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PREPARATION OF Nb – Nb_3Al/Al_2O_3 NANOCOMPOSITE POWDER BY MECHANO-CHEMICAL REACTION

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Abstract

Mechano-chemical processing route appears to be an advanced technique for synthesis of nano – sized materials of composite type. The work is focused on the synthesis of Nb-Nb_3Al/Al_2O_3 composite by mechanical alloying (MA). For these purposes, a mixture of niobium (V) oxide and pure aluminium powders was subjected to high energy ball milling. The structural and phase analyses of powder particles before and after milling for different times was conducted by scanning electron microscopy (SEM) and X – ray diffractometry (XRD). Thermal properties were detected by using differential scanning calorimetry (DSC). Formation of the Nb/Nb_3Al nanocomposite was proved, as a side effect of the reactions almost alumina matrix was formed during mechano-chemical reaction for the Nb_2O_5 / Al ratio used.

Keywords: mechanical alloying, mechano-chemical synthesis, intermetallics, niobium aluminate.

1. INTRODUCTION

Composites are an important group of engineering materials that contain a combination of two or more different materials with a clear interface between them [1]. They are typical by dispersion of reinforcement phase in a matrix phase; the reinforcement can be of different shape and dimension mostly in the form of a particulates, short (chopped) fibres, or continuous fibres. Composites exhibit properties that are an average of the matrix and reinforcement properties according to rule of mixture [2], e.g. typically for Young's modulus, hardness or strength. But thanks to synergy of different reinforcing and toughening mechanisms they may possess extraordinary enhancement of selected properties, e.g. fracture resistance. In such a case the key role is seen in a well-defined interface properties between the matrix and the reinforcement phases in addition to controlled thermal expansion coefficient and elastic properties of both the reinforcement and the matrix.

Aluminium based alloys are widely used as aerospace and automotive components, because of their high specific strength, stiffness and good formability. A sintering technology of aluminium alloys powder has been considered to be a low cost manufacturing process for light weight parts and other light weight applications [3, 4]. Thanks to their attractive mechanical properties the lower density aluminium alloys and their composites prepared by powder metallurgy route appear to be important candidate materials for applications and sinterability conditions of aluminium composites powder. Sintering of aluminium powder has difficulty to wet with another particle due to its oxide layer, Al_2O_3. The thickness of this oxide layer can be up to 100 nm. High melting point of Al_2O_3 hinders diffusivity of aluminium during sintering. So approaches must be investigated how to remove this oxide layer during sintering and/or exploit the oxides for properties improvement e.g. by formation of oxide nanoparticles dispersion inside the aluminium grains. Magnesium is considered to be an agent to remove oxide layer due to its reactive behaviour at lower temperature to form spinel, $MgAl_2O_4$ [5]. Another way is seen in intermetallic phase formation inside the metallic matrix that could bring both the strengthening and fracture resistance enhancement of the aluminium alloy.

Among intermetallic compounds, niobium aluminides appears to be one of potential solution [6]. The Nb-Al phase diagram shows that the $Nb(Al)_{ss}$ solid solution phase is extensive and the other two intermetallic phases are stable under high temperature even above 1000°C, besides, the stoichiometric Nb_3Al phase only exists at high temperature in equilibrium. With temperature falling, the composition of the Nb_3Al deviates from the stoichiometric ratio, which results in T_c declining [7].

Mechano-chemical activation as a type of in-situ method is a solid state powder processing which induces chemical reactions in a mixture of as-received powders at room temperature or at least at temperatures comparably lower than standard sintering ones. An increase in the kinetic of reactions during high energy ball milling can be a result of microstructural refinement, repeated cold intensive deformation and fracture of particles [8]. The mechano-chemical technique has been widely used to fabricate interpenetrating phase composites with nanosized microstructures. A mechano-chemical was process proposed by Iizumi et al. [9].

This work is focused on mechano-chemical reactions in Nb_2O_5 / Al composite system. The work could show whether there is any possibility for formation of intermetallic phase of the type Nb_3Al that could be further used for reinforcement of the aluminium matrix.

2. EXPERIMENTAL

Mixtures of pure aluminium (particle size 45±20 μm, GTV) and niobium (V) oxide (purity 99.9 %, particle size 44 μm, Aldrich) in the stoichiometric ratio of 25 wt.% Al were used as initial materials. Fig. 1 shows the morphology of the as received powders. Al powder has an accidental morphology while Nb_2O_5 spongy.

