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Z. WITCZAK*, S. DYMEK**

EFFECTIVNESS OF DISPERSION STRENGTHENING IN THE NiAl INTERMETALLIC ALLOY PRODUCED BY SELF-SUSTAINING HIGH-TEMPERATURE SYNTHESIS

EFEKTYWNOŚĆ DYSPERSYJNEGO UMOCNIENIA REAKTYWNIE SPIEKANEGO ZWIĄZKU MIĘDZYMETALICZNEGO NiAl

The stoichiometric NiAl intermetallic alloy strengthened by nano-particles of Al_2O_3 was produced by self-sustaining high-temperature synthesis (SHS). The particles, in the volume quantity of 2.5 and 5%, were introduced into the material at the stage of mechanical mixing of elemental nickel and aluminium powders. Two methods of mechanical mixing of powders were employed: a conventional one, where the powders were mixed in a ball rotational mixer (in air) and the ultrasonic method, where the powders were mixed by high intensity ultrasound in a liquid (acetone) or gaseous (helium) medium. The mixed powders were subjected to the SHS process. All synthesised materials were densified by hot hydrostatic extrusion (hydroextrusion) at the same conditions (1000°C, 4:1 reduction ratio). The effectiveness of the applied technological procedure was estimated from the mechanical properties of the produced materials. Mechanical properties were measured by means of uniaxial compression tests. Beside the as-received materials, the materials after high-temperature annealing were tested. This permitted evaluation of the thermal stability of the materials. Strength and plastic properties of the materials were determined from an acoustic emission being monitored during the test. As a measure of the quality of the synthesized alloys, the product of the yield strength and the maximal true plastic strain was proposed. Using this measure, it was established that the ultrasonic method of doping nano-particles is more effective, and that the most desireable quantity of the Al_2O_3 dispersoid in the NiAl matrix is less than 5% by volume.

Keywords: intermetallic NiAl, dispersion strengthening, ductility, microcracking, acoustic emission

Zbadano wpływ technologii wprowadzania nanocząstek Al_2O_3 do osnowy stechiometrycznego związku międzymetalicznego NiAl na efektywność procesu dyspersyjnego umacniania stopu. Nanocząstki, w ilości 2,5 i 5% obj., były wprowadzane mechanicznie do materiału na etapie mieszania proszków wyjściowych niklu i aluminium przed procesem samopodtrzymującej się wysokotemperaturowej syntezy (SHS). Zastosowano dwie procedury mieszania: tradycyjną, w mieszalniku kulowym (w powietrzu) oraz ultradźwiękową w ośrodku ciekłym (aceton) i gazowym (hel). Po procesie syntezy wszystkie materiały były dogęszczane przez wyciskanie hydrostatyczne na gorąco (1000 °C, współczynnik wyciskania 4) w jednakowych warunkach. Efektywność całego procesu technologicznego oceniano na podstawie własności mechanicznych wytworzonych materiałów, bezpośrednio po hydroekstruzji oraz, w celu oszacowania ich stabilności termicznej, po wysokotemperaturowym wyżarzaniu. Własności mechaniczne mierzone były w próbie jednoosiowego ściskania. Dzięki monitorowaniu, metodą emisji akustycznej, całego procesu odkształcania materiału można było określić nie tylko jego wytrzymałościowe, ale również plastyczne własności. Zaproponowano używanie iloczynu granicy plastyczności i odkształcenia plastycznego w próbie ściskania jako miarę jakości materiałów półkruchych, takich jak związki międzymetaliczne. Przy użyciu tego wskaźnika stwierdzono, że metoda ultradźwiękowa jest efektywniejsza od tradycyjnej, oraz, że pożądana zawartość cząstek umacniających Al_2O_3 w osnowie NiAl mieści się w przedziale 0-5% objętościowych.

