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EFFECT OF TEMPERATURE ON THE STRUCTURE AND MECHANICAL PROPERTIES OF MECHANICALLY ALLOYED Al-NiO COMPOSITE

WPŁYW TEMPERATURY NA STRUKTURĘ I WŁAŚCIWOŚCI KOMPOZYTU Al-NiO WYTWORZONEGO METODĄ MECHANICZNEJ SYNTEZY SKŁADNIKÓW

Mechanical alloying of high-purity aluminum and 10 wt.% NiO powders combined with powder vacuum compression and following hot extrusion method was used to produce an Al-NiO composite. Mechanical properties of as-extruded materials as well as the samples annealed at 823 K /6 h, were tested by compression at 293 K – 770 K. High mechanical properties of the material were attributed to the highly refined structure of the samples. It was found that the structure morphology was practically not changed during hot-compression tests. Therefore, the effect of deformation temperature on the hardness of as-deformed samples was very limited. The annealing of samples at 823 K/6 h induced a chemical reaction between NiO-particles and surrounding aluminum matrix. As a result, the development of very fine aluminum oxide and Al_3Ni grains was observed.

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

Kompozyt na osnowie aluminium zawierający dodatek 10%mas. NiO wytworzono metodą mechanicznej syntezy stosując mielenie proszków aluminium i tlenku niklu oraz mechaniczną konsolidację uzyskanego proszku metodą prasowania próżniowego i wyciskania w temperaturze 673 K. Własności mechaniczne uzyskanego kompozytu, jak również próbek wyżarzonych w 773 K/6 godz., badano w zakresie 293 K-770 K w próbie ściskania. Badania strukturalne wykazały silne rozdrobnienie składników strukturalnych zarówno w materiale wyciskanym, jak również w próbkach wyżarzonych, co jest przyczyną wysokich własności mechanicznych uzyskanego kompozytu. W przypadku próbek odkształcanych „na gorąco” praktycznie nie obserwuje się istotnych zmian morfologii struktury. Jednakże wyżarzanie w 823 K/6 godz. spowodowało zmiany strukturalne wywołane reakcją chemiczną między cząstkami NiO a osnową, której skutkiem było utworzenie silnie dyspersyjnych wydzieleń tlenku aluminium i ziarn fazy międzymetalicznej typu Al_3Ni.

1. Introduction

Mechanical alloying (MA) and powder metallurgy methods (P/M) are often used with success for the processing of fine-grained and high-strength metallic materials. In particular, low-density composites based on aluminum or magnesium matrices are very useful for numerous applications in the automobile and aircraft industries because of their high strength-to-density ratios. One of the advantages of the above-mentioned methods is strengthening of light metals resulted from an addition of highly refined ceramics such as transition metal oxides or metal silicides [1-7]. Metallurgical methods are useless for the production of such composites, as the liquid matrix and reinforcements are very reactive at high temperatures. On the other hand, the consolidation of the components in the solid state by application of the MA and P/M procedures, makes it possible to effectively retard the chemical reactions between them.

Light composites based on an aluminum matrix and reinforced with heavy-metal oxides (MeO) can be categorized into two groups if the structural effect of the chemical reaction between the matrix and the reinforcement is considered. Due to the high affinity of oxygen to aluminum, most MeO compounds are reduced and very fine Al_2O_3 particles are formed. The first group of composites was distinguished for the Al−MeO systems, in which the released Me-metal hardly dissolves in the matrix and does not create any intermetallic compounds in the aluminum matrix. For example, fine Me-particles were reported to form in annealed composites reinforced with PbO, SnO, Bi_2O_3, Sb_2O_3, or GeO_2 particles [4, 8]. The basic issue pertaining to the application of a particular composite is related to the possible increase in the material porosity during exposure to high temperatures. Chemical reactions between the oxide particles and the surrounding matrix usually result in the local reduction in the material specific volume. As a consequence, the nucleation of Me-particles and

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aluminum/magnesium oxides is accompanied by the growth of voids in the vicinity of pre-existing MeO particles.