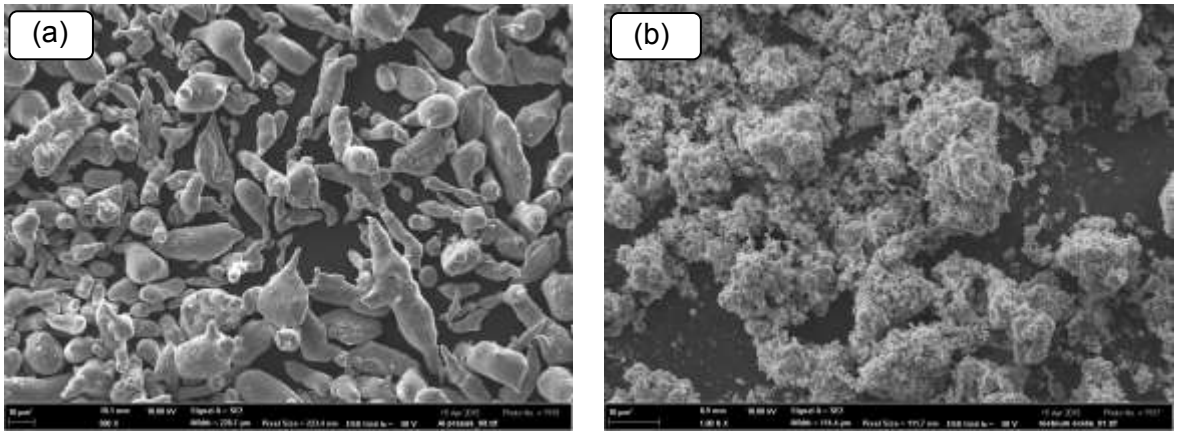

Fig. 1 SEM morphology of as received powders: (a) Al; (b) Nb_2O_5.

Milling was carried out at room temperature using a high-energy planetary ball mill (Fritch Pulverisette 6). High chromium-carbon hardened steel vial containing the powders and balls (of 15 mm in diameter) is fixed onto a rotating disc and rotates in the opposite direction to that of the larger platform. The rotation speed of the vial and platform were fixed at 300 rpm. The mass of powder charge was 15 g and the weight ratio between steel balls and powder charge was controlled about 15:1 in all cases. The powder sample and milling balls were loaded into the vial, which was filled with Ar gas to avoid powder surface contamination. No process control agent (PCA) was used during milling.

Phase transformation and mean crystallite size during milling were determined by X – ray diffraction method (XRD) in a Philips X´PERT diffractometer using filtered Co Kα radiation (λ = 1,790307 Å). The morphology of milled powder particles was examined by scanning electron microscopy (SEM) using ZEISS Ultra Plus electron microscope.

Thermal behaviour was studied by differential scanning calorimetry (DSC) using Setsys Evolution calorimeter from Setaram. The powder samples were placed in a crucible and heated in dynamic Ar atmosphere up to 1200 °C at a rate of 10 K/min. The heating of the samples was conducted in Ar atmosphere.

3. RESULTS AND DISCUSSION

3.1 XRD analysis and crystallite size

XRD analysis enabled Nb_2O_5 to investigate the effect of ball milling time on phases formation. 25 wt.% aluminium and 75 wt.% Nb_2O_5 powders were mixed as stoichiometric mixture to produce Nb – 38 wt.% Nb_3Al nanocomposite. Fig. 2 shows the XRD patterns of powder mixture after different milling times. The diffraction patterns of initial powder mixture show several peaks corresponding to Al and Nb_2O_5. As can be seen, XRD patterns of powder mixture after 2 h of milling time disappear due to the reaction between Nb_2O_5 and Al. But remainder of pure Al is expected to be present in the composite mixtures. Note, that there may be overlapping of Nb and Al diffraction lines. There has been a displacement reaction during ball milling with niobium (V) oxide. At longer milling times the activation energy required for reaction between Nb_2O_5 and Al is provided through mechanical activation and this reaction occurs. So, after 12 h of milling time the Nb_3Al and Nb peaks are presented in the XRD pattern.

