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EFFECT OF MAGNESIUM ADDITION ON PROPERTIES OF Al-BASED COMPOSITE REINFORCED WITH FINE NiO PARTICLES

WPŁYW DODATKU Mg NA WŁAŚCIWOŚCI KOMPOZYTU NA OSNOWIE Al UMOCNIONEGO DYSPERSYJNYMI CZĄTKAMI NiO

An Al(Mg)−NiO composite was manufactured using combined mechanical alloying (MA) and powder consolidation methods that yielded well-consolidated and very-fine grained bulk material. Compression tests at 293 K – 773 K revealed high mechanical properties of the material. Preliminary annealing at 823 K/6 h was found to result in the flow stress reduction at 573 K – 773 K. However, the effect of preliminary annealing on the flow stress value was relatively low for Al(Mg)-NiO if comparing to similar tests performed for the Al-NiO composite. Structural observations revealed very-fine grained structure of both as-extruded and annealed Al(Mg)-NiO composites. The chemical reaction between the composite matrix and reinforcements (NiO) at sufficiently high temperatures resulted in fine grains and spinel-type particles' development. With respect to the similarly produced Al-NiO composite, a magnesium addition was found to intensify chemical reaction between Al(Mg)-based matrix and NiO particles. As result, fine Al_3Ni particles were observed in both hot-extruded material and Al(Mg)-NiO samples annealed at 823 K/6 h.

Keywords: Mechanical alloying, Al-Mg-NiO, metal matrix composite, nanocrystalline material, powder processing, powder consolidation, solid-state chemical reaction, SEM, STEM, TEM

Kompozyt Al(Mg)−NiO wytworzono metodą mechanicznej syntezy stosując mielenie składników proszkowych i mechaniczną konsolidację uzyskanego proszku kompozytowego w procesie prasowania próżniowego i wyciskania „na gorąco". Uzyskano jednorodny materiał charakteryzujący się dużym rozdrobnieniem składników strukturalnych. Próby ściskania w temperaturze 293 K – 773 K wykazały wysokie własności mechaniczne kompozytu. Wyżarzanie próbek w 823 K / 6 godz. spowodowało nieznaczne obniżenie wartości naprężenia uplastyczniającego w zakresie 573 K – 773 K, jednakże w znacznie mniejszym stopniu niż w porównywanym przypadku kompozytu nie zawierającego dodatku magnezu (Al-NiO), który opisano we wcześniejszej pracy. Obserwacje struktury wyjściowych próbek kompozytowych i próbek wyżarzonych w 823 K / 6 godz. wykazały zmiany strukturalne wywołane reakcją chemiczną między osnową kompozytu (Al-Mg) a dyspersyjnymi cząstkami zbrojenia (NiO), której skutkiem jest utworzenie silnie dyspersyjnych wydzieleń tlenków typu spinelu, oraz submikronowych ziarn typu Al_3Ni. W porównaniu z kompozytem Al-NiO, dodatek magnezu powoduje zwiększenie szybkości reakcji chemicznej, która przejawia się utworzeniem ziarn fazy międzymetalicznej Al_3Ni zarówno w materiale wyjściowym – wyciskanym „na gorąco" – jak również w próbkach wyżarzonych w 823 K / 6 godz.

1. Introduction

Searching for new high-strength and low-density metallic materials is well-motivated by the demands of modern aviation and car industries. However, the application of some products at high service temperatures calls for materials which, in addition, exhibit sufficiently good structural stability and, subsequently, desirable mechanical properties. Light-metal-based composites reinforced with dispersed metal oxide particles (*Me*O) have been proposed as materials that fit the specific requirements mentioned above [1-6].

Our recent research on mechanically alloyed (MA) Al-NiO composite presented the effect of annealing and deformation temperature on the mechanical properties of the material. At high temperatures the composite properties were affected by specific structural processes induced by a chemical reaction between the Al-matrix and the NiO reinforcements [7].

