EXAMINATION OF ALUMINUM MATRIX COMPOSITES OBTAINED BY POWDER METALURGY AND STRENGHTENED BY AgO AND CeO$_2$ PARTICLES

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Abstract

The main advantage of mechanical alloying (MA) is a possibility to combine together different components that are difficult or even impossible to combine by conventional melting methods due to their high reactivity in liquid or semi-liquid state. In the present work, results of experiments performed on Al-AgO and Al-CeO$_2$ composite rods manufactured by means of mechanical alloying method was presented. Structure of as-extruded composites was analysed using SEM/TEM observations and X-ray diffraction analysis (XRD). It was found that intermetallic phases were formed at elevated temperature as a result of chemical reaction of strengthening particles and aluminium matrix. In order to determine composites thermal stability, samples were subjected to annealing in temperature range 473 K - 873 K. The effect of annealing on the sample microhardness was determined and compared with respect to structural processes resulting from chemical reaction of CeO$_2$ and AgO and aluminium matrix. It was found that adequate intermetallic grains start to form during production process (MA, hot extrusion) and their coarsening was intensified during following annealing at high enough temperature.

Keywords: Powder metallurgy, mechanical alloying, powder's consolidation, aluminum composite

1. INTRODUCTION

Dynamic development of automotive and aviation industry in recent years forcing a trend towards new, light and high strength materials, which can meet high modern construction standards. Traditional materials produced using metallurgical methods very often don't meet requirements imposed on them by industry, therefore, in order to overcome this issues, the material engineering must develop new methods of designing and material production technologies with strictly defined properties of the product [1-5]. Plastic consolidation is widely used as effective process for densification of powder, chips and belts. Into a group of modern, construction materials, which allow maintain high level of performance parameters, MA composites can be classified. Their mechanical properties are mainly determined by strengthening mechanisms and structural process mostly caused by increased temperature of the material during processing. Composites based on light metals strengthened by metal oxide particles constitute a specific group of metallic composites manufactured by mechanical synthesis [6-9]. Use of light matrix in these materials results in acquiring low specific gravity weight and high strength at the same time. Literature data indicates that metallic composites strengthened in particular by metallic oxides are characterised by high hardness level. As an example, Al-Sb$_2$O$_3$:145HV, Al-Nb$_2$O$_5$:150HV, Al-MnO$_3$:240HV composites can be mentioned [10-19]. Composites strengthened by metallic oxides can be separates into two groups. First group consists of composites, in which the metal released from metallic oxides during chemical reaction in Al-matrix, practically does not dissolve in the matrix and does not form intermetallic phase with aluminium. Examples of that composites are Al-PbO i Al-SnO$_2$ [10, 20]. Annealing of aforementioned composites at the temperature range of 500°C to 600°C showed that SnO$_2$ and PbO oxides reacts with aluminum, forming pure metal precipitates (Sn, Pb). After reduction of oxides, released oxygen combines with aluminum forming nanometric, needle-shaped Al$_2$O$_3$ particles, which additionally influence matrix strengthening, prevent recrystallization process and further grain coarsening at elevated temperatures. Described structural processes result from the following chemical reactions:

$$3\ SnO_2 + 4\ Al \rightarrow 3\ Sn + 2\ Al_2O_3$$

$$3\ PbO + 2\ Al \rightarrow 3\ Pb + Al_2O_3$$
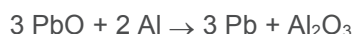
Composites from this group are thermally stable up to the temperature of about 400°C, and after exceeding this temperature hardness is usually dropping while porosity is increasing, which depends on a result of chemical reaction mentioned above [10,20]. In case of the second group of metallic composites, metal oxides react with a matrix and result in intermetallic phases precipitation [14-16]. Examples of such composites are Al-CuO and Al-Nb$_2$O$_5$ where reaction between structural components can be separated into two steps as follows

$$8\ Al + 3\ CuO \rightarrow 3\ Cu + 6\ Al + Al_2O_3 \rightarrow 3\ Al_2Cu + Al_2O_3$$

$$28\ Al + 3\ Nb_2O_5 \rightarrow 6\ Nb + 18Al + 5\ Al_2O_3 \rightarrow 6\ Al_3Nb + 5\ Al_2O_3$$

If the first step results in a local reduction of a volume of chemical reaction products, the material porosity rises. However, following growth of intermetallic grains may result in locally increasing volume of the grain. Therefore, summarized effect of a local volume alterations may become compensated and result in negligible porosity of the material. It was reported that chemical reaction in Al-CuO composite takes place already during hot extrusion stage, which leads to formation of equilibrium phase θ (Al$_2$Cu) while in Al-Nb$_2$O$_5$ equilibrium phase Al$_3$Nb forms after annealing at 600 °C [10-12]. Therefore, experiments described below were also performed to determined the thermal stability of already tested composites.