The second group of composites was recognized with respect to the development of Al_xMe_y intermetallic phase that follows the chemical reaction between MeO particles and the surrounding aluminum (magnesium) matrix. The diffusion of the released Me-atoms into the surrounding matrix triggers the growth of intermetallic grains. The latter process is usually suppressed due to the development of nano-sized aluminum/magnesium oxides in the neighboring matrix. Numerous materials reinforced with compounds such as Nb_2O_5, Sc_2O_3, WO_3, MnO_2, MoO_2, HfO_2, Fe_2O_3 belong to the mentioned group of MA composites [8-9, 10]. It is worth to emphasize that the most pronounced intermetallic grain coarsening occurs in some composites when the grain growth is accompanied by the volume expansion effect, i.e. the local reduction of the material density. The expansion of the growing particles provides a sustained diffusion stream of the Me-element through the interphase boundary. Therefore, the growing intermetallic grains can reach a size of over 75 μm, as reported for the MA Al$-V_2O_5$ composite annealed at 873 K / 100 h [7].

Expansion or shrinking effects induced by chemical reactions between MeO particles and aluminum or aluminum-magnesium matrices may be approximately estimated from the specific volumes of substrates and products. High porosity of the composite is expected if the chemical reactions result in a local increase in the product density, i.e. when the specific volume of products is reduced in relation to the initial volume of substrates. If the subsequent growth of intermetallic grains yields a local expansion effect, the porosity induced by the chemical reaction may become suppressed.

The experiments on the MA Al−NiO composite described in the present paper were performed in order to investigate new composite system that would be suitable for manufacturing high-strength and low-weight materials. In particular, the effect of temperature on structural evolution at high temperatures and the related properties of the composites was investigated.

2. Experimental

A mechanically alloyed Al-NiO composite was manufactured from high-purity components. The mixture of fine-grained powders with the compositions 91.8 wt% Al – 8.2 wt% NiO was milled in an argon atmosphere for 30 h using an attritor mill. Methanol was used as a process control agent to avoid the agglomeration of powder particles.

The obtained MA powders were packed into an AA6061 aluminum alloy container, compressed under a pressure of 550 MPa and degassed at 623 K/1 h in vacuum under a pressure of 1.3÷13.3 μPa. The material was extruded at 673 K using a cross-section reduction ratio of λ =22.8. The obtained rods, 7 mm in diameter, were machined in order to remove a thin layer of AA6061 coating, and then 8 mm long samples were excised for the compression tests. A set of samples was annealed at 823 K/6 h to investigate an effect of annealing on the material structure and the related properties. The mechanical properties of the Al-NiO composite were tested in compression at 298 K-773 K and the constant true strain rate $\dot{\varepsilon}$ =5·10^{-3}s^{-1}. In order to reduce friction between the anvils and the sample, flaked graphite was used.

3. Results and discussion

3.1. Mechanical tests

True stress *vs.* true strain curves received for the as-extruded Al-NiO composite and samples annealed at 823 K/6 h are shown in Fig. 1a and Fig. 1b, respectively. High-temperature flow stress characteristics are typical for aluminum alloys undergoing dynamic recovery. The decrease at 293 K – 423 K, which follows the maximum on $\sigma_t - \varepsilon_t$ curve, may be attributed to flow localization and sample bending rather than any structural softening processes. Moreover, the development of local micro-cracks in some samples may also intensify a flow stress decrease at larger strains, especially for the samples deformed at 293 K. The flow stress decrease at
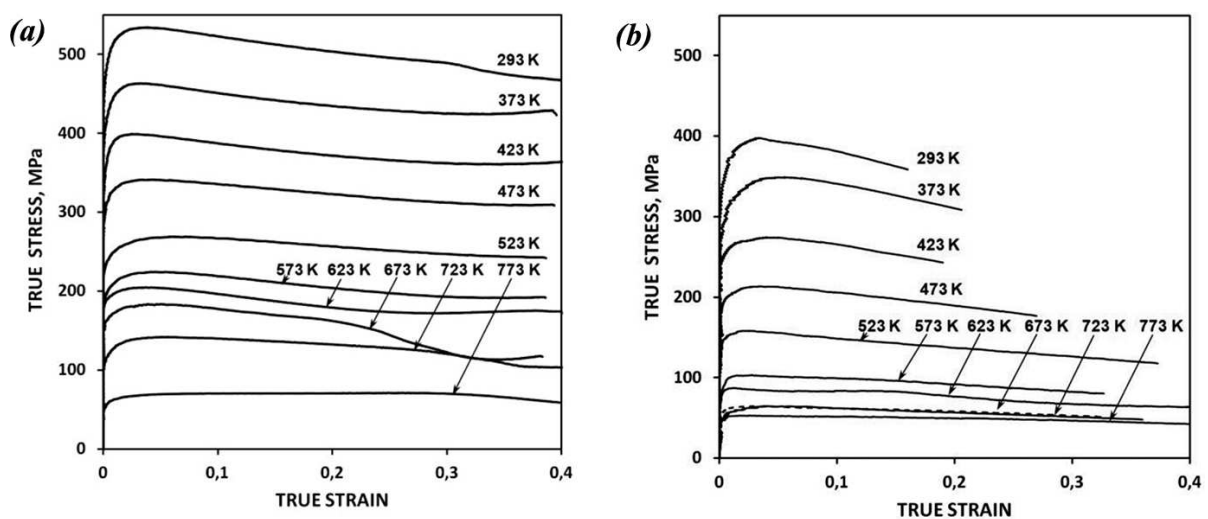