1. Introduction

Intermetallic materials offer great potential for structural applications, however, a number of technological issues must be solved before these materials can be of practical use. This is especially relevant with respect to NiAl. This intermetallic compound with cP2 (B2) ordered crystal structure is of potential for versatile applications because of its high melting point, low density, good thermal conductivity and excellent oxidation resistance [1]. However, conventionally processed polycrystalline NiAl suffers from room temperature brittleness, low high-temperature strength and inadequate creep resistance [1]. During an extensive research on NiAl span-

* INSTITUTE OF HIGH PRESSURE PHYSICS, POLISH ACADEMY OF SCIENCES, 01-142 WARSZAWA, 29/37 SOKOŁOWSKA STR., POLAND
** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND

ning the last two decades, many features and properties have been found and characterized. It was found that fairly good plastic properties of NiAl appear at a stoichiometric composition when its microstructure was refined to the submicrocrystalline size [2,3]. However, since this material is well suited to high temperature applications it should also be resistant to a long, high-temperature exposition, i.e. to a diffusion controlled grain growth which, on the other hand, results in the lost of low temperature ductility. This problem may be overcome by introducing into the microstructure a small amount of thermally and chemically stable dispersed very fine particles (nano-particles). Such dispersion strengthened material is also believed to exibit improved creep resistance.

Several processing methods were utilized to produce submicron microstructure with a dispersed second phase. The most common one was mechanical alloying followed by hot extrusion of alloyed powders [4]. Only recently, a self-sustained high-temperature synthesis (SHS) technique has been developed for production of intermetallic alloys directly from elemental powders [5]. The advantages of this process include low energy inputs, short-time requirements and simplicity. This work was aimed at producing a NiAl alloy by SHS with a simultaneous incorporation of Al_2O_3 nano-particles in the form of dispersoid into its microstructure.

2. Material and technology

Nano-particles of aluminium oxide (particle size 10-20 nm) were blended with nickel and aluminium elemental powders (purity ~ 99.7 and ~ 99.9%, particle size ~ 3 and 5 μm respectively). The mixture served as a raw material to the SHS process. The nickel powder contained some fine graphite flakes (~ 0.2%) as a leftover from its carbonyl technology. Two compositions of the mixture with 2.5% or 5% volumetric parts of Al_2O_3 in a stoichiometric NiAl were produced. Two methods of intensive powder mixing were applied. In the first one, the suspension of powders in a fluid was exposed to high intensity ultrasound. Two media were used: a liquid acetone (further denoted as *Ac*) at atmospheric pressure and a gaseous helium (*He*) compressed to the pressure of ~ 200 MPa to induce an acoustic impedance of this gas high enough for the propagation of ultrasound. In the case of acetone, the powder mixture had to be thoroughly dried by heating before the next operation, *i.e.* compaction. As a reference material a pure stoichiometric NiAl (without dispersoid) was prepared using a traditional method of rotating ball mixer. Each mixture of powders was compacted into a rod of 40 mm in diameter by cold isostatic pressing at the pressure of ~ 0.3 GPa and enclosed in the thick-wall cylinder. The cylinder was heated to about 600°C to initiate an exothermic SHS reaction. The X-ray phase analysis showed that the sintered material was a porous composite (8-10% vol. porosity) of the single-phase NiAl matrix with the Al_2O_3 dispersoid. To densify the materials and refine their microstructure, the materials were subjected to hot hydrostatic extrusion under the following parameters: extrusion ratio of 4, temperature of 1000°C and pressure of 0.6 – 1.0 GPa.

3. Experimental procedure

The specimens for compression tests were excised from the centres of extruded rods parallel to their axes using a spark discharge technique. The samples were precisely machined to obtain accurate parallelepiped form of dimensions 6×3×3 mm. Several samples were annealed in a vacuum at 500°C for 2 h and then slowly cooled down in the furnace to stabilise the concentration of point defects in the material [6,7]. These samples will be designated as the extruded ones (extruded material). To show the effect of high temperature annealing on the material another part of samples were annealed at 900°C for 20 hours also followed by very slow cooling. These samples will be further referred to as the annealed samples (annealed material).