2. EXPERIMENTAL

Examined composite Al-CeO$_2$ was prepared from a powder mixture of aluminum (an average grain size of 10 µm and purity of 99.9%) with 9.1 wt.% addition of CeO$_2$ (an average grain size of 1-8 µm and purity of 99,5%). Rare earth oxides to which CeO$_2$ is classified are one of the most thermally stable materials, therefore using this oxide as strengthening particle is fully justified [21]. Cerium oxide is characterized by density of 7.13 g/cm^3 and melting temperature of 2600°C. Crystallographic lattice is fluorite-type with lattice parameter of 0.511 nm [22, 23]. Subsequent examined material was Al-AgO composite produced from mixture of aluminum (an average grain size of 10 µm and purity of 99.9%) and 12.8 wt.% AgO oxide powders (an average grain size of 60 µm and purity of 99,5%). Silver oxide (AgO) is characterized by density of 7.48 g/cm^3 [24, 25]. **Table 1** presents chemical composition of examined composites.

Table 1 Chemical composition of examined composites

	at.%	wt.%
Al - CeO$_2$	Al - 4.5 CeO$_2$	Al - 9.1 CeO$_2$
Al - AgO	Al - 6 AgO	Al - 12.8 AgO

Powder mixtures (700 g each) were milled in Attritor mill for 30 h. Steel balls with a diameter of 9.5 mm were used for milling procedure. The milling was carried out using stirrer rotation speed of 120 rpm. Protective atmosphere of argon was used during milling in order to prevent powders from oxidation and accidental self-ignition of the powder mixture. Addition of methanol (5 wt.%) into a charge was used to prevent against formation of powder agglomeration which could deposit on steel balls and grinder mixing blades or the container walls. As milled powders were subjected to cold pressing under load of 500MPa and, after degassing in vacuum for 1 hour, powders were submitted to hot pressing (400°C) under load of 100MPa. Last stage of manufacturing process was hot extrusion at the temperature of 400°C that resulted in receiving of the rods with a diameter of 7mm. Composite samples were subjected to Vickers hardness tests in accordance with a standard PN EN ISO 6507-1 applying load of 19.61 N (HV2). The samples were cut from as-extruded rod, then annealed at the temperature range of 200-600 °C. Analysis of phase composition was carried out with

use of X-ray diffractometer Rigaku MiniFlex II. Diffraction analysis was performed using 2θ angle ranging from 20 to 70 degree. Diffractometer has been equipped with Cu lamp which generated Kα characteristic X-radiation with a wave length of 0.15418 nm. Microstructure observations were performed with use of JEM 2010 electron microscope and accelerating voltage of 200 kV. Thin foils for microstructure observations were finally thinned using PIPS-691 GATAN ion thinner. For microstructure observations also scanning electron microscopy Hitachi SU-70 was used.