Fig. 1. Effect of deformation temperature on the true stress vs. true strain characteristics for MA Al-NiO composite: a) as extruded material; b) samples preliminarily annealed at 823 K/6 h

ε_t ~0.25 for the sample deformed at 673 K resulted from an accidental fracture of the sample. The remaining samples deformed at high temperatures did not fracture over the applied strain range ($\varepsilon_t \leqslant 0.4$).

A set of samples was annealed at 823 K/6 h to examine the effect of temperature on the structure and properties of the composite. It was found that preliminary annealing of the composite resulted in a *ca.* 100 MPa reduction in flow stress for the samples deformed at 293 K-673 K (Fig. 1b). Fracture of as annealed samples at $\varepsilon_t = 0.2 - 0.3$ was observed in the temperature range of 293 K – 473 K. Remaining samples, deformed at higher temperatures, did not fracture regardless of some fine micro-cracks developed during the test.

The flow stress maximum decreased monotonically with increasing deformation temperature for both as-extruded and annealed samples, as shown in Fig. 2. For comparison, some data reported for similar MA Al-Nb$_2$O$_5$ and MA Al-V$_2$O$_5$ composites are also displayed in the Figure [7, 11].
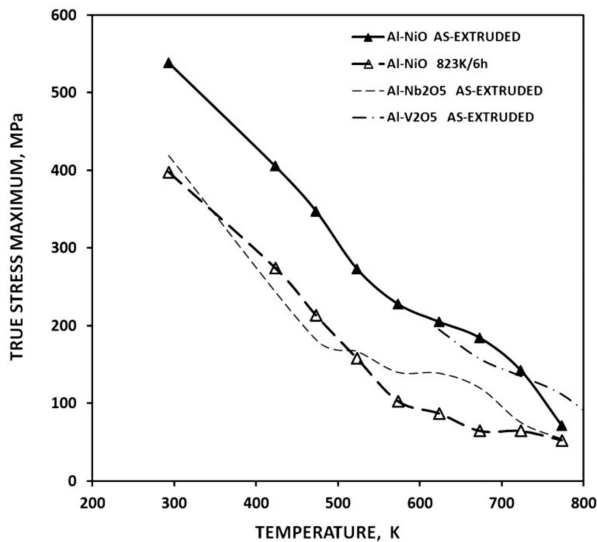

Fig. 2. Maximum flow stress vs. temperature relationship for as-extruded MA Al-NiO composite and samples preliminarily annealed at 823 K/6 h. Some data for similar as-extruded MA Al-Nb$_2$O$_5$ and MA Al-V$_2$O$_5$ composites are displayed for comparison [7, 11]

Samples deformed with true strain of $\varepsilon_t \cong 0.4$ were water-quenched immediately after deformation. Vickers hardness tests were performed using an indenter load of 0.98 N (0.1 kG). It was found that increasing the deformation temperature did not result in significant reduction in the material hardness, that remained within the range of 138 HV-143 HV for the samples deformed at 293 K-673 K. A slightly lower hardness value of 132 HV was obtained for the sample deformed at 723 K. However, the scatter of results makes the hardness vs. deformation temperature analysis difficult to interpret unambiguously. Hardness results for preliminarily annealed and hot deformed samples were not displayed in the figure since the sample fractured before the limit value of $\varepsilon_t \cong 0.4$ was reached.
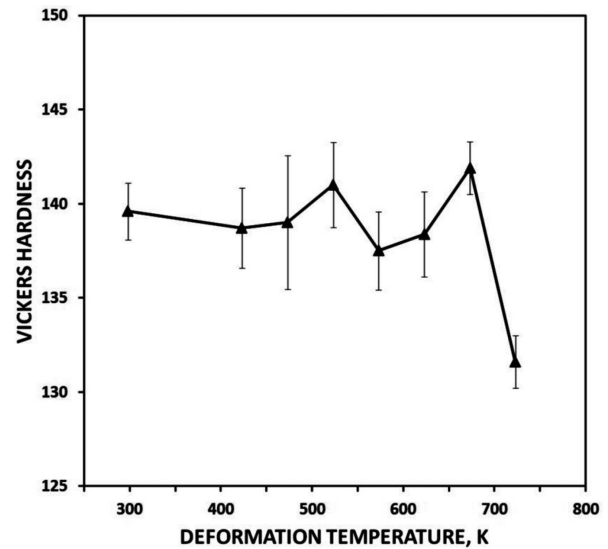