The microstructure of the produced materials was examined on longitudinal sections of samples (after adequate preparation) using light and scanning electron microscopes (LM and SEM). Polished and non-etched surfaces were observed for a rough estimation of the distribution of dispersoid in the material, while the etched ones for the measurement of the grain size. The average grain size was calculated using the intercept method.

Compression tests were performed at an average strain rate of ~ 3×10^{-3} s^{-1} using a stiff testing machine supplied with an acoustic emission (AE) analyser [8]. The accuracy of measurements was at the level of ±1 N for the load and ±1 μm for the displacement.
Simultaneously with the load-displacement curve, an acoustic emission activity was registered at the level of discrimination of the AE signal energy sufficient to solely detect the process of microcracking in the material [9]. At least two specimens were tested for each material.

4. Results and discussion

The extruded materials were strongly textured with a sharp <110> fibre texture which remained stable even under long high-temperature annealing [10]. Microscopic observations showed some inhomogeneous residual

porosity (0.01-0.02 relative porosity) giving a fibre feature to the microstructure. Pores were irregularly shaped and strongly elongated. The grains (size and shape) were also inhomogeneous. The average grain size was estimated at ~ 15 μm. Typical microstructure of the produced materials is shown in Figs 1 and 2. Despite the fact that the temperature of the SHS process reaches 1800°C [11], higher even than the melting point of NiAl, the produced material revealed some scattering in chemical composition (measured by energy dispersive spectrometry in SEM). This was most likely due to Al powder particles that were too coarse taken into the process. The annealed materials revealed different grain sizes depending on the concentration of Al_2O_3 dispersoid. The grain growth was particularly significant in pure NiAl in which the grain size reached an average size of about 100 μm. It is worth noting that the grain size depended on the method of mixing powders before the SHS process. Essentially no grain growth was observed in materials mixed *via* ultrasonic methods.

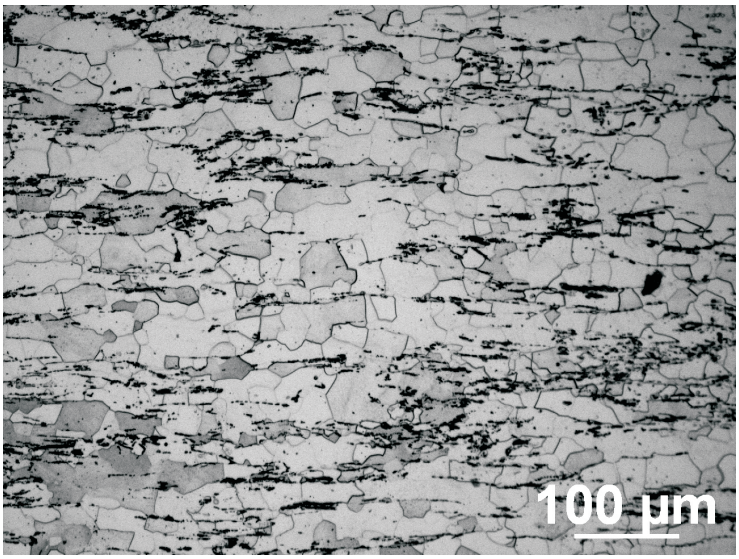

Fig. 1. Typical microstructure of the produced materials; light microscope

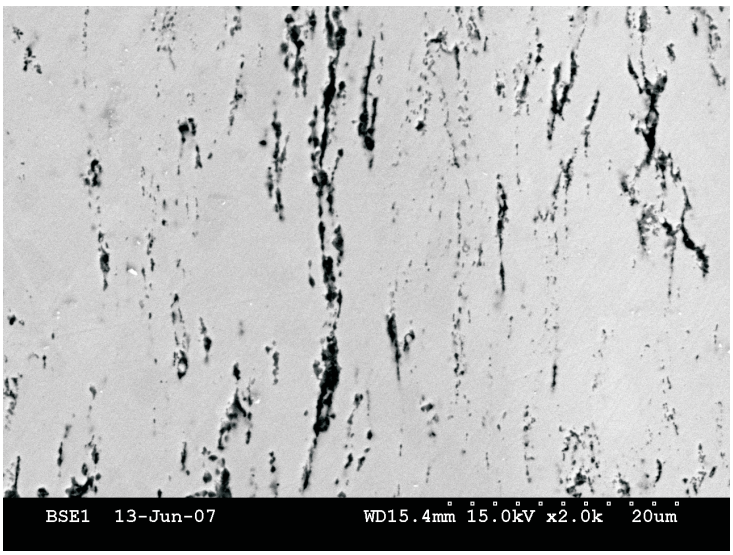

Fig. 2. Typical microstructure of the produced materials; scanning electron microscope

The results of compression tests are presented in Figs. 3-6. The true strain – true stress curves, $\sigma(\varepsilon)$, and the corresponding cumulative (summed) number of AE events, $\Sigma AE(\varepsilon)$, are shown in each figure. Square open points at the $\sigma(\varepsilon)$ curves correspond to the onset of AE activity marked by vertical arrows on the $\Sigma AE(\varepsilon)$ curves. The points indicate the critical value of strain, ε_c, that is a value of pure plastic deformation at which an additional mechanism of deformation is activated. This mechanism usually operates in semi-brittle materi-

als (like NiAl) under compressive loading. It is based on the mutual displacement of large blocks of the material along microcracks created during deformation. This displacement is accompanied by a smaller plastic deformation within the blocks. Such a mechanism, well described in the mechanics of rocks, which show a semi-brittle behaviour under the load with hydrostatic component of the stress tensor, is termed a cataclastic flow (cataclasis) [12]. The more brittle the material, the lower ε_c will be, and the bigger the difference between ε_c and the compressive strain, ε_m, corresponding to the maximum on the $\sigma(\varepsilon)$ curve becomes. This can be clearly seen on the presented graphs (Fig. 3-6) for all materials containing 5% of Al_2O_3. The value of ε_c is proposed to serve as the most accurate indicator of ductility in compression tests of semi-brittle materials. Consequently, the value of the corresponding stress, σ_c, may be considered as a strength parameter of the material similar to the yield stress, σy. However, from a material quality viewpoint, both parameters: yield stress, σ_y, and critical strain, ε_c, are important. Hence, for the sake of material comparison, we introduced the following combined quantity q:

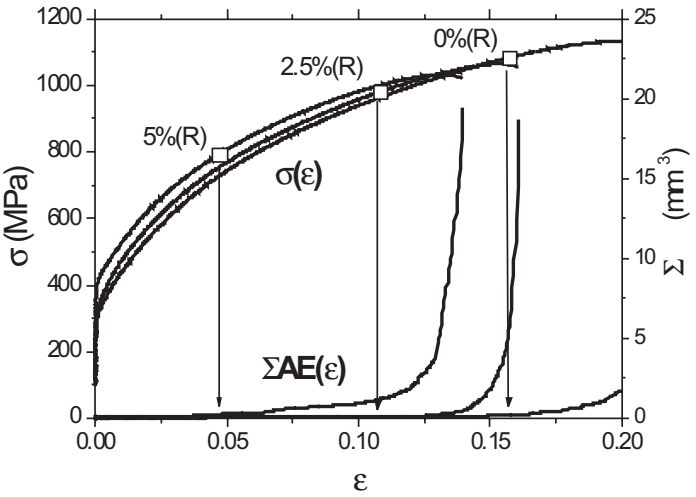

Fig. 3. Compression curves, $\sigma(\varepsilon)$, and acoustic emission activity, $\Sigma AE(\varepsilon)$, for the reference material (R) with various quantity (vol. %) of Al_2O_3 dispersoid in the state as extruded

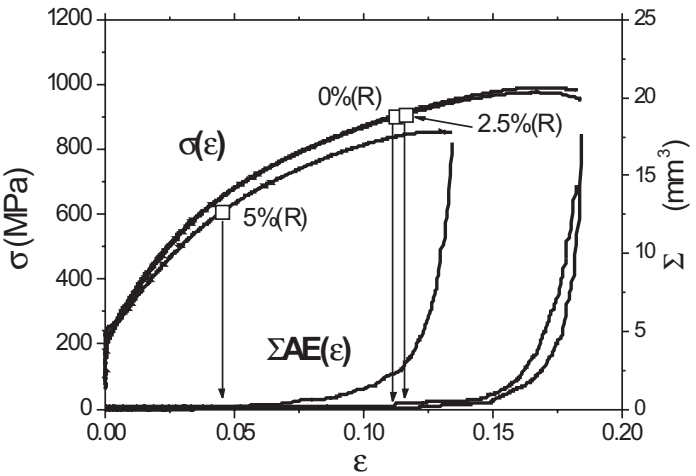

Fig. 4. Compression curves, $\sigma(\varepsilon)$, and acoustic emission activity, $\Sigma AE(\varepsilon)$, for the reference material (R) with various quantity (vol. %) of Al_2O_3 dispersoid in the state as annealed

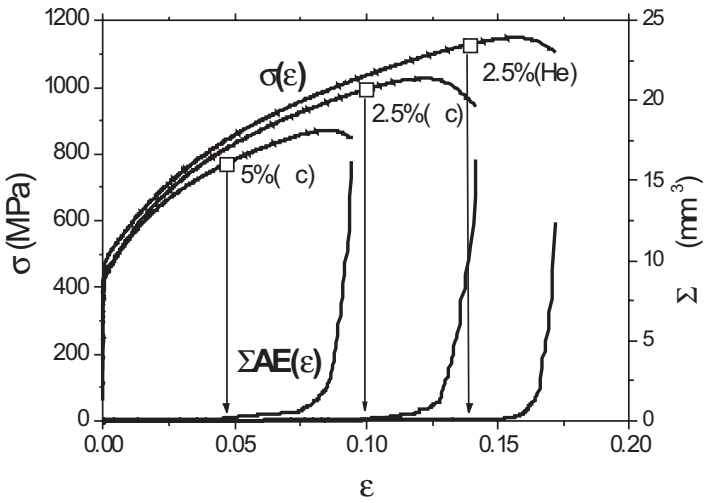

Fig. 5. Compression curves, $\sigma(\varepsilon)$, and acoustic emission activity, $\Sigma AE(\varepsilon)$, for the material after ultrasonic preparation in acetone (*Ac*) and helium (*He*) with various quantity (vol. %) of Al_2O_3 dispersoid in the state as extruded

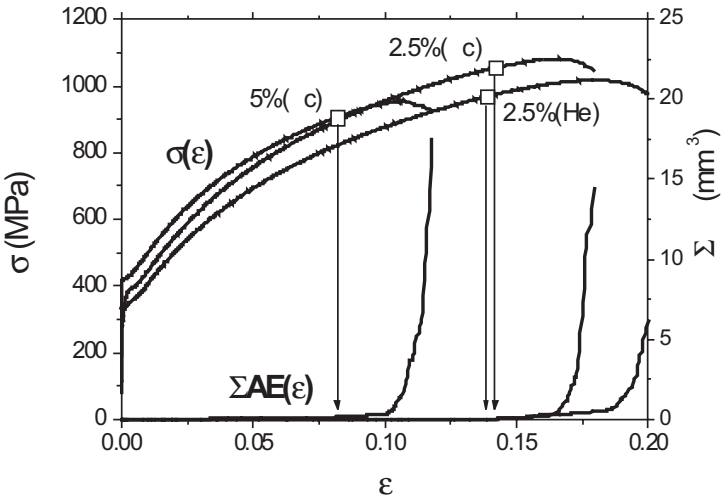

Fig. 6. Compression curves, $\sigma(\varepsilon)$, and acoustic emission activity, $\Sigma AE(\varepsilon)$, for the material after ultrasonic preparation in acetone (*Ac*) and helium (*He*) with various quantity (vol. %) of Al_2O_3 dispersoid in the state as annealed

$$q = \sigma_y \varepsilon_c \tag{1}$$

as a parameter describing the mechanical properties of semi-brittle intermetallic alloys, in our case the NiAl-Al_2O_3 alloy. The higher value of q, the better is the quality of the material; hence, the problem of technological optimisation now has a clear criterion – maximizing the value of q.

The values of σ_y, ε_c, and q are shown in the table for all investigated materials (Table 1). Two principal parameters of the microstructure, which affect the values of σ_y and ε_c, are the concentration of dispersoids and the grain size of the base material. While the former one can be easily controlled, the latter is a quantity strongly dependent on the parameters of the technological route. First of all, it depends on the dispersoid concentration and its distribution in the matrix. From the obtained results (Table 1) a reasonable dependence is seen that the higher concentration of dispersoid, the higher σ_y and the lower ε_c will be. Let us assume, for the sake of qualification, that $q \approx 50$ MPa is a sufficient level of quality; this is accomplished for $\sigma_y \approx 500$ MPa and $\varepsilon_c \approx 0.1$. Only two materials containing 2.5% of Al_2O_3, both produced via ultrasonic technology (independently of their

state, as-extruded or as-annealed), might be considered as "good" in the sense of this criterion. The materials with 5% concentration of dispersoid do not satisfy the criterion of quality $q \geqslant 50$ MPa because they are too brittle in either state. The pure NiAl that satisfied the criterion in the as-extruded condition ($q \approx 53$ MPa) lost its quality due to the grain growth during annealing (decrease in both ductility and strength). The low quality of the material containing 2.5% of dispersoid, which was produced via the traditional route, indicates that this kind of mixing technique is not appriopriate since it does not hinder the grain growth and thus deteriorates the residual ductility. The remarkable discrepancy between the values of q for 2.5% and 5% of Al_2O_3 shows that the optimal concentration of dispersoid should be expected in the lower range of concentration (< 2.5%).

TABLE 1

Strength and plastic properties of investigated materials (as-extruded, E, and annealed, A)

Material	E σ_y (MPa)	A σ_y (MPa)	E ε_c	A ε_c	E $\sigma_y \cdot \varepsilon_c$ (MPa)	A $\sigma_y \cdot \varepsilon_c$ (MPa)	E Λ (MPa)	A Λ (MPa)
0% (R)	335	227	0.157	0.112	52.6	25.4	127.5	73.6
2.5% (R)	356	241	0.108	0.116	38.4	28.0	80.4	77.6
5% (R)	434	258	0.047	0.045	20.4	11.6	29.9	20.1
2.5% (Ac)	448	375	0.101	0.142	45.2	53.3	78.4	113.5
5% (Ac)	462	426	0.047	0.082	21.7	34.9	29.9	58.9
2.5% (He)	497	341	0.139	0.139	69.1	47.4	124.5	101.8

An another parameter of plastic potential of the material can be defined as the quantity of mechanical work, Λ, needed for an achievement of a critical deformation, ε_c (Eq. 2):

$$\Lambda = \int_0^{\varepsilon_c} \sigma d\varepsilon \tag{2}$$

which is also presented in Table 1. Similar conclusions can be drawn about plasticity of the material, however, this parameter seems to be less universal as it does not take into account sufficiently enough the strength properties of the material.

5. Conclusions

1. Dispersion strengthening of NiAl-based intermetallic alloys by the nano-sized powder of Al_2O_3 as a dispersoid is a potential production technique for high temperature applications.
2. The dispersoid can be doped into the material when the powder metallic components of intermetallic are mixed before the SHS process.
3. Ultrasonic mixing is more efficient than conventional mechanical mixing in the rotational ball mixer. The liquid and gaseous technology gives similar results, however, the first of them is a cheaper process. It can be improved through optimisation of the parameters of the mixing process.
4. The optimal concentration of dispersoid, giving simultaneously sufficient ductility and resistance to long high temperature exposition, falls into the range of 0 – 5 vol. % of dispersoid.

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