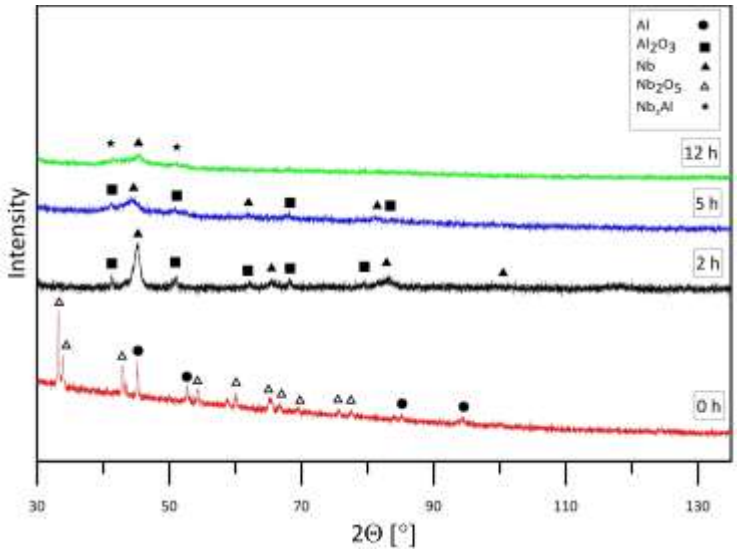

Fig. 2 XRD patterns of Al – Nb_2O_5 powder mixture after 0, 2, 5 and 12 h of milling.

Except for unreacted Nb there are also present Al, Nb_3Al and Al_2O_3 In the mixture. From the diffraction pattern is not easily identifiable signals of the separate phases but this follows from the mass balance of reaction products. Phase Nb_3Al was formed by reaction between free Nb and Al. Free Al stayed in the structure due to still unreacted powder.

Ball milling for 12 h led to broadening of Nb diffraction peaks evidencing crystallite refinement - decrease of crystallite size. The crystallite size of Nb for different milling time is presented in Table 1.The crystallite refinement is caused by severe plastic deformation of powder particles due to impact force of colliding balls during milling process.

Table 1 Crystallite size of Nb after different milling time

Milling time	Crystallite size [Å]
2	110
12	35

3.2 Powder morphology analysis

The changes in morphology of powder particles during milling process are shown in the following Fig. 3. Fig. 3 (a) shows the as-blended powder mixture. The morphology of particles is consisting of Al and Nb_2O_5. After 2 hrs of milling (Fig. 3 (b)) the powder particles are composed of cold welded small units. The powder particles became spherical due to the gradually repeated cold welding, fracturing and severe plastic deformation. The particle size decreases with increasing milling time because the powders are crushed by the collision between the powder and the milling media. But, after 12 h of milling time, as shown in Fig. 3 (d), the particle size increased because of extensive the reaction between Al and Nb_2O_5. This reaction is in fact of exothermic nature and thus increases the temperature locally and causes the particle size to grow.

