

INVESTIGATION OF THE ELECTROLESS NICKEL PLATED SiC PARTICLES IN METAL MATRIX COMPOSITES

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Abstract

Electroless nickel (EN) plating was used to coat SiC particles, using three different pre-treatment methods (acidic pre-treatment, surface oxidation, palladium chloride activation). The acidic pre-treatment is able to activate the surface of the particles hardly. Consequently, the electroless nickel deposit formation is only particular. A coherent oxide layer is developed on the surface of the substrate after the surface oxidation. This ensures the homogeneous nickel nuclei formation after using the electroless nickel plating. Finally the palladium chloride activation creates homogeneous palladium nuclei on the surface of the silicon carbide particles. A coherent and continuous nickel layer is formed on the surface containing elemental palladium nuclei. The EN plated SiC particles were added to an Al alloy powder to produce Al/SiC composite by compression and sintering. During sintering (580°C 5h), the nickel coating of the silicon carbide particles and the matrix react with the formation of different Al-Ni phases. The arrangement and chemical composition of these intermetallic phases was studied and discussed in this paper as function of the pre-treatment method of SiC particles.

Keywords: *surface coating, acidic pre-treatment, surface oxidation, palladium chloride activation, aluminium alloy matrix composites*

INTRODUCTION

In the production of the powder metallurgical Al/SiC composites the interfacial bond between the reinforcing phase and the matrix has a great importance. To ensure strong adhesion between the phases, surface coating of the ceramic particles is sometimes used. The surface can be coated by metals, or surface oxidation can also be used.

The aim of surface oxidation is to prevent Al-carbide (Al_4C_3) formation (harmful reaction: $\text{Al}_4\text{C}_3 + 12 \text{H}_2\text{O} \rightarrow 4 \text{Al}(\text{OH})_3 + 3 \text{CH}_4$) [1] by developing a silicon oxide layer between the silicon carbide particles and the metallic aluminium matrix [2-3]. Metallic coatings are prepared by galvanization [4], mechanical alloying [5], or physical or chemical vapour deposition (PVD, CVD) [6], as well as by chemical reduction [7].

The selection of metallic coating is essential, as it has a double role. On the one hand it helps to improve adhesion between the particles and the matrix, on the other hand, it might dissolve in the matrix and influence its mechanical properties. Thus, only those metals should be chosen as SiC-coating for the Al/SiC composite, which can improve the mechanical properties of the Al-matrix. Copper [8] and nickel [9] have been used in the past in Al/SiC composites, as both of them can improve the strength and heat resistance of Al-alloys.

Electroless nickel (EN) plating was chosen in this paper to coat the SiC particles. However, covalently bonded SiC cannot be coated by a metal without surface pre-treatment.

In this paper, the following three different pre-treatment methods will be studied to improve the quality of EN coating.

1. Acidic sodium-hypophosphite (AP) has already been used for coating the surface of the composite [10] or that of an aluminium alloy [11]. However, this method has not been used for SiC particles before.
2. Surface oxidation (SO) is another possibility to activate a surface. However, SO has not yet been used before as a pre-treatment method for EN plating of SiC particles. Nevertheless, SO of SiC particles is a promising method, as in this way surface covalent bonds are replaced by surface ionic bonds, having stronger adhesion to metallic phases [12].
3. A 2-step pre-treatment including sensitisation of the surface by stannous chloride followed by its activation by palladium chloride provides palladium nucleation (PCP) on the surface. This PCP pre-treatment method was applied to electroless nickel and copper coating of a Teflon substrate [13], and to Ni-Fe-P layer on carbon nanotubes [14]. The same method was applied to coat boron carbide particles [15] and nano silicon carbide particles [16]. The PN method has not been used for SiC particles before.

It has been found earlier that the Ni-coating of the SiC particles reacts with the Al-matrix during sintering, leading to the formation of different Al-Ni intermetallic phases at the Al/SiC interface [17]. The mechanical properties of the coating were also studied [10]. It is important to know how the composition, structure and properties of the Al/SiC composite depend on the pre-treatment methods used to coat the SiC particles.