Fig. 3. Hardness of as-extruded Al-NiO samples deformed with $\varepsilon_t \cong 0.4$ via compression at 293 K-773 K

4. Structural observations

The structure of the as-extruded composite and the sample annealed at 823 K/6 h was observed by means of SEM in order to estimate the material porosity and the distribution of NiO-particles (Fig. 4). The porosity of the material was estimated using a common statistical point method with a grid of 10x10 points superimposed on SEM images. The initial porosity of the as-extruded Al-NiO composite was 3.4% and increased to 9% after annealing at 823 K/6 h. Unfortunately, the resolution of SEM/EDX was insufficient to distinguish very fine Ni-rich intermetallic grains from NiO particles. Aluminum oxide particles were also too fine to be detected in the matrix.
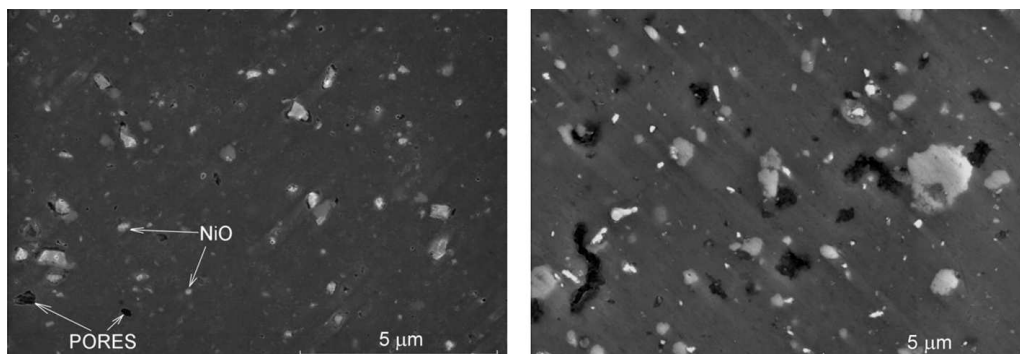

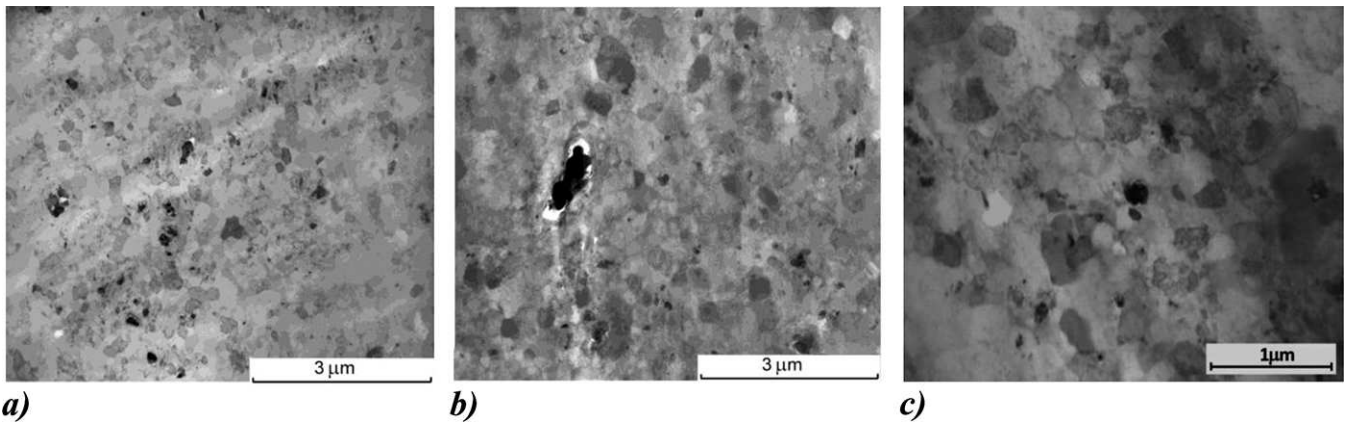Fig. 4. SEM microstructure of Al-NiO composite: (a) as-extruded material; (b) sample annealed at 823 K/6 h