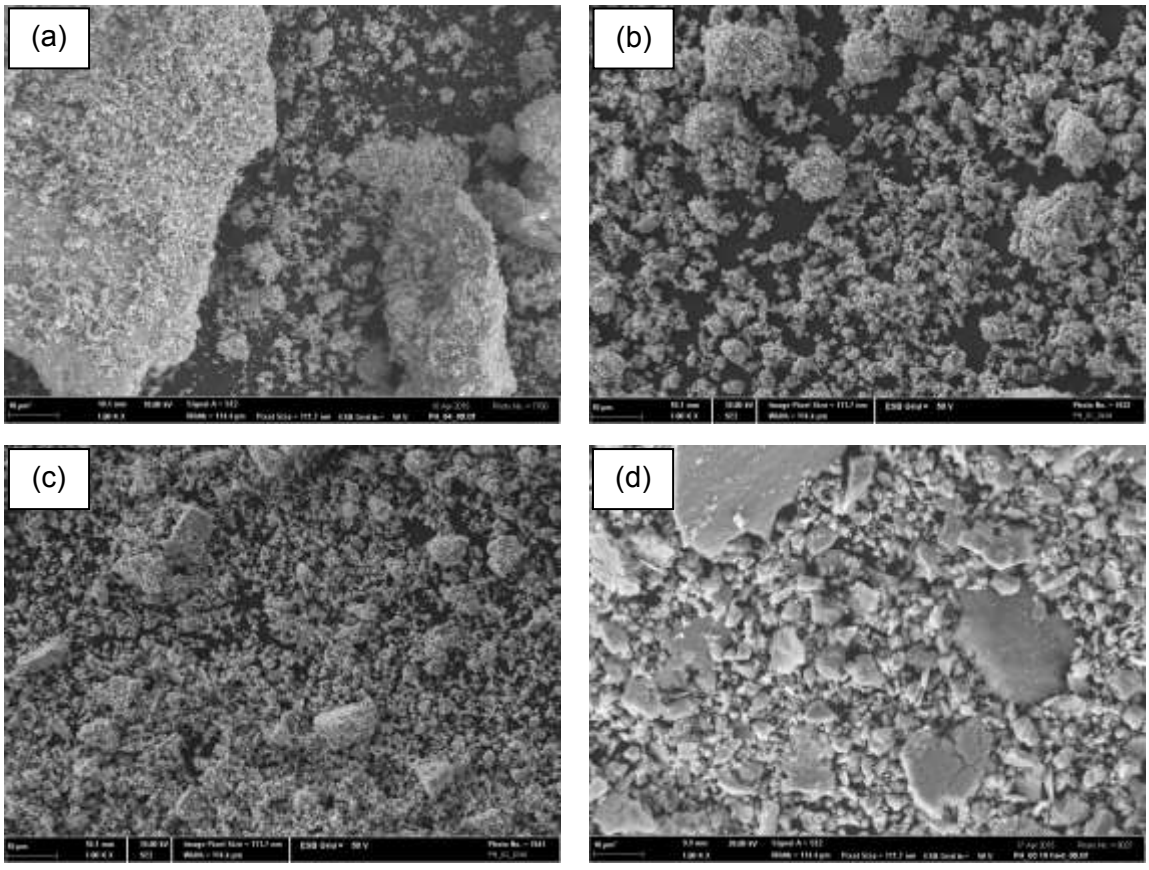

Fig. 3 SEM images of the Al – Nb_2O_5 powders after: (a) 0 h; (b) 2 h; (c) 5 h and (d) 12 h of milling times.

3.3 Thermal analysis

DSC technique was used to detect the phase transformations in the samples. The effect of milling time on the reaction between aluminium and niobium (V) oxide was carried out.

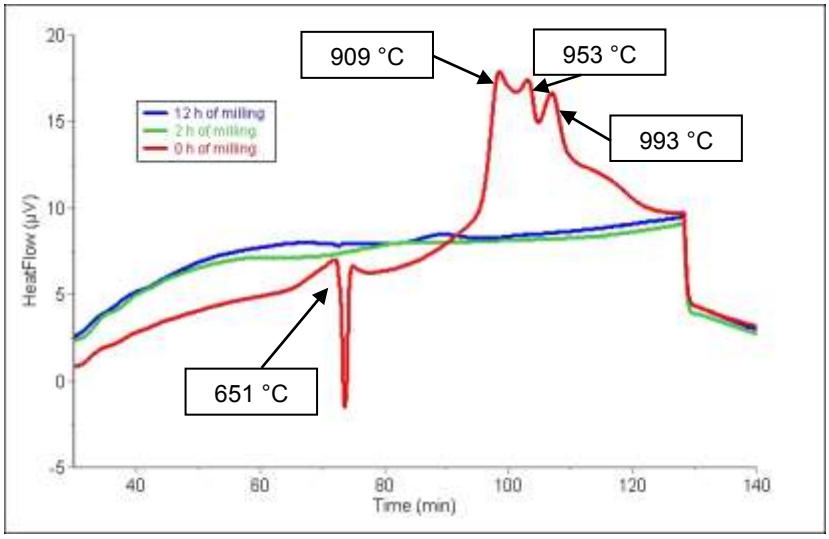

Fig. 4 The DSC analysis (at 1200 °C) of Al/Nb_2O_5 system after different milling time

As observed in Fig. 4 for the initial Al/Nb_2O_5 powder mixture (0 h of milling – red line), four peaks appear in DSC curve. As can be seen, the first peak is an endothermic reaction which corresponds to the melting point of pure aluminium. The other peaks that are seen on the DSC curve are the exothermic peaks at 909, 953 and 993 °C. These three exothermic peaks may correspond to the reduction of Nb_2O_5 by Al and subsequent formation of the intermediate niobium oxides during the reaction [10]. After 2 h of milling (green line) no peaks are observable. The structure is formed by Nb in alumina matrix that are stable up to 1200°C according to this measurement. Only further ball milling induces mechanochemical reaction leading to Nb_3Al phase formation. After 12 h of milling (blue line on DSC diagram) one exothermic peak can be observed. The exothermic peak in the range of 767 – 852 °C can be assigned to intermediate phase from free Nb and further intermetallic Nb_3Al formation.

CONCLUSION

Formation of Nb_3Al nanostructured phase during mechanochemical reaction was investigated. Mechanical ball milling has been found to be a process applicable for producing this phase. XRD analyses showed that during milling (2 – 5 h) there is only exchange reaction between Al and Nb_2O_5 resulting in formation of Al_2O_3 and Nb. After 12 hours of milling only the intermetallic phase Nb_3Al was formed. Crystallite size decreased with increasing milling time. From the analysis of morphology it is evident that particle size is reduced during milling. But, in case of milling for 12 h the particle size was again increased. This was caused by the exothermic reaction between the products of previous stages of ball milling. It was also deducted from the calorimetric studies that the as-blended powder showed reduction of Nb_2O_5 to intermediate niobium oxides at higher temperatures. After 12 h of milling time DSC curve showed formation of intermediate phases and intermetallic Nb_3Al.

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