EXPERIMENTAL PROCEDURE

Commercially available Al-powder as a matrix and SiC powder as reinforcement were chosen for the production of the composite materials.

The Al powder of grade 123 Ecka (ECKA Granules) contains 4.5 wt.% Cu, 0.7 wt.% Si, 0.5 wt.% Mg and 1.5 wt.% of Microwax C as a lubricant. The particle size of the initial powder is in the range of 100-200 μm . According to Fig.1b, the initial material is a mechanical mixture of pure metal particles. However, upon sintering an alloy is formed (see Fig.1a) with an eutectic temperature of 580°C.

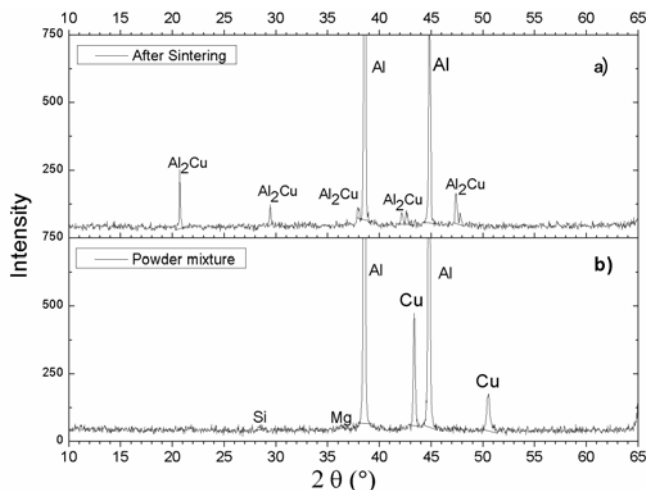


Fig.1. X-ray diffraction spectra of Ecka granulate: a - XRD spectra of the sintered powder mixture, b - XRD spectra of the Ecka Alumix 123 powder mixture.

As reinforcement silicon carbide of P220 grade was used (Saint Gobain Grains & Powders). Particle size distribution was established by Quantimet 500 Image Workstation computer image analysis. The particle size was measured by Leica Qwin software [18]. The most particles were from 100 μm to 180 μm in diameter. The most frequency was showed in the case of 125 μm , so the average particle size can be accounted 125 μm .

A Micrometrics TriStar 3000 type gas-adsorption device was used with nitrogen gas (99.999%) to examine the specific surface area of the silicon carbide particles. Specific surface area of SiC particles estimated by the BET (Brunauer, Emmett, Teller) method at the temperature of 77 K is 0.14 m^2/g [17]. According to the low specific surface area, the silicon carbide particles do not contain any pores. This is in accordance with the SEM observations (see Fig.2).

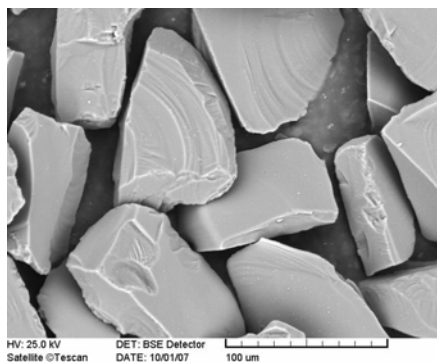


Fig.2. SEM photomicrograph of SiC particles.

A Bruker D-8 advanced type ceramic X-ray tube as X-ray source, a long fine focus, Cu anode, and a voltage of 40 kV, 40 mA as well as a valve current were used for the X-ray investigations. The evaluation was performed with EVA 2005 software. The individual phases were identified by using a PDF-2 (Powder Diffraction File) database. The X-ray diffraction spectrum (Fig.3) show that SiC powder used is not a stoichiometric phase. Two elemental carbon peak appeared in the XRD spectrum, particular Graphite C 2H and Graphite 3R (Graphite C 2H PDF code: 00-041-1487) (002) Miller index plane with 100% reflection; Graphite 3R PDF-kód: 00-026-1079) (003) Miller index plane with 100% reflection) (mean chemical composition in atomic percent: 54.4% C, 45.6% Si determined by SEM-EDX).

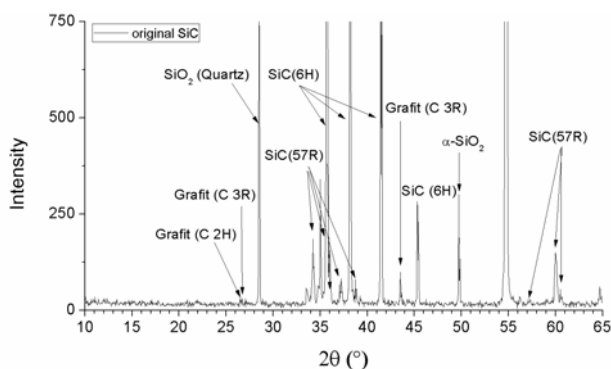


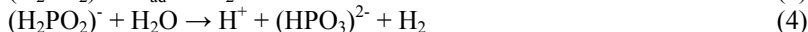
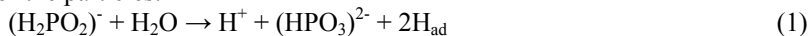
Fig.3. XRD spectrum of SiC particles.

Ultrasonic cleaning of SiC particles was applied in acetone for 25 minutes at room temperature. Then, the SiC particles were pre-treated by three different methods (for details see Table 1).

Tab.1. Characteristic parameters of different pre-treatments of SiC particles.

Type of pre-treatment		Chemical composition	Parameters	Result
Acidic pre-treatment (AP)		Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 30 g/l, and Lactic acid 98% ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$), 20ml/l	T = 85°C, t = 35 min after flushing with distilled water or drying at 105°C for 15 min	development of a thin hypophosphite layer
Surface oxidation (SO)		Air atmosphere	T = 1000°C and 1100°C, t = 1, 3, 5 and 7 hours	continuous, compact oxide (SiO_2) layer
Palladium chloride pre-treatment (PCP)	Sensitization	Stannous chloride, SnCl_2 , 15g/l Hydrochloric acid HCl (cc. 37%), 55cm ³ /l	T = 298 K (25°C), t = 10 min	Sn^{2+} ions adsorb on the surface of silicon carbide particles
	Activation	Palladium chloride, PdCl_2 , 0,5 g/l Hydrochloric acid HCl (cc. 37%), 2ml/l	T = 298 K (25°C), t = 25 min	palladium nuclei form on the surface of SiC particles

Then, the pre-treated SiC particles were EN plated by immersing them into an acidic nickel bath, containing nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) 28g/l, sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) 30g/l, sodium acetate hydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) 35g/l, and lactic acid ($\text{C}_3\text{H}_6\text{O}_3$, 90%) 20ml/l. According to the following reactions a Ni-P layer formed on the surface of the particles:



The EN plated SiC particles were used as reinforcing phase to produce Al/SiC composite samples by a powder metallurgical process, including the following three steps:

1. mechanical mixing of the powders (10 wt.% SiC + 90% Al-alloy),
2. pressing of the powder mixture with pressure of 400 MPa,
3. sintering at 575°C±5°C for 5 hours in high purity nitrogen (99.999%).

Cylindrical samples with a diameter of 7.6±0.1 mm and length of 8.5±0.5 mm were produced in this way. Three types of composite samples were fabricated. Sample "AP-MMC" was obtained after acidic pre-treatment, sample "SO-MMC" was obtained after surface oxidation, while sample "PCP-MMC" was obtained after palladium chloride activation of the surface of SiC particles.

RESULTS AND DISCUSSION

The Ni coating of the SiC particles and the Al-alloy react to form Al_xNi_y phases by diffusion during sintering. According to the SEM photos (Figs.4-6) the arrangement of these intermetallic phases depends on the pre-treatment method of the SiC particles as follows. The quantity of Al_xNi_y phases formed after the sintering was determined by X-ray diffraction. This method is able to detect compounds instead of the elements (seen SEM). But, if the quantity of a phase is than 5 %, the phase must be present in the sample.

In sample AP-MMC the SiC particles are coated by Ni only partly. This is due to the weak adhesion of the hypophosite layer to the SiC particles. Thus, the Ni-coating can be easily separated from the SiC particles, and as a result, the intermetallic phase can be found both near and far from the SiC particles (Fig.4).

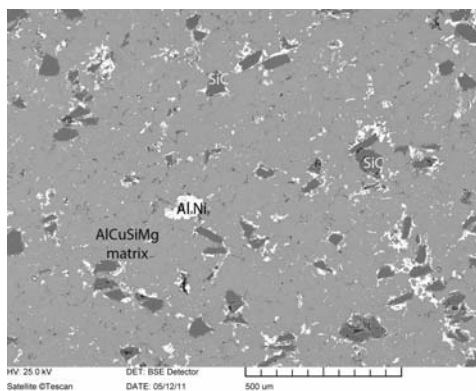


Fig.4. Arrangement of Al-Ni phases in the Al/SiC(Ni)_p composite (in the case of acidic pre-treatment).

The intermetallic phases appear to be Al_3Ni_2 and Al_3Ni . In this case, the Ni-content of the composite was found to be 0.7 wt. %.

In sample SO-MMC the adhesion of the Ni coating to the SiC particles is higher compared to sample AP-MMC. In this case, spherical Ni-particles cover the surface of SiC in a homogeneous way. The intermetallic phases are located around the particles (Fig.5).

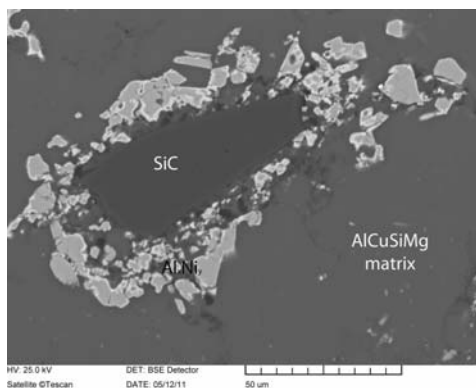


Fig.5. Arrangement of the Al-Ni phase in the Al/SiC(Ni)_p composite (in the case of surface oxidation pre-treatment).

According XRD, those phases are mostly Al_3Ni_2 . In this case, the Ni-content of the composite was found to be 1.1 wt.%.

In sample PCP-MMC, Ni forms a continuous coating on the surface of the SiC particles. Thus, the intermetallic phases form a thin interlayer between the particles and the matrix (Fig.6). The main intermetallic phase is AlNi (Fig.7). In this case, the Ni-content of the composite was found to be 5.5 wt.%.

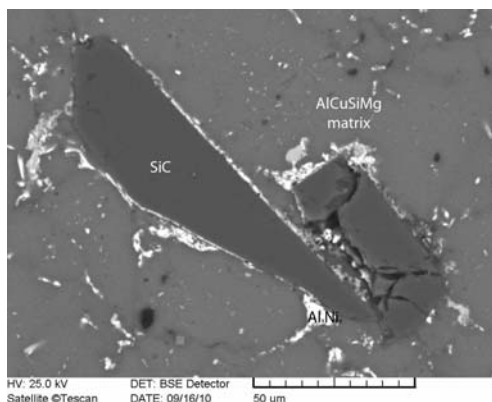


Fig.6. Arrangement of Al-Ni phases in Al/SiC(Ni)p composite (in the case of palladium-chloride activation).

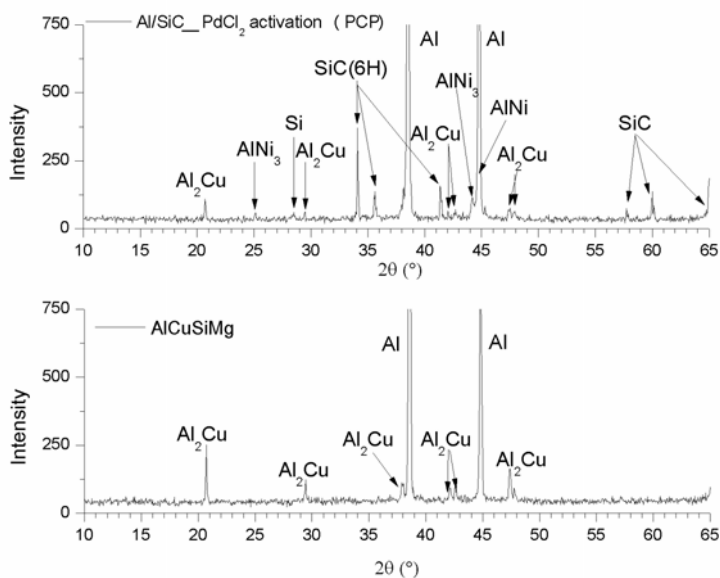


Fig.7. XRD spectrum of the composite sample (palladium chloride activation): a) XRD spectra of the Al/SiC(Ni)p composite (PCP-MMC), b) XRD spectra of the sintered matrix (AlCuSiMg).

Thus, the stronger is the adhesion of the Ni-coating to SiC as a result of the pre-treatment, the less this Ni-layer can separate from the particles during compression and

sintering and thus the closer the intermetallic phases appear to the SiC/Al interface. On the other hand, stronger adhesion of Ni to SiC particles also leads to a higher specific amount of Ni deposited per a unit surface area of the SiC particles. As a result, the total nickel concentration found in the composite also follows the above trend: the stronger is the Ni-SiC adhesion, the higher is the Ni-content of the composite. A higher Ni-content also leads to the formation of the strongest (AlNi) intermetallic compound (Table 2).

Tab.2. Determination of Al-Ni phases.

Samples	Quality of the electroless nickel layer	Al ₃ Ni ₂	AlNi ₃	Al ₃ Ni	AlNi
AP-MMC	not continuous, deposit fragments forms intermetallic phase reservoirs	peak appeared, but quantity of this phase cannot be appraised	0.6%	peak appeared, but quantity of this phase cannot be appraised	0.3%
SO-MMC	not continuous, deposit nuclei fixed to the particles locally	0.7%	0.8%	not appeared	peak appeared, but quantity of this phase cannot be appraised
PCP-MMC	compact, continuous deposit on the surface of the silicon carbide particles	not appeared	0.5%	not appeared	6.6%

According to the data of Table 2 the AlNi phase must be detected in the PCP-MMC sample, while the AlNi₃ phase may be present in the PCP-MMC. The SO-MMC sample contains Al₃Ni₂ and AlNi₃ only as indication. Finally the AP-MMC has AlNi₃ and AlNi phase can be detected to small extent.

CONCLUSIONS

SiC particles reinforced Al matrix composites were produced by compression and sintering. The surface of the SiC particles was electroless nickel plated, after three different surface pre-treatments (acidic pre-treatment, surface oxidation, and palladium chloride activation). Electroless Ni layer and Al react during sintering to form intermetallic phases. These phases were investigated by SEM and X-ray diffraction. The arrangement and phase identification of these phases were performed and the findings were connected to the surface pre-treatment. The quantity of Al₃Ni₂, Al₃Ni, AlNi₃ intermetallic phases is low (only indication), but the AlNi phase (> 5%) must be present in the composite samples.

The three pre-treatment methods can be arranged in the following row in their ability to ensure weaker → stronger adhesion between the Ni coating and the SiC particles: acidic pre-treatment → surface oxidation → palladium chloride activation. The same trend

is followed in finding the intermetallic phase further → closer to the SiC/Al interface and in forming lower → higher average Ni content in the composite. Higher Ni-content also leads to the formation of the strongest intermetallic phase (AlNi).

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