It was concluded that the transformation of structural components in a thermodynamically unstable Al-NiO system leads to the development of very fine aluminum oxide and Al_3Ni particles. However, the coarsening of structural components is controlled by the diffusion process, which becomes relatively slow for substances in the solid state. The commonly used metallurgical procedure would therefore be useless for the production of similar composites.

The experiments described in the present paper were performed on an MA Al(Mg)-NiO composite, and their purpose

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was to test the effect of magnesium addition on the structure and properties of the material with respect to the MA Al-NiO composite investigated in the earlier work [7]. Magnesium was added principally to reduce the material density and enhance the strengthening effect of the aluminum matrix. It is worth stressing that the available data on the structural processes and related mechanical properties of similar Al(Mg)-*Me*O systems leads the conclusion that, besides from the solution strengthening effect, magnesium addition also affects the transformation of structural components at sufficiently high temperatures [8-13].

2. Experimental

A mixture of high purity aluminum-magnesium alloy and nickel oxide powders, containing 86.92 wt% Al – 4.88 wt% Mg – 8.2 wt% NiO, was milled for 30 h in an Attritor ball mill using an argon protective atmosphere. MA-powders were then vacuum-compressed and hot extruded under the same conditions as those reported for the Al-NiO composite [7].

As-extruded MA Al(Mg)-NiO composite samples, 7 mm tall and 5 mm in diameter, were tested over the temperature range of 293 K – 773 K in compression tests performed at constant true strain rate of $5 \cdot 10^{-3}$ s^{-1}. In order to reduce friction between the anvils and the sample, flaked graphite was used. A set of samples was annealed at 823 K/6 h to investigate the effect of annealing on the material structure and properties.

Hitachi S-70 scanning electron microscope (SEM), JEM2010 analytical transmission electron microscope equipped with scanning transmission electron microscopy device (STEM) and X-ray energy dispersive system (EDS) were used for the material structure examination and chemical analysis of structural components.

3. Results and discussion

Mechanical tests

A set of true stress *vs.* true strain curves recorded for as-extruded material and samples preliminarily annealed at 823 K/6 h are shown in Fig. 1. High-temperature flow stress characteristics are typical for aluminum alloys undergoing dynamic recovery. Flow stress decreasing at 393 K – 473 K that follows the maximum on the $\sigma_t - \varepsilon_t$ curve, may be attributed to flow localization and sample bending rather than any structural softening processes. Local micro-cracks observed in the as-extruded material deformed at room temperature may also contribute to the flow stress reduction observed for larger strains, i.e. $\varepsilon_t = 0.3{-}0.4$.

A set of samples was annealed at 823 K/6 h to investigate the annealing effect on the structure and the related mechanical properties of the material (Fig. 1b). Neither the as-extruded nor the annealed samples deformed at high temperatures fractured over the applied strain range ($\varepsilon_t \leqslant 0.4$). It is worth noting that the ductility of tested materials was relatively high when comparing to the Al-NiO composite investigated earlier that became brittle at 293 K-473 K after annealing at 823 K/6 h [7].

The effect of deformation temperature on the maximum flow stress is shown in Fig. 2 for as-extruded Al(Mg)-NiO material and the samples annealed at 873 K/6 h. For comparison, the maximum flow stress data for similarly manufactured Al-NiO samples [7] and some other MA composites reported in the literature are also displayed in figure [11-13]. The effect of magnesium addition on the strengthening of the as-extruded Al(Mg)-NiO composite was practically negligible at low deformation temperatures (293-423 K). However, above ~500 K the flow stress value for the as-extruded Al(Mg)-NiO samples was lower than that for the Al-NiO composite. The latter effect of flow stress reduction with temperature may, to some degree,