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

A set of STEM microstructures for the as-extruded material and the sample annealed at 823 K/6 h is shown in Fig. 5a and Fig. 5b, respectively. The STEM examinations revealed a fine-grained structure of the composite matrix. The grain size was estimated from STEM microphotographs as an average intercept length using statistical line cross-section method. The grain size for the Al-NiO composite, i.e. the average intercept length with a standard deviation, was 183±75 nm and 304±140 nm for the as-extruded and annealed samples, respectively. It is worth mentioning that no evident coarsening of structural components was observed for samples deformed by compression at 773 K (Fig. 5c).

A detailed analysis of fine structural components was performed using TEM, EDX and SAD pattern analysis methods. The TEM structure of the as-extruded Al-NiO composite is shown in Fig. 6a. The most of particles in the as-extruded Al-NiO composite were characterized by a Ni/O atomic ratio that corresponded closely to the NiO stoichiometry. However, the EDX analysis also revealed a nickel content of over 95 at.% for numerous particles that were also surrounded by a thin aluminum oxide layer. The typical constituents of the structure, i.e. the reduced Ni-rich granules (Ni) surrounded by an aluminum oxide layer (Al_2O_3) and the nano-sized aluminum oxide particles in the matrix, are marked in Fig. 6a. The structure of some fine (Ni, Al)-rich particles such as the P-particle marked in the figure is probably of the Al_3Ni type. However, diffraction spots corresponding to the Al_3Ni crystal structure were indistinguishable on SAD patterns taken from the analyzed area containing the fine P-particle. On the other hand, Al_3Ni grains were often observed in the sample annealed at 823 K/6 h, as shown in Fig. 6b. The inserted SAD pattern corresponds to the orthorhombic structure of the Al_3Ni phase (*Pnma*, a=0.6611 nm, b =0.7366 nm, c =0.4812 nm) [12].

The initial stage of a chemical reaction between Al-matrix and NiO particles was also detected for the as-extruded sample deformed with $\varepsilon_t \sim 0.4$ by compression at 773 K (Fig. 7). Ni-rich particles observed on the Ni-element distribution map (Fig. 7b) were surrounded by a thin oxygen-enriched layer (Fig. 7c). This peculiar distribution of oxygen and nickel suggests the beginning of a chemical reaction between NiO and the Al-matrix; this reaction leads to the nucleation of Ni-rich particles and a thin layer of aluminum oxides at preliminary Al/NiO interphase boundaries.
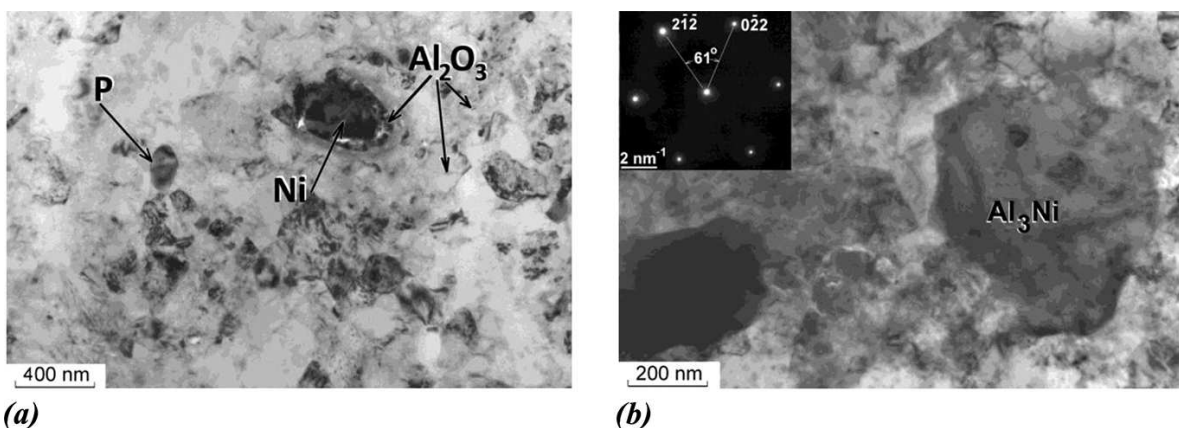

Fig. 6. TEM structure of Al-NiO composite: a) the as-extruded sample (as-reduced nickel-oxide particle (Ni), the surrounding necklace of Al_2O_3 nano-particles, and what is presumably an intermetallic grain (P) are marked in the image); b) sample annealed at 823 K/6 h (inset: SAD pattern taken from the particle marked Al_3Ni in the TEM image)
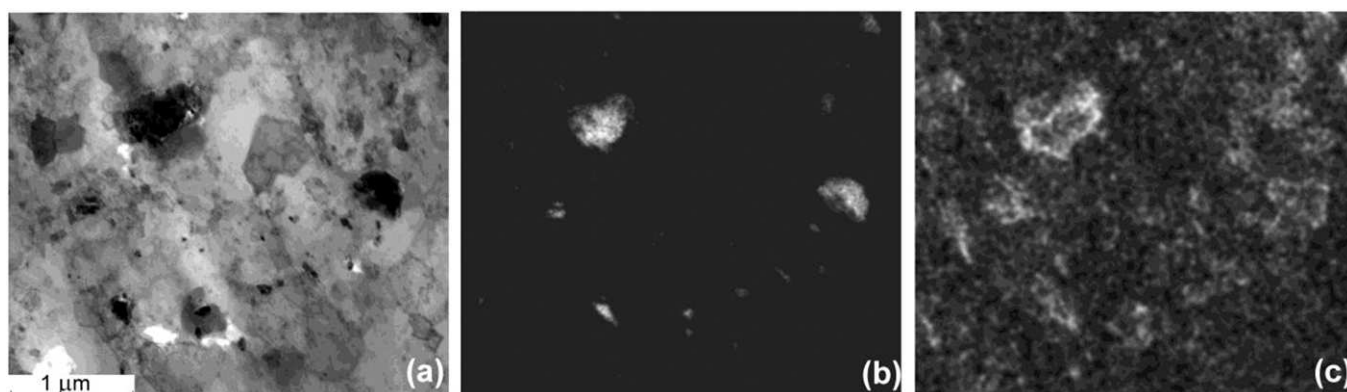
Fig. 7. Element mapping for as-extruded sample deformed at 773 K with ε_t = 0.4: a) STEM image; b) nickel distribution; c) oxygen distribution

5. Summary

In summary, the mechanical alloying of components and the procedure applied for the consolidation of MA-powders yielded a well-consolidated bulk Al-NiO composite. The highly refined structure of the material yielded high mechanical properties, which are slightly higher than those for similarly produced MA Al-Nb$_2$O$_5$ and MA Al-V$_2$O$_5$ composites [7, 11]. Preliminary annealing of samples at 823 K/6 h was found to result in a pronounced deterioration of mechanical properties, which stems from the recovery process and an overlapping effect of specific transformation of the composite structure, induced at high temperature by a chemical reaction between components. TEM observations of as-extruded materials lead to the conclusion that chemical reactions between NiO particles and surrounding matrix occur already during the hot consolidation of MA-powders.

The calculation of substrates/products density ratio corresponding to the mentioned chemical reaction in the annealed Al-NiO composite leads to the conclusion that the decay of NiO particles and Al$_3$Ni + Al$_2$O$_3$ formation is accompanied by a local volume reduction Δv = -8.4%. Relatively high porosity of as-annealed Al-NiO samples may be responsible for the fracturing of the samples during compression at 293 K − 423 K.

Hot compression tests hardly change the morphology of structural components. The grain coarsening during short-time test, or the structure transformation induced by the solid-state chemical reaction, are very limited to result in a noticeable change of the material microstructure. Since dislocations were practically absent inside fine Al$_3$Ni particles, it was concluded that the particles did not deforme during compression tests. Moreover, the hot deformation process did not result in noticeable changes in the dislocation substructure of the matrix. Fine subgrains in as-deformed samples were similar in size to those observed for the as-extruded material. The subgrain coarsening during annealing or hot deformation was very limited, mostly due to the high density of nano-sized oxides and intermetallic particles in the composite matrix.

Acknowledgements

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