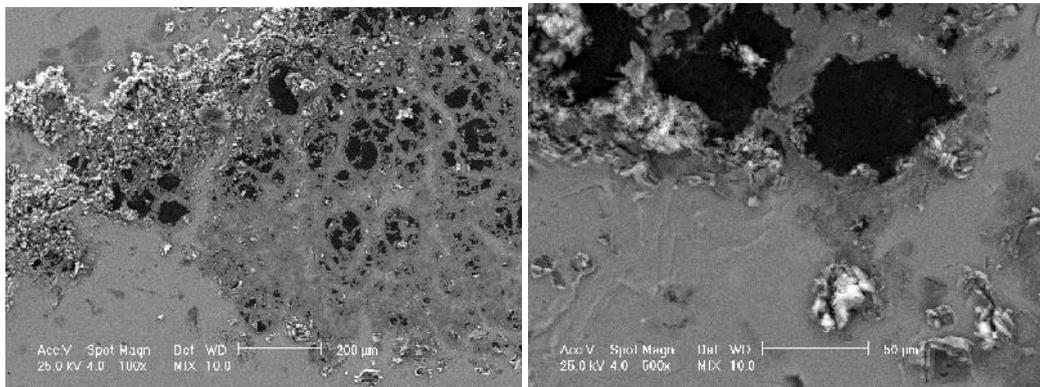


Figure 4. SEM images from top part of the AlSi7/AlN composite sample

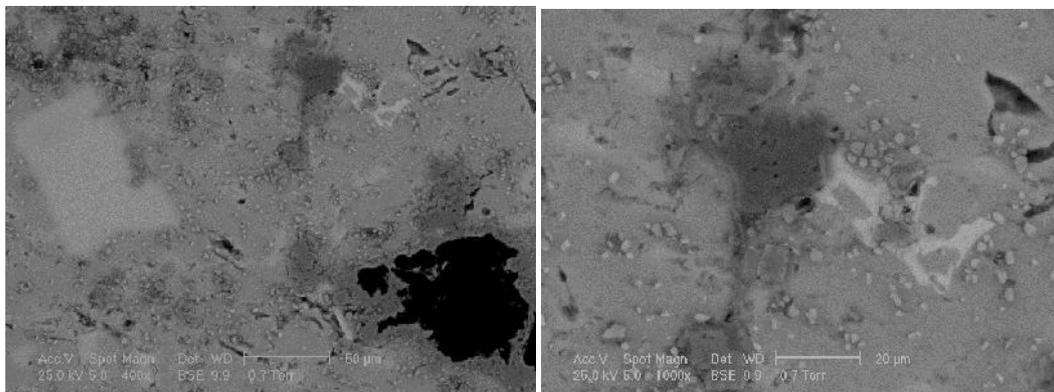


Figure 5. SEM images from the top part of the AlSi12Mg/SiC composite sample.

SEM images revealed dense agglomerations of AlN particles near the areas with high concentration of porosities, in the top part of the AlSi7Mg/AlN composite(Figure 4). The average particle size ranged from 1 to 5µm. SiC particles found in the samples taken from the top part of the AlSi12Mg/SiC composite (Figure 5) present a better distribution in the alloy mass, and they can be clearly distinguished even in lower magnification images.

The X ray diffraction patterns (figures 6 and 7) indicated a phase composition formed of Al-α solid solution, primary Si, Mg₂Si, MgO, spinels, SiC as moissanite and AlN. MgAl₂O₄ spinel is formed mainly as a result of the reaction between the trace oxygen as impurity from the injected gas and the magnesium contained in the melt. The phase composition for both composite system is presented in table 3.

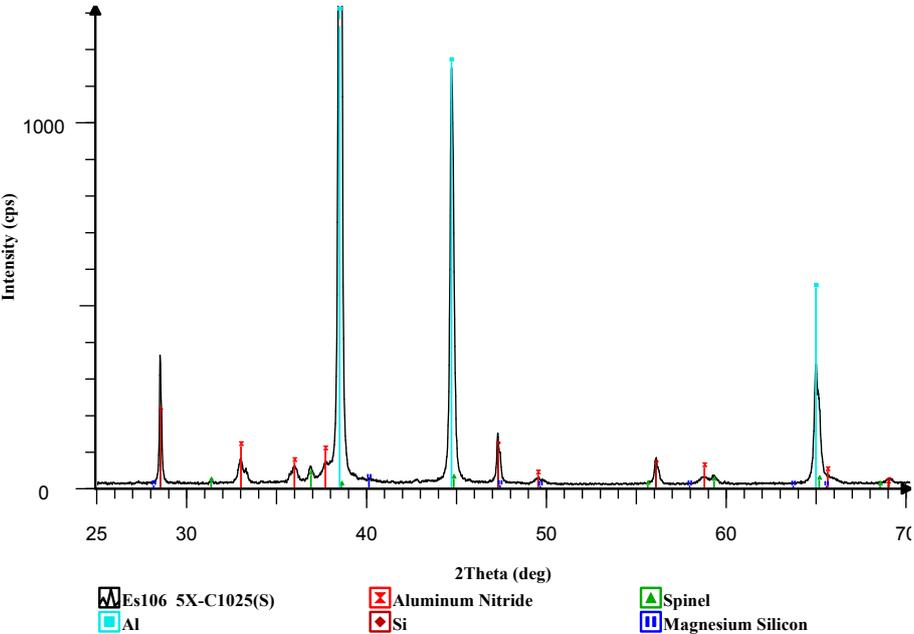


Figure 6. X-ray diffraction pattern of a sample from the top part of the AlSi7Mg/AlN composite sample

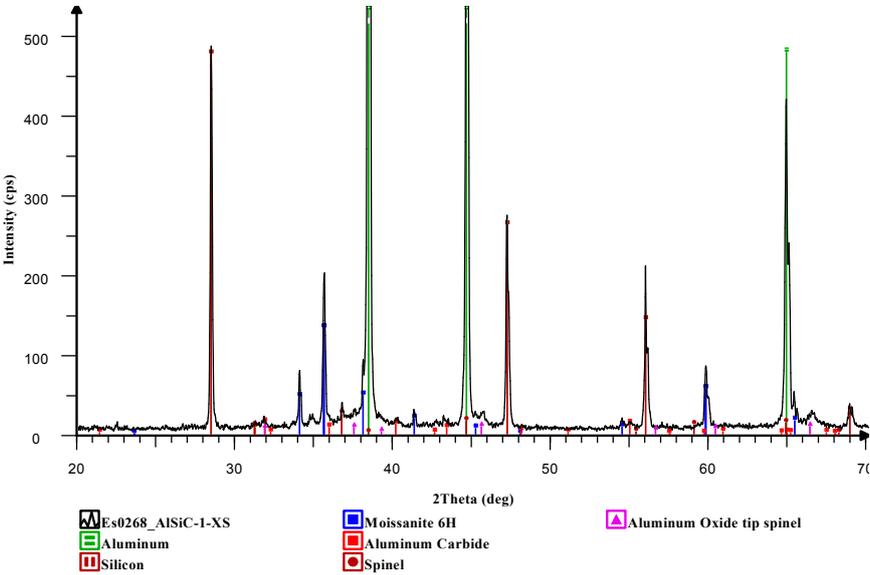


Figure 7. X-ray diffraction pattern of the superior and inferior part of the AlSi12Mg/SiC composite sample

Table 3. Phase composition of the top part of the samples, for both composite systems.

Composite system	AlSi/AlN					AlSi/SiC				
	Al	Si	AlN	MgAl ₂ O ₄	M ₂ Si	Al	Si	SiC	MgAl ₂ O ₄	Al ₂ O ₃
S-Q(wt.%)	82.8	5.2	9.3	2.2	0.5	71.3	12	11.8	1.7	1.7

4. CONCLUSIONS

Aluminum metal matrix composites reinforced with AlN and SiC, obtained in-situ by the reaction of a precursor gas (nitrogen and methane) with matrix alloy, were characterized by chemical analyses, optical microscopy, SEM and X-ray diffraction. The chemical and microstructural investigations indicated a higher concentration of reinforcing particles in the top part of the product. The obtained particles were distinguished as large agglomerations (for SiC) or cluster strings in the grain boundary area (for AlN) and presented small dimensions ($<5\mu\text{m}$ for AlN and $<10\mu\text{m}$ for SiC) and irregular shapes. SEM determinations show different distributions and morphologies of the particles for the two composite systems; and indicate that the agglomeration of AlN particles is more probable in zones with high concentration of micropores. XRD analyses confirmed the formation of AlN and SiC particles in the melt, together with spinels formed by the oxygen impurities from the injected gas.

REFERENCES

- [1] Kainer U. K., Metal Matrix Composites. Custom-made Materials for Automotive and Aerospace Engineering, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
- [2] Suresh S., Mortensen A., Needleman A., Fundamentals of metal matrix composites, published by Butterworth-Heinemann, 1993, pp. 3-22.
- [3] Koczak M.J., Premkumar M.K., Emerging technologies for the in-situ production of MMCs, JOM, vol.45, no.1 (1993), 44-48
- [4] Apelian D., Processing challenges of light weight, high specific strength metallic materials, Worcester Polytechnic Institute.
- [5] Cup C., Shen Y., Meng F., Review on Fabrication Methods of In Situ Metal Matrix Composites, Journal of Materials Science and Engineering, vol. 16, no.6 (2000), 619-626.
- [6] Surappa M. K., Aluminium matrix composites: Challenges and opportunities, Sadhana, vol. 28 (2003), parts 1 & 2 , 319-334.
- [7] Borisov V. G., Ljudmila P. Borisenko, Alexandr V. Ivanchenko, Alexandr P. Bogdanov, Metal for production of metal base composite material, US Patent 5305817, 1994.
- [8] Varin R.A., Intermetallic-Reinforced Light-Metal Matrix In-Situ Composites, Metallurgical and Materials Transactions A, vol. 33A (2002), 193-201.
- [9] Tong X.C., Fang H.S., Al-TiC Composites In Situ-Processed by Ingot Metallurgy and Rapid Solidification Technology: Part I. Microstructural Evolution, Metallurgical and Materials Transactions A, vol. 29A (1998), 875-891.
- [10] Tong X.C., Fang H.S., Al-TiC Composites In Situ-Processed by Ingot Metallurgy and Rapid Solidification Technology: Part II. Mechanical Behavior, Metallurgical and Materials Transactions A, vol. 29A (1998), 893-902.
- [11] Song I. H., Kim D. K., Hahn Y. D., Kim H. D., Synthesis of In-Situ TiC-Al Composite by Dipping Exothermic Reaction Process, Metals and Materials International, vol. 10, no. 3 (2004), 301-306.
- [12] Song I. H., Hahn Y. D., Kim H. D., Kyung K. D., Method for making high volume reinforced aluminum composite by use of dipping process, Patent US6406516, 2002.
- [13] Zhao Y. T., Zhang S. L., Chen G., Aluminum matrix composites reinforced by in situ Al₂O₃ and Al₃Zr particles fabricated via magnetochemistry reaction, Transactions of Nonferrous Metals Society of China, vol. 20 (2010), 2129-2133.
- [14] Koczak M. J., Kumar K.S., In situ process for producing a composite containing refractory material, U.S. patent 4808372, 1989.
- [15] Wu B., Reddy R. G., In-situ Formation of SiC Alloy Composites Using Methane Gas Mixtures, Metallurgical and Materials Transactions B, vol. 33B (2002), 543-550.
- [16] Zheng Q., Reddy R. G., Mechanism of in situ formation of AlN in Al melt using nitrogen gas, Journal of Materials Science, vol. 39 (2004), 141- 149.
- [17] Borgonovo C., Apelian D., Aluminum Nanocomposites via Gas Assisted Processing, Materials Science Forum, vol. 690 (2011), 187-191.