3. RESULTS AND DISCUSSION

Results of microstructure observation confirmed, that process of mechanical alloying (under protective argon atmosphere) combined with extrusion at elevated temperature allows to obtain composite with negligible porosity and highly refined structural components. Grain size of aluminum matrix was determined by statistical intercept method with a use of STEM structure images. After mechanical consolidation and hot extrusion, measured grain size of Al-CeO$_2$ and Al-AgO composites were 244±1.1 nm and 259±1.6 nm respectively. In both materials, evenly distributed strengthening particles in aluminum matrix were observed. Strengthening particles in Al-CeO$_2$ composite were found to be evidently finer with respect to these observed for Al-AgO composite (**Figures 1, 2**). Both examined composites are characterized by lack of visible porosities which confirms that conditions of the powder mechanical consolidation during extrusion process were well-selected.
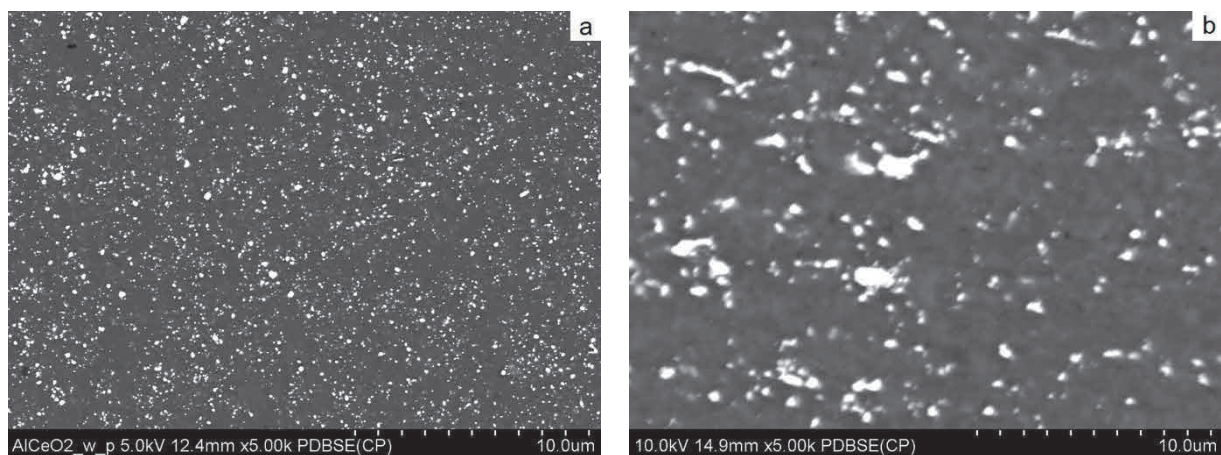

Figure 1 Microstructure of as-extruded composites revealed by means of SEM: a) Al-CeO$_2$; b) Al-AgO
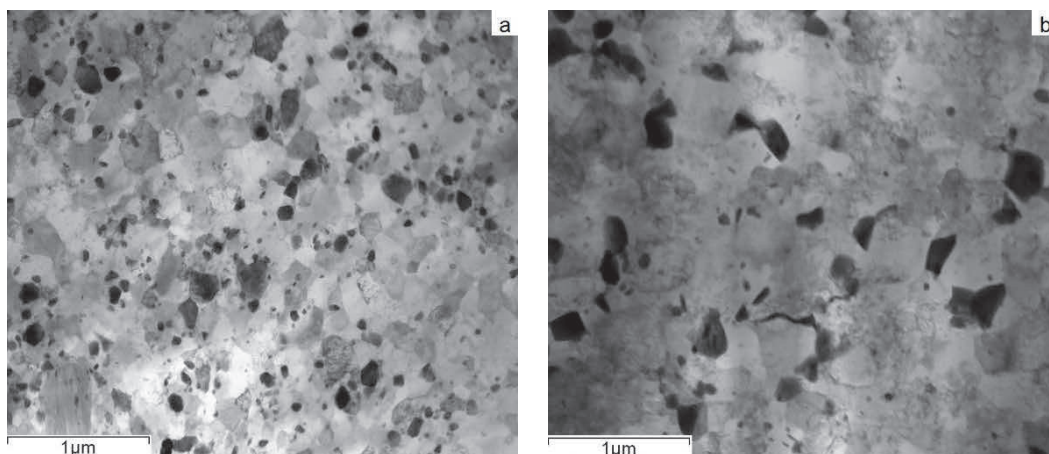

Figure 2 Microstructure of as-extruded composites revealed by means of TEM: a) Al-CeO$_2$; b) Al-AgO