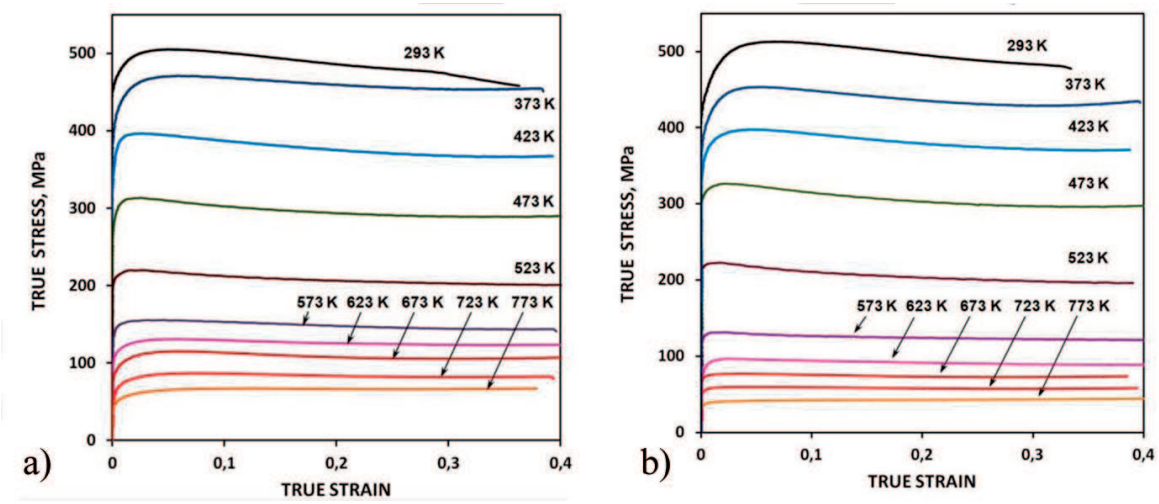

Fig. 1. Effect of deformation temperature on flow stress in the MA Al(Mg)-NiO composite: a) as-extruded material; b) samples annealed at 823 K/6 h

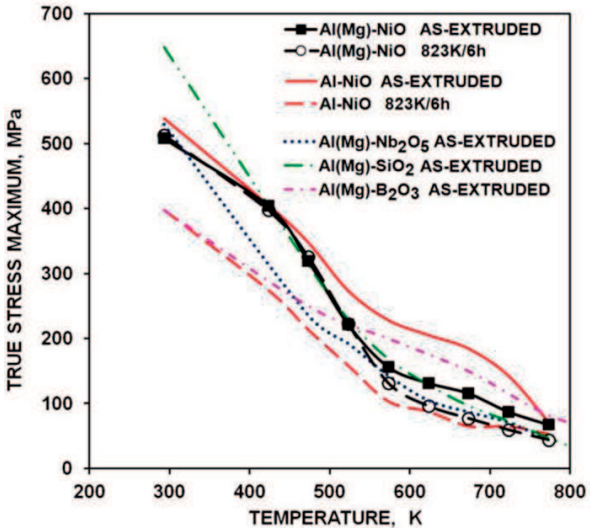

Fig. 2. Maximum flow stress vs. deformation temperature for the as-extruded material and samples annealed at 823 K/ 6 h. For comparison, the data for Al-NiO and Al-NiO annealed at 823 K/6 h as well as the data for similarly produced as-extruded MA composites Al(Mg)-Nb_2O_3, Al(Mg)-SiO_2 and Al(Mg)-B_2O_3 are shown in the figure [11-13]

be attributed to the decline in s*olidus* temperature due to the magnesium addition. The *solidus* temperature for aluminum (933 K) is reduced to approx. 850 K for the Al-4.88 wt% Mg alloy. Consequently, the low flow stress values for Al(Mg)-NiO tested over the range of high temperatures (Fig. 1b) is affected by relatively high homological temperature, *i.e.* $T/T_{melting}$ ratio.

Samples deformed *via* compression were water-quenched immediately after completion of deformation at $\varepsilon_t \cong 0.4$. The samples were cut along the direction of compression and Vickers hardness tests, using an indenter load of 0.98 N, were performed on a flat surface of each sample. A slight hardness decrease, i.e. from 141 HV to 134 HV, was observed for the as-extruded samples when deformation temperature raised

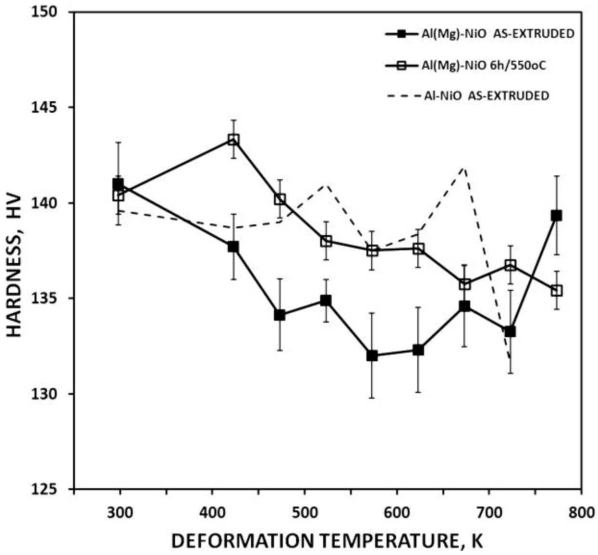

Fig. 3. Vickers hardness vs. deformation temperature for the as-extruded Al(Mg)-NiO composite (filled marks) and samples annealed at 823 K/ 6 h (open marks). For comparison, the data for hot-deformed Al-NiO samples are shown in the figure [7]

from 293 K to 723 K (Fig. 3). The hardness of samples preliminarily annealed at 823 K/6 h was decreased from 140 HV to 137 HV for samples deformed at 423 K and 773 K, respectively. It was found that the hardness of the hot-deformed samples tended to increase after preliminary annealing of the Al(Mg)-NiO composite. Similar effects of the composite hardening, that occur due to the annealing procedures, were reported for Al-based MA composites reinforced with Nb_2O_5, V_2O_5, WO_3, HfO_2, MnO_2 particles [14, 15]. Unfortunately, the scatter of the present results and the variation in average hardness values were too high to make further analysis possible.

Structural examination

In order to analyze the structural processes that affect the mechanical properties of the tested material, structural examinations were performed using SEM, TEM, STEM and energy dispersive X-ray analysis (EDS) methods. The SEM micrographs of the as-extruded Al(Mg)-NiO material and the sample annealed at 823 K/6 h were useful for evaluating the morphology of structural components at relatively low magnification and the statistical assessment of the material porosity. The SEM microstructure of as-extruded and annealed samples is shown in Fig. 4a and Fig. 4b, respectively. It is assumed that the chemical reaction between the NiO particles and the Al(Mg) matrix results in the growth of Al_3Ni and $MgAl_2O_4$ (spinel) particles at high annealing temperatures. The expected local volume reduction accompanying this reaction, should be Δv = -9.0%. However, the porosity of both as-extruded and annealed samples, as observed by means of SEM, was lower than 1%. For comparison, the porosity of the as-extruded MA Al-NiO composite was equal to 3.4% and was reported to increase to 9% after annealing at 823 K/6 h [7]. The reason of such a pronounced difference between the experimental and calculated data is unclear and requires additional research.

The STEM microstructures typical for the as-extruded Al(Mg)-NiO composite and the sample annealed at 823 K/6 h are shown in Fig. 5a and Fig. 5b, respectively. The average grain size was estimated from STEM microphotographs as intercept length using statistical line-cross-section method. During annealing at 823 K/6 h the average grain size of the material was reduced from 368±253 nm to 321±104 nm for the as-extruded and annealed samples, respectively. The finer grain size of the as-annealed material result ad likely from the recovery process as well as the development of fine intermetallic grains that form due to the aforementioned chemical reaction. It is worth noting that the average increase in grain size observed for the Al-Ni composite was found to result in an evident decrease in the flow stress value during hot compression tests [7]. On the other hand, neither the average grain size nor the flow stress value for the hot deformed Al-(Mg)-NiO composite were affected by the preliminary annealing to the extent observed for Al-NiO samples.

Structural observations were also performed for samples deformed in a hot compression test. However, the STEM microstructure of hot deformed samples was practically not varied with deformation temperature and look very similar to the microstructure shown in Fig. 5c.

Most relatively dark grains, $\leqslant 1.5\ \mu$m in size, were found to contain 20-30 at% Ni suggesting the development of the

Al_3Ni phase. TEM observations performed at relatively high magnification and a careful analysis of structural components in as-extruded Al(Mg)-NiO material confirmed the presence of the Al_3Ni grains, as shown in Fig. 6a. The SAD pattern, shown in the inset, confirmed that the crystal structure corresponded to the Al_3Ni-type. It was found that very few relatively large NiO particles were deoxidized to Ni-rich particles containing 80-90 wt.% Ni. The particles were surrounded by nano-sized (Mg,Al)-rich oxide agglomerates, as shown in Fig. 6b. The SAD pattern shown in Fig. 6c indicates the development of Ni-type and $MgAl_2O_4$-type (spinel) structures, with the diffraction spots distribution characteristic for very fine particles. However, the Al/Mg atomic ratio detected by means of EDS for the agglomerate of nano-sized oxides surrounding the Ni-rich particle was close to 78/22. The detected excess of magnesium resulted likely from the nucleation of both MgO and spinel particles at an early stage of NiO-particle chemical decomposition. Unfortunately, the most intense {200}MgO, spots marked in Fig. 6c, are too close to the {111} Ni-ring to

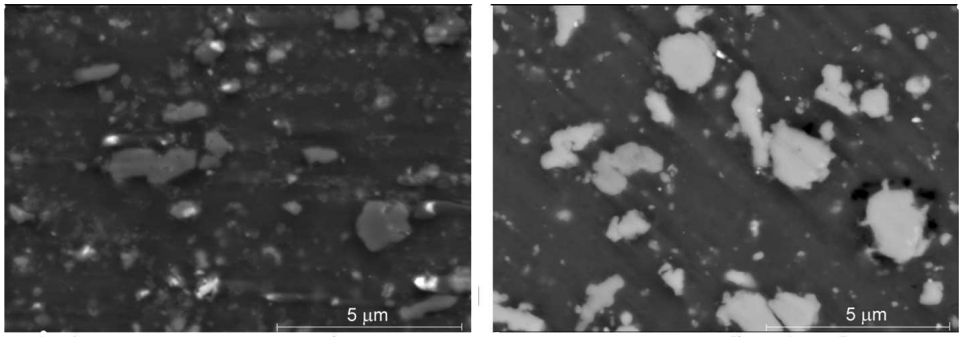

Fig. 4. SEM microstructure of Al(Mg)-NiO composite: (a) as-extruded material; (b) sample annealed at 823 K/6 h

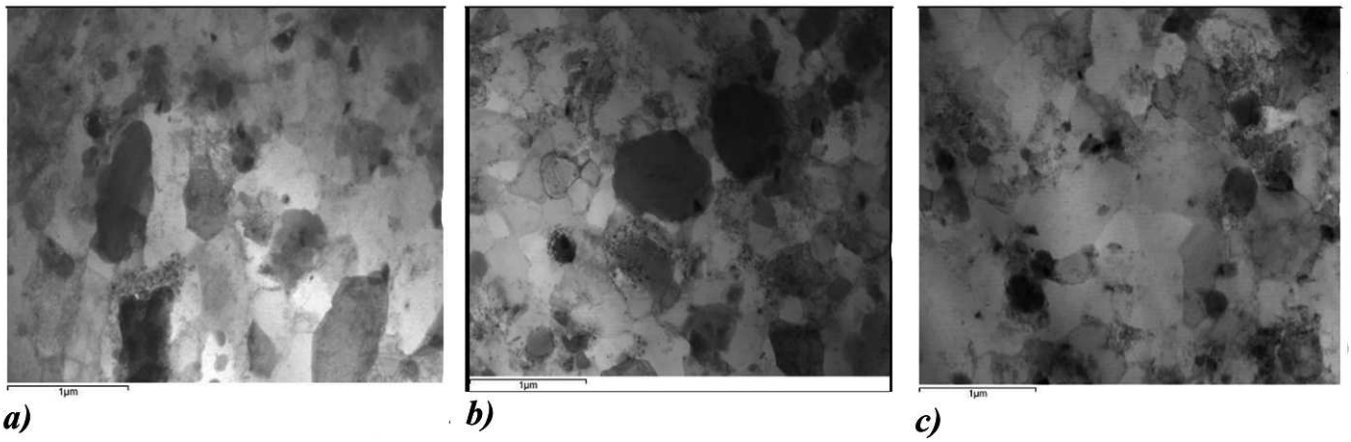

Fig. 5. STEM microstructure of Al(Mg)-NiO composite: (a) as-extruded material; (b) sample annealed at 823 K/6 h; (c) as-extruded sample deformed at 773 K with ε_t = 0.4

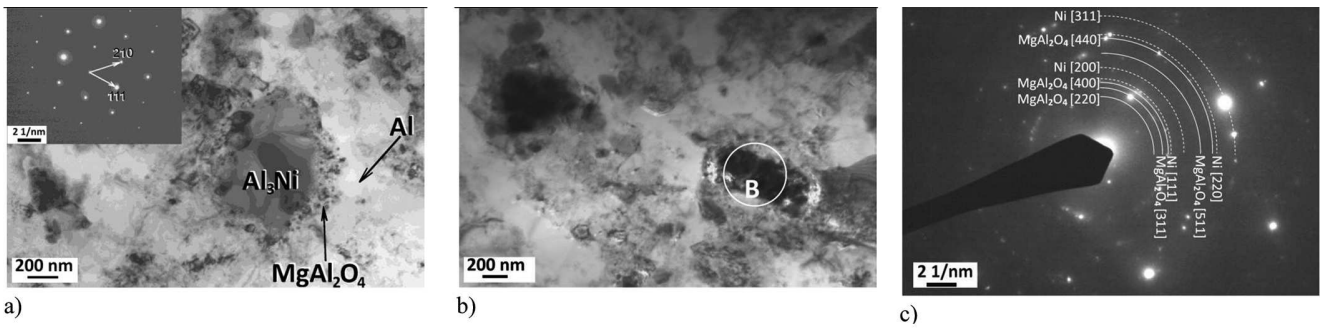

Fig. 6. Microstructure of as-extruded Al(Mg)-NiO composite: a) TEM image and the SAD pattern taken from an Al_3 Ni grain (inset); the fine oxygen-rich particles in the Al-matrix (Al) surrounding the Al_3 Ni grain were identified as a spinel-type, $MgAl_2O_4$; (b) TEM image and the SAD pattern (c) obtained for the area marked as 'B'; positions of diffraction spots for nickel and spinel structures were marked in the diffraction image

be distinguished as discrete objects. However, it is worth mentioning that an occurrence of the spinel-type particles was also reported at other as-annealed MA Al(Mg)-based composites reinforced with some heavy-metal oxide particles [8-13].

The particles with the Ni-type crystal structure were not found in the sample annealed at 823 K/6 h. Likewise, only Al_3Ni grains and very fine spinel-type particles were observed for the sample deformed by compression at 773 K. The results lead the conclusion that the chemical reaction between the initial components of MA Al(Mg)-NiO composite was practically complete both for the as-annealed samples and for the samples hot-deformed at 773 K.

In summary, the structural processes revealed by means of TEM/EDS analyses account for the mechanical properties of the material shown in Figs 1-3. It is commonly accepted that Mg-addition rises aluminum alloy mechanical properties due to the solution strengthening effect. However, the flow stress maximum vs. deformation temperature data for both as-extruded and preliminarily annealed Al(Mg)-NiO samples, shown in Fig. 2, point to the relatively low magnesium strengthening efefct if compared to the data reported for the MA Al-NiO composite [7]. It seems reasonable to conclude that the advanced transformation of NiO particles into thermodynamically stable Al_3Ni and $MgAl_2O_4$ components in the Al(Mg)-NiO composite extruded at 673 K is responsible for the flow stress decrease observed for a wide range of deformation temperatures. Therefore, the effect of preliminary annealing (823 K/6 h) on the flow stress vs. deformation temperature characteristics was very limited, as shown in Fig. 1b, because the chemical reaction occurred practically during the hot extrusion of the composite, i.e. before sample annealing.

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