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NiAl-Al_2O_3 intermetallic matrix composite prepared by reactive milling and consolidation of powders

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Reactive milling of nickel oxide and aluminium powders corresponding to the stoichiometric reaction 3NiO + 5Al resulted in the formation of intermetallic matrix composite NiAl-Al_2O_3, with 28 wt% of alumina. Prolongation of the milling process allowed obtaining the microstructure with nanosize range of crystallites of both phases, as showed XRD measurements and TEM observations. The refinement of microstructure was accompanied with an increase of lattice strain as a result of ball milling. The particles size and morphology changed from several tens of micrometers and polyhedron shape observed immediately after the reaction took place, to several micrometers and spherulitic shape after long-term milling.

Two consolidation techniques of nanocomposite powders were applied: explosive compaction and hot-pressing under high pressure. Both methods allowed obtaining the samples of high density (up to 99% of theoretical one) and microhardness above 13 GPa. Simultaneously, a nanocrystalline structure of the material was preserved. © *2004 Kluwer Academic Publishers*

1. Introduction

During the last years significant research and development efforts have been focused on structural intermetallics [1]. Intermetallic compounds enjoy intense study by materials scientists and engineers, looking for very strong tough structural materials at elevated temperatures, magnetic alloys, superconductors, catalysts or hydrogen storage materials. Especially aerospace industry generates new needs for high temperature structural materials with properties better than exhibited by ceramics or by conventional superalloys. In many cases intermetallics show higher melting temperatures than superalloys and, having metallic bonding, the possibility of better toughness than ceramics. Some intermetallics, e.g. TiAl, exhibit a high strength to weight ratio, some aluminides have good resistance to oxidation at elevated temperatures. However, the main obstacles for the use of intermetallic compounds as structural materials are their low ductility and toughness at ambient temperature and, in some cases, insufficient creep resistance at high temperature. It was showed that macroalloying [2] or microalloying has been successful in increasing ductility in some intermetallics. On the other hand, for optimisation of room temperature toughness and high temperature strength, microstructural modifications are required. For these reason it has been recognized that intermetallic matrix composites (IMCs) may be appropriate materials for structural applications, replacing in some cases intermetallics. Thus, IMCs become the subject of intensive research [3, 4]. Generally, any two-phase material with an intermetallic compound as the principal phase could be considered an IMCs. The second phase could be in the form of particulates, whiskers or chopped fibers (discontinuous reinforcement) or in the form of continuous fibers or filements (continuous reinforcement). From engineering point of view most of IMCs fall into the last category, since the largest improvement in mechanical properties is observed in this type of composites.

Many synthesis and processing methods of intermetallics and IMCs exist, like ingot metallurgy, powder metallurgy, rapid solidification or spraying. But it should be pointed out that processing of intermetallics requires a special importance because of their complex crystal structure, often restrictive stoichiometry limits and limitations coming from the equilibrium phase diagrams. Among the processing methods is mechanical alloying (MA). The use of MA as a processing tool for IMCs is limited to the case of discontinuous second reinforcing phase. This phase is typically a hard ceramic or metalloid compound. Mechanical alloying involves the synthesis of materials by high-energy ball milling of powders. It was first developed by Benjamin in order to produce oxide-dispersion-strengthened (ODS) alloys for high temperature structural applications [5]. An increasing interest in MA as non-equilibrium processing method was observed after discovering that amorphous alloys could be made by MA starting either from the intermetallic compound or from the mixture of elemental powders. Since that time there have been many studies using MA of mixture of elemental powders or mechanical milling (MM) of single-phase powders (such as intermetallic compounds) to synthesize nonequilibrium structures, including extended solid solutions, metastable crystalline phases, quasicrystals and nanocrystalline materials. MA as a processing route offers some advantages, like the relative simplicity and flexibility of the process at a cost low relative to some other fabrication techniques.

In the mechanical alloying science there is a part called mechanochemistry [6]. This term is applied to the process of reactive milling in which chemical reactions and phase transformations take place due to the application of mechanical energy. The process includes exchange reactions, reduction/oxidation reactions, decomposition of compound and phase transformations. Most of the reactions studied have been displacement reactions, where a metal oxide is reduced by a more reactive metal (reductant) to the metal or intermetallic compound. Usually the reactions are characterized by a large negative free energy change, and depending on milling conditions, can occur as a gradual transformation or a self-propagating combustion. Processing parameters such as grinding ball diameter, ball-to-powder weight ratio, use of a process control agent and proportion of the reactants (off-stoichiometry) play an important role on the kinetics, type of the reaction and type of the product phases obtained.