Results of XRD analysis (**Figure 3**) suggest that particles of CeO_2 were not reduced during extrusion. Both CeO_2 and Ce_4O_7 oxides in as extruded material were identified, which suggest high stability of material during extrusion at 400°C. CeO_2 and Ce_4O_7 particles are characterized by A1 lattice. Because mentioned oxides differ only slightly in cell parameters (a_{CeO_2} = 0.54113 nm, $a_{Ce_4O_7}$ = 0.55260 nm) it can be assumed that they concern the same oxide (CeO_2) of which crystallographic data has been used in TEM/SAD examinations [26]. Analysis of results for Al-AgO composite lead to the conclusion, that AgO particles are subjected to reduction in aluminum matrix during hot extrusion while intermetallic phase Ag_2Al was formed in the material (no presence of AgO particles and Al_2O_3 were detected in XRD diagrams (**Figure 3**).
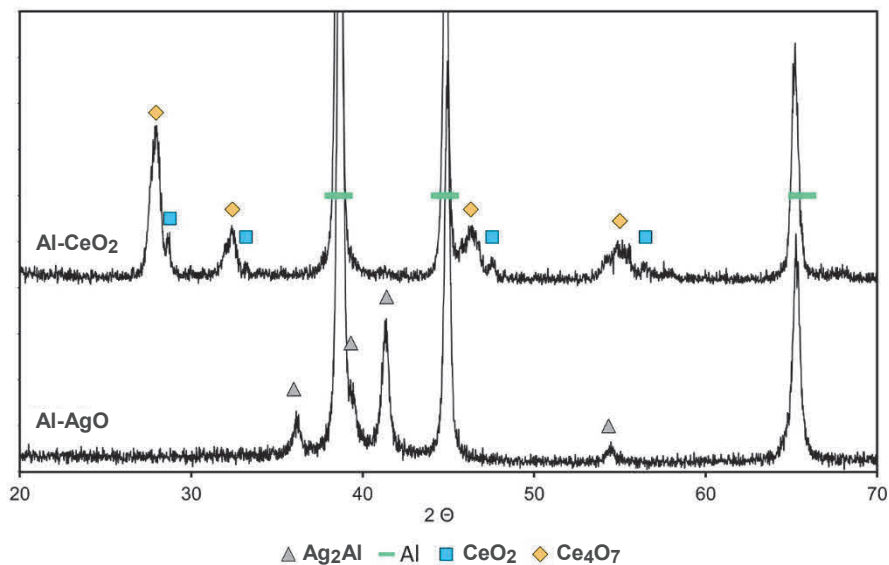

Figure 3 X-ray diffraction analysis results for as extruded Al-CeO_2 and Al- AgO composites. Identified peaks of the oxides CeO_2 and Ce_4O_7 and intermetallic phase Ag_2Al-type are marked in the figure.
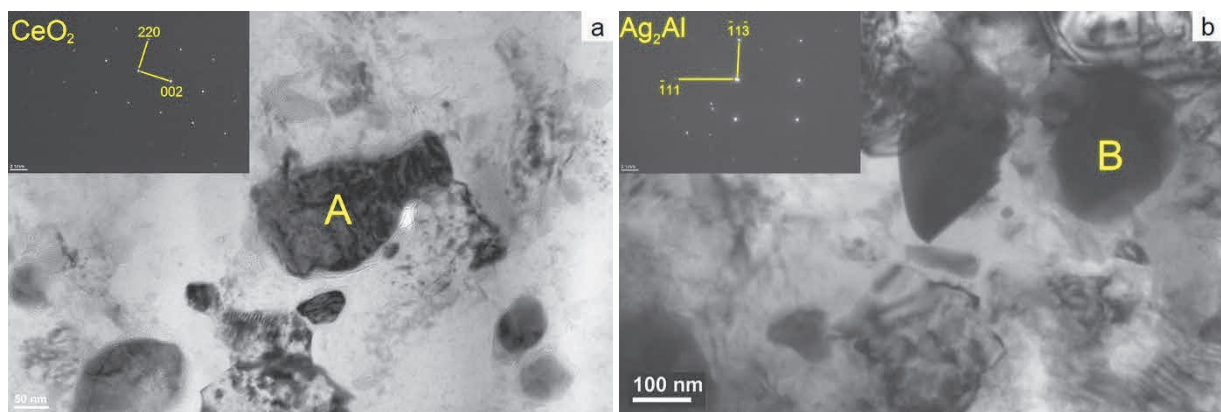

Figure 4 TEM structures of as-extruded composites: a) Al-CeO_2; b) Al-AgO. Diffraction patterns for CeO_2 and Ag_2Al particles, marked A and B in TEM pictures, are inserted in figure a) and b), respectively

Hardness of as-extruded Al-AgO composite is much higher with respect to Al-SnO and Al-PbO composites in which contact of strengthening particles with aluminum matrix does not lead to formation of intermetallic phases as reported elsewhere (**Figure 4**) [10, 14]. Hardness of Al-CeO_2 composite is comparable with as-extruded Al-Nb_2O_5 that is material in which intermetallic grains of $NbAl_3$ - type were found [12]. Composite Al-HfO_2 is characterized by presence of intermetallic phase $HfAl_3$ [13] and hardness of 164 HV (**Figure 5a**). One of the most desired properties of metallic composites - besides mechanical properties - is the stability of their structure at high temperature. Formation of intermetallic phases as a result of interaction between

strengthening particles and matrix is basically dependent on composite annealing conditions. Hardness of composites vs. annealing temperature is presented in **Figure 5b**. Experiments were performed in wide temperature range (473K - 873K) at constant annealing time of 2h.
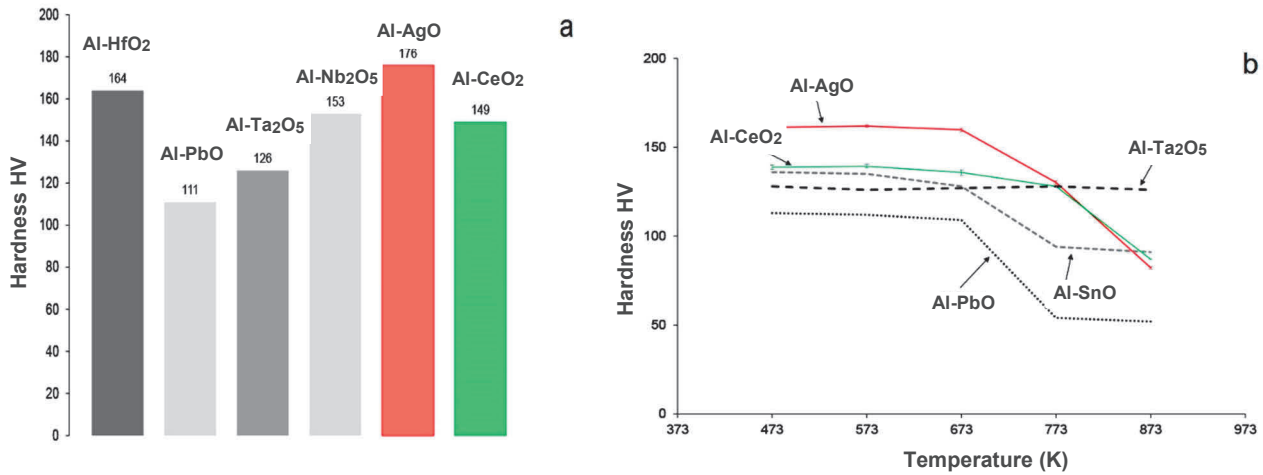

Figure 5 Hardness of some composites reported in literature: a) as-extruded; b) samples annealed at 473K - 873K for 2 hours [10,12]

Hardness of Al-CeO$_2$ composite is practically remained during annealing for 2 h in temperature range 473 K-773 K and become reduced after annealing at 773 K and 873 K from 128 HV to 87 HV (**Figure 4b, Table 2**). In case of Al-AgO composite initial hardness is higher than that for Al-CeO$_2$ and it does not change during annealing in temperature range of 473 K-673 K. At higher annealing temperatures, the sample hardness was found to decrease from 160 HV to 82 HV for annealing temperatures 673 K and 873 K, respectively (**Figure 4b, Table 2**). For comparison, Al-Ta$_2$O$_5$ composite maintains almost constant hardness value during annealing in the same time-temperature conditions (**Figure 4b**). In temperature range of 473 K-673 K both Al-CeO$_2$ and Al-AgO composites are characterized by comparable hardness regardless of annealing time. Changes in hardness along with annealing time were observed at the temperature range between 773 K and 873 K (**Table 2**).

Table 2 Effect of annealing time and temperature on hardness of Al-CeO$_2$ and Al-AgO composites

	Al-CeO$_2$		Al-AgO	
	2 h	24 h	2h	24h
473 K	139 HV	138 HV	161 HV	159 HV
573 K	139 HV	137 HV	162 HV	161 HV
673 K	136 HV	137 HV	160 HV	154 HV
773 K	128 HV	108 HV	130 HV	113 HV
873 K	87 HV	76 HV	82 HV	84 HV

4. CONCLUSIONS

1) High hardness of Al-AgO and Al-CeO$_2$ composites result from efficient refining of components during mechanical alloying and advantageously performed consolidation of MA-powders by means of vacuum pressing and following hot extrusion (673K).

2) Plastic consolidation of components during hot extrusion was found to be very effective procedure to avoid pores and voids in as-extruded Al-AgO and Al-CeO$_2$ composites.

3) TEM and XRD analyses confirmed the development of intermetallic phases (Ag_2Al) in hot extruded material and no presence of AgO particles and Al_2O_3 were detected. Structure and hardness measurement of Al-CeO_2 samples revealed relatively good thermal stability of the examined composite.

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