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IN-SITU SYNTHESIS OF Al-Si/SiC$_P$ COMPOSITES BY REACTIVE GAS INJECTION METHOD

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S-a studiat procesul de obținere in-situ a materialului compozit Al-Si/SiC$_p$ prin barbotare de gaz metan în topitura de aliaj de aluminiu. Produsul obținut a fost caracterizat prin spectroscopie optică în plasmă DCP, microscopie optică şi difracție de raze X. S-a determinat un conținut superior de particule de SiC în partea superioară a produsului. Particulele de SiC au avut forme colțuroase şi au fost de dimensiuni mici (<10μm). Analiza termodinamică a sistemului a evidențiat formarea de SiC în detrimentul Al_4C_3, ceea ce demonstrează fezabilitatea procesului.

It was studied the in-situ process for the obtaining of Al-Si/SiC$_p$ composite material by bubbling methane in aluminum alloy melt. The obtained product was characterized by optical emission plasma spectrometer DCP, optical microscopy and X-ray diffraction. It was determined a higher content of SiC particles in the top part of the product. The SiC particles were of angular shapes and had small sizes (<10μm). The thermodynamic analyses of the system revealed the formation of SiC instead of Al_4C_3, which demonstrates the feasibility of the process.

Keywords: composites, in-situ, SiC

1. Introduction

Metal matrix composites (MMC) have received a great attention from the research community during the past decades. Their improved physical and mechanical properties, such as high mechanical resistance and low density, are the main reason for the potential replacement of conventional materials in key sectors of the industry. Nevertheless the main withdraws in the large scale valorification of the MMC are the high production costs and the limitations imposed by their processing routs [1]. The high number of preparation stages, the high cost of the initial materials and the complex equipment required for the production of metal matrix composites are mainly dictated by the required quality of the matrix/reinforcement interface and the homogeneity of the material. The in-situ synthesis of metal matrix composites has the advantage of a "natural" grown

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interface, free of impurities, which eliminates the reinforcement treatment stages and plays an important role in the enhancement of the fatigue resistance of the material. There have been performed numerous trials in producing in-situ MMC by different methods (SHS, DIMOX, XD, PRIMEX, RD, Mixalloy, Osprey, Direct nitridation, Mixed Salt Reaction, etc.) [2,3], but unfortunately most of them require complex techniques that either imply expensive equipment or are characterized by less ability to sufficiently control the in-situ process. The synthesis of aluminum metal matrix composites (AlMMC) by reactive gas injection method (RGI), initiated by Kocsak and Kumar [4], is a relatively simple technique were the reinforcing particles are formed in-situ by the reaction of the injected gas with the molten matrix alloy. Different systems have been studied in the past, where the precursor gas was CH_4, N_2, NH_3, or a mix of these, and the molten alloy was composed of Al, Si, Ti, Ta, etc. Wu and Reddy [5] studied the synthesis of Al-Si/SiC composites by RGI method. The research work showed notable results regarding the quantity of the obtained reinforcement (30 wt.%) at a formation rate of 12.5 mg/(L·s). In the process described by the authors the composite material was obtained by the overflowing of the melt over the crucible and later collected from a bottom tray, thus only a small part of the starting alloy was converted into composite material, lowering the overall process efficiency. The authors suggested a possible reaction mechanism and described the kinetics of the system. The calculations based on the theoretical findings allowed the verification of the experimental data, but no in-detail explanations were provided. The silicon percentage in the starting alloy was kept higher than 7%, in conformity with the predictions of Lee et. all in [6], who showed that a silicon concentration less than the critical value can result in Al_4C_3 formation at the surface of the methane bubbles or emerged SiC particles.

The present paper discusses the experimental and thermodynamic findings in the study of the in-situ synthesis of Al-Si/SiC composites by RGI method. The resulted product was collected directly from the elaboration crucible and sent to chemical and microstructural characterization. The thermodynamic calculations were made with the support of specialised software: HSC and Thermocalc

2. Experimental procedure

The experiments were carried out in a vertical tube electric furnace (Fig. 1). The starting aluminum alloy Al-Si (300 grams, 12÷20% Si) was placed in a crucible, in a sealed reaction chamber. The sealed chamber was provided with a water cooled lid, protective atmosphere, a thermocouple to record the process temperature, a pressure gauge and a gas flowmeter. The system was purged with argon for 30 minutes before the experiments and was maintained during the whole process at 0.1 bars.

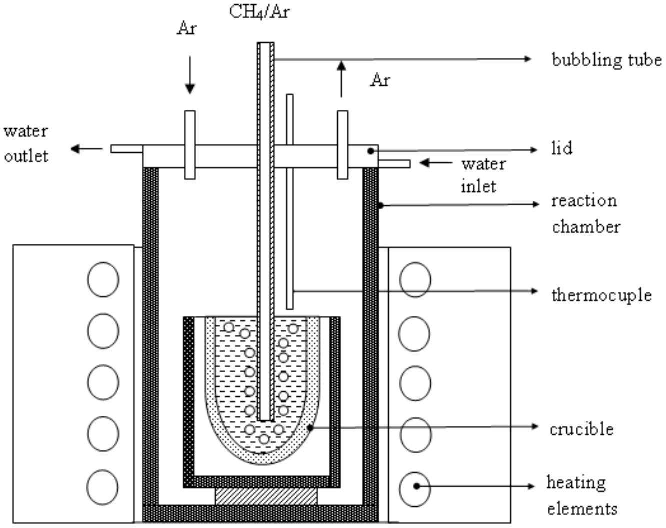

Fig. 1. Experimental installation

The charge was melted and maintained at process temperature (900 - 1200ºC) for 30 minutes, before the beginning of the bubbling process. The bubbling tube (high density graphite, 30 cm long) was lowered into the melt close to the bottom of the crucible. The reactive gas (CH_4/Ar mixture) was injected in the alloy melt through four nozzles provided at the bottom of the tube, at a constant flow rate value. The entire process was visually inspected by the means of an eye-hole through 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 (10 wt.%SiC). After the bubbling process was ended, the resulting material was cooled in the furnace till room temperature. The obtained material was than prepared for chemical and structural characterization.

The process mechanism is described by several stages. The reactive gas enters into the system through several orifices at the bottom of a tube which is immersed in the molten alloy. Because of the small diameter and the high length of the bubbling tube, the gas is already heated to the process temperature when enters in the melt. While in the tube, at over 900°C, methane dissociates in carbon and hydrogen. Thus, the gas entering the melt consists of carbon particles and a mixture of hydrogen and argon. The carbon particles will eventually diffuse to the gas/liquid interface, get adsorbed and than desorbed in the melt, near the bubble surface. The silicon from the alloy will than react with the carbon particles diffused in the melt and form SiC.

3. Results and discussions

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

The results obtained from samples extracted from different parts of the product revealed a gradual distribution of the SiC particles. Even if the SiC has a higher density than the alloy, the determined concentration of particles in the top part was much higher than that in the middle or bottom part of the product (table 1). This fact could be explained by the difference in the surface tension in the particle-alloy-gas system and the upwards stirring action implied by the gas bubbles during the process. There is also an indication that the small size of the particles (<10μm) allowed their rejection by the solidification front. A similar compositional distribution was also noticed for the silicon content, which is explained by the lower solid/gas surface tension of silicon compared to aluminum.

The optical characterization of the samples was accomplished with an Axio Scope A1m Imager from Zeiss, Germany, with bright field, dark field, DIC and polarization capabilities, and high-contrast EC Epiplan 10X/50X/100X lenses. Pictures were taken with a polarized camera provided with the equipment.

Figs. 2 and 3 show micrographs taken from the top and middle part of the product. There can be seen typical Al-Si near eutectic structure (light color), with occasional thin-shaped primary silicon (light grey color). The top part of the product (Fig. 2) presents darker zones as particle agglomerations and gas micropores generated during the bubbling process. Instead, in the middle part of the product there is a little indication of SiC particles presence at provided magnification.

Fig. 4 shows a higher magnification of a SiC particles agglomeration from the top part of the composite, and shows specific configurations of angular SiC particles of darker grey color surrounded by black boundary zones.

Table 1

Chemical composition (wt.%) from different parts of the in-situ AlSi12/SiC composite

Level	Si	SiC	Fe	Cu	Ti	Mn	Al
top	12.98	7.60	0.091	0.076	0.001	0.025	base
middle	12.03	3. 57	0.093	0.094	0.001	0.028	base
bottom	11.40	0.86	0.061	0.079	0.001	0.025	base

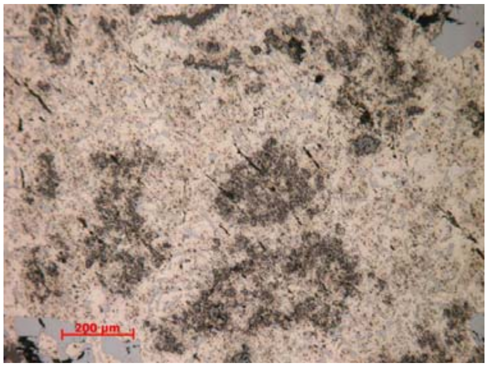

Fig. 2. Top part of the composite at low magnification. Al-Si eutectic (light color areas), primary Si (light grey thin-shape), SiC particle agglomerations (dark color areas) and porosities.

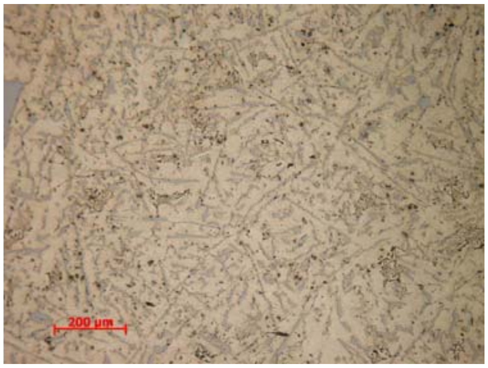

Fig. 3. Middle part of the composite at low magnification. Al-Si eutectic (light color areas), little primary Si (light grey plate like) and porosities

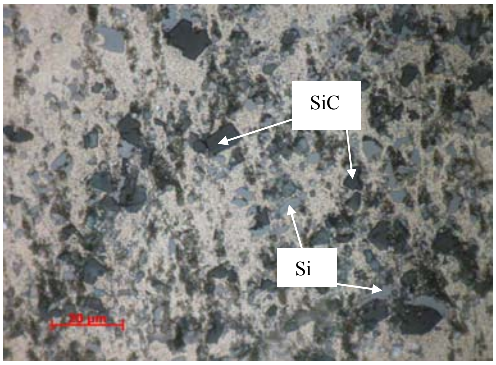

Fig. 4. Top part of the composite at higher magnification and obtained with polarized lenses. Al solid solution (light color background), primary Si (light grey plate like), SiC particles (dark grey with black contour) and porosities (whitish).

X-ray diffraction of the sample taken from the top part of the product is presented in Fig. 5. Phase characterization was performed using a BRUKER D8 DISCOVER X-ray diffractometer, Germany. The obtained data were processed using the FPM (Full Pattern Matching) module from the DIFFRAC^{plus} BASIC (Bruker AXS) program package and the ICDD PDF-2 Release 2006 database. The quantitative representation of the phase system is showed in table 2. The results show 11.8% SiC, as moissanite 6H, little Al_4C_3 and some oxides as spinels.

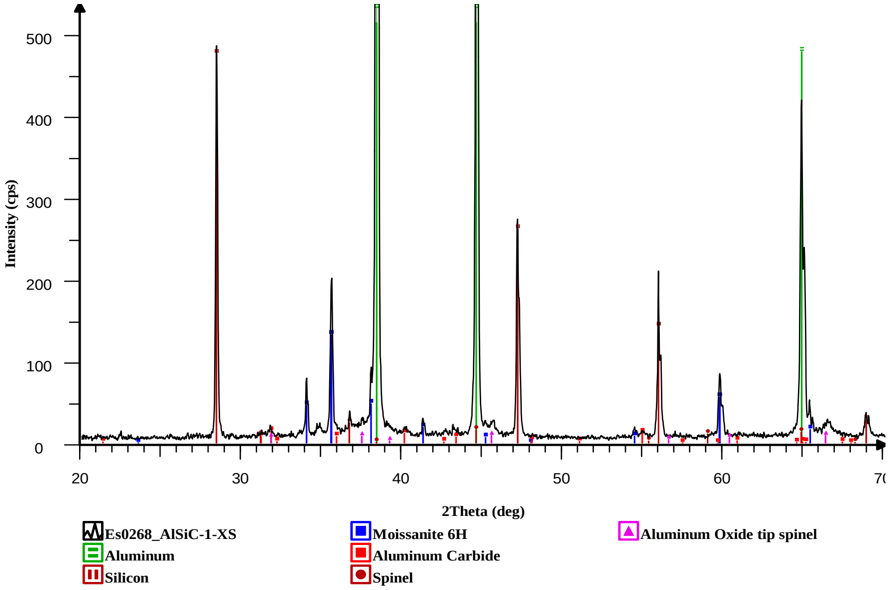

Fig. 5. X-ray diffraction pattern of a sample from top part of the composite

Table 2

Phase identification and composition for the top part of the product

Compound Name	Formula	S-Q(%ms.)	PDF Reference
Aluminum	Al	71.3	00-004-0787 (*)
Silicon	Si	13	00-027-1402 (*)
Moissanite 6H	SiC	11.8	01-072-4564 (A)
Aluminum Carbide	Al_4C_3	1.6	00-035-0799 (*)
Spinel	$MgAl_2O_4$	1.7	00-021-1152 (*)
Aluminum Oxide, spinel type	Al_2O_3	1.7	00-050-0741 (I)

The in-situ process for the synthesis of Al-Si/SiC by bubbling reactive gas in the alloy melt was described by the reactions system presented in table 3. The reactions system was estimated based on possible combinations of chemical elements entering in the process. The reactions that have as result the intended process products (C and SiC) were called primary and the others secondary.

Table 3

Reaction system

Reaction	Type
$CH_4 = C + 2H_2$	primary
$Si + C = SiC$	primary
$Si + CH_4 = SiC + 2H_2$	primary
$3SiC + 4Al = Al_4C_3 + 3Si$	secondary
$4Al + 3C = Al_4C_3$	secondary
$4Al + 3CH_4 = Al_4C_3 + 6H_2$	secondary
$Si + 2H_2 = SiH_4$	secondary
$2Al + 3H_2 = 2AlH_3$	secondary
$H_{2(g)} = 2H_{(g)}$	secondary

The thermodynamic calculations for each reaction were obtained by the means of specialized software HSC, for the temperature interval of the process (600°C ÷1500°C) and considering standard values for Gibbs free energy (ΔG^0). Figs. 6 and 7 show the graphical representation for the free energy and reaction constant over a wide range of temperatures. The synthetic representation of the results from table 4, shows the direction of the chemical reactions on the 600°C ÷1500°C temperature interval. The assessment of the thermodynamic data indicates that not only the reactions for SiC formation have a high level of probability, but also the secondary reactions for the formation of aluminum carbide (Al_4C_3). In this case a comprehensive analysis of the most probable reactions is needed.

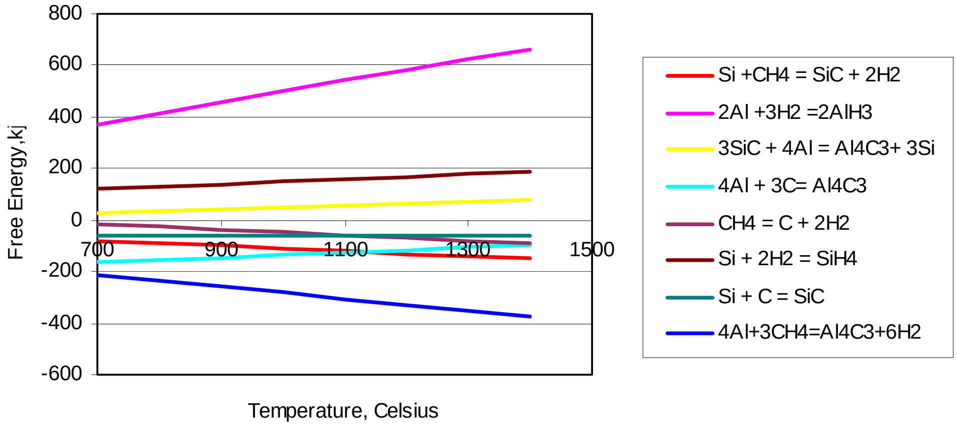

Fig. 6. Free energy calculations (HSC)

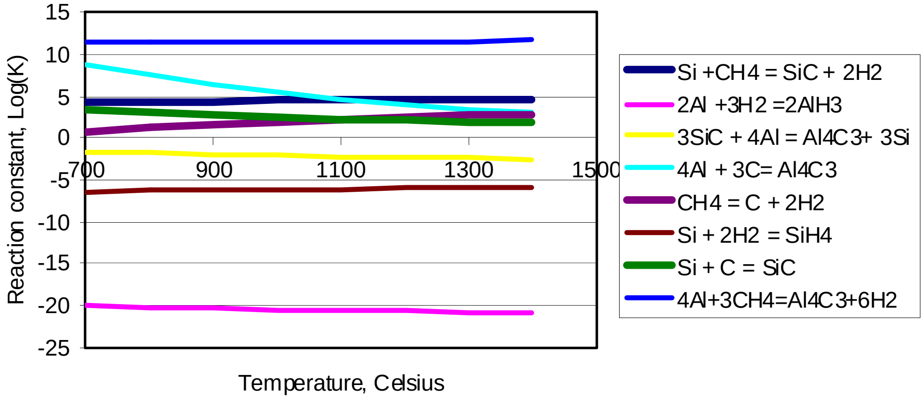

Fig. 7. Equilibrium constant calculations (HSC)

Table 4

Free energy and reaction equilibrium constant calculations

Reaction	ΔG^0, kJ			Log K		
	900 ^{0}C	Sense	1.100 ^{0}C	900 ^{0}C	Sense	1.100 ^{0}C
$Si + CH_4 = SiC + 2H_2$	**-100,4**	→	**-120,8**	**4,47**	→	**4,60**
$2Al + 3H_2 = 2AlH_3$	458,0	←	542,6	-20,4	←	-20,6
$3SiC + 4Al = Al_4C_3 + 3Si$	42,0	←	56,5	-1,87	←	-2,15
$4Al + 3C = Al_4C_3$	**-145,1**	→	**-125,6**	**6,46**	→	**4,78**
$CH_4 = C + 2H_2$	**-38,1**	→	**-60,1**	**1,70**	→	**2,29**
$Si + 2H_2 = SiH_4$	139,0	←	158,7	-6,19	←	-6,04
$Si + C = SiC$	**-62,3**	→	**-60,7**	**2,78**	→	**2,31**
$4Al + 3CH_4 = Al_4C_3 + 6H_2$	**-259,4**	→	**-306,0**	**11,55**	→	**11,64**
$H_{2(g)} = 2H_{(g)}$	311,0	←	287,7	-13,85	←	-10,95

The overall reaction for the formation of Al_4C_3 from SiC and Al is represented by:

$$\begin{gathered} 3SiC + 4Al = Al_4C_3 + 3Si \\ \Delta G^o_{1000^o C} = 49.238\ kJ/mole \end{gathered} \tag{1}$$

The HSC calculations for this reaction are considering an ideal system, where Si and Al are pure substances. But, for the studied process, silicon represents more than 10% of the aluminum alloy, and finds itself in a dissolved state, which is a non-ideal situation. In this case, the thermodynamic assessment has to take in consideration the activities of the substances in the system. A more accurate interpretation of the reaction (1) is represented by reaction (2).

$$4[Al]_{alloy} + 3SiC_{(s)} = Al_4C_{3(s)} + 3[Si]_{alloy} \tag{2}$$

The free energy of reaction for non-ideal systems is calculated with reaction:

$$\Delta G_{1000^o C} = \Delta G^o_{1000^o C} + RT \ln K \tag{3}$$

where

$$K = (a_{Si})^3 / (a_{Al})^4 \tag{4}$$

Thus the reaction constant K depends on the activities of silicon a_{Si} and aluminum a_{Al} . The activity values for an alloy with 12%Si and atomic fractions of $x_{Al} = 0.8858$, $x_{Si} = 0.1163$, at 1000°C, determined with ThermoCalc are presented in Fig. 8. Substituting $a_{Al} = 0.61$ and $a_{Si} = 0.134$ in (2) we get K= 0.01737781 and:

$$\Delta G_{1000^o C} = \Delta G^o_{1000^o C} + 1273 \cdot R \ln K = 6.344\ kJ/mole \tag{5}$$

The positive *ΔG* shows that the reaction is oriented towards the formation of SiC, but the small value of it (lower than 60kJ [7]) implies a possible instability

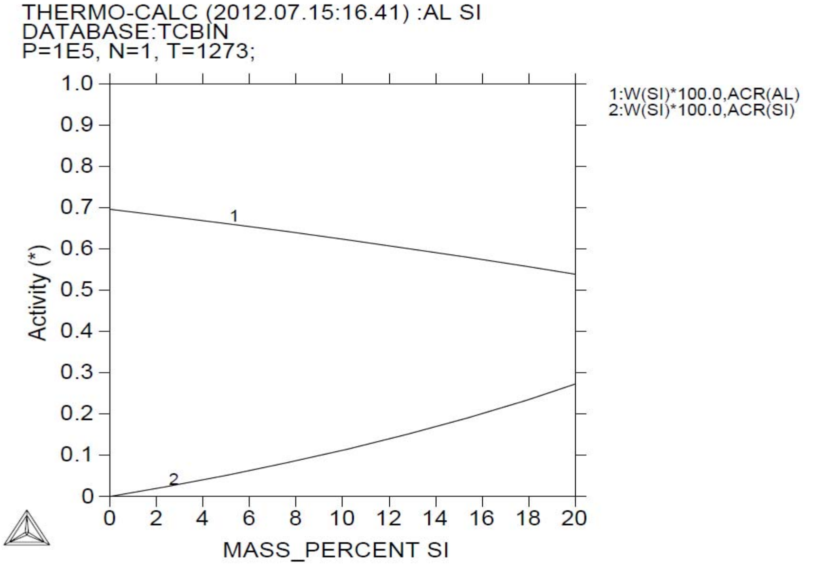

Fig. 8. Al-Si activity diagram by ThermoCalc.

towards the formation of both species, silicon and aluminum carbides. According to the previous works of Wu and Reddy [5], because of the high agitation and the surface energy difference between silicon and aluminum a silicon-rich layer is formed around the gas bubble. This way the activity of Si near the bubble can increase considerably and shift the equilibrium towards a more probable formation of SiC (ΔG greater than 60kJ).

6. Conclusions

In-situ SiC particles were successfully synthesized by the bubbling of a methane/argon gas mixture in the aluminum alloy melt. The chemical and microstructural evaluation indicated a higher concentration of reinforcement particles in the top part of the composite, with small dimensions (<10µm) and angular shapes. The thermodynamics of the system, investigated with specialized software HSC and ThermoCalc, indicated that at the process temperature (900-1100ºC) the formation of SiC in the aluminum alloy (AlSi12) is more probable than the formation of Al_4C_3. Tough, the direction of the reaction between the two compounds could be easily influenced (ΔG < 60kJ) by the concentration of the silicon near the bubble surface. Further investigations are needed to determine the influence of alloy/gas surface tension and boundary layer silicon diffusion to the probability of SiC formation.

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