The resulting products depend on the composition of starting powder mixture, e.g. the reduction reaction of nickel oxide by aluminium can give us a metal matrix:

$$3\mathrm{NiO} + 2\mathrm{Al} \rightarrow 3\mathrm{Ni} + \mathrm{Al_2O_3}$$

or intermetallic matrix composite:

$$3\mathrm{NiO} + 3\mathrm{Al} \rightarrow \mathrm{Ni_3Al} + \mathrm{Al_2O_3}$$

$$3\mathrm{NiO} + 5\mathrm{Al} \rightarrow 3\mathrm{NiAl} + \mathrm{Al_2O_3},$$

with different intermetallics as a matrix (Ni_3Al or NiAl).There have been some attempts to produce IMCs with nickel aluminides mentioned above. Due to their good oxidation resistance they are likely candidates for application above 1000°C. MA technique, standard powder metallurgy route or melt infiltration were used to incorporate particles or fibres of Al_2O_3 in the nickel aluminides matrix [7]. However, the observed ductility and fracture toughness were low, although some increases of tensile strength and creep strength were found.

The aim of our studies was to obtain "*in situ*" nanocrystalline NiAl-Al_2O_3 intermetallic matrix composite by reactive milling and compaction of the powder. Some advantages from "*in situ*" processing were expected, when both phases are formed directly during the reactive milling. Prolongation of milling time could allow nanocrystalline structure formation. Finally, it was expected that the applied powder compaction methods would result in preserving nanocrystalline nature of a composite.

2. Experiment

2.1. Milling details

The mixtures of nickel oxide and aluminium powders were prepared, allowing taking place the stoichiometric reaction: $3\mathrm{NiO} + 5\mathrm{Al} \rightarrow 3\mathrm{NiAl} + \mathrm{Al_2O_3}$. This reaction resulted in a formation of a composite with 28 wt% contribution of alumina. The starting powders were characterized by mean particle size below 10 μm and purity of 99.9%. Fritsch Pulverisette P5 planetary ball mill was used for reactive ball milling processes. The following milling parameters were applied: 250 rpm, ball-to-powder weight ratio 10:1, mass of the powder 10 g. Hardened steel vials and balls (10 mm diameter) were used. All powder handling was performed in a glove bag under an argon atmosphere.

2.2. Techniques used for sample characterization

The X-ray investigations (XRD) were performed on a Philips PW 1830 diffractometer using Cu K_α radiation ($\lambda = 0.15418$ nm). Differential scanning calorimetry (DSC) measurements were carried out in a Perkin Elmer DSC 7 unit within the temperature range 50–700°C, applying the heating rate of 20 K/min. Scanning electron microscopy (SEM) observations of the powder particles size and morphology were performed using a XL30 LaB_6 device. A laser particle size analyser Fritsch Analysette 22 was used for determination of average powder particles size and their distribution. Structural observations of the powders by transmission electron microscopy (TEM) were carried out with a Jeol 1200EX microscope. The average hardness of the compacts was measured using a Zwick microhardness tester under a load of 100 g imposed for 15 s, and their density using a Gilbertini E154 balance equipped with a device for measuring the density of solids (Archimedes method).

2.3. Methodology of crystallite size and lattice strain calculations

The X-ray diffraction line profile obtained in a diffractometer is broadened due to instrumental and physical (crystallite size and lattice strain) factors. Therefore, it is necessary to determine "pure" diffraction line profile for a given reflection, whose breadth depends on the physical factors only. It can be done by removing the instrumental broadening factor from the experimental line profile. In the present work the "pure" line profile breadth of each reflection was calculated from the parabolic approximation correction:

$$\beta(2\theta) = B(1 - b^2/B^2) \quad \text{(in radians)},$$

where B and b are the breadths (in radians) of the same Bragg peak from the XRD scans of the experimental and reference powder, respectively. The reference powder was the powder of NiAl after annealing for 3 h at 1100°C. Both B and b were calculated as the full widths at half maximum (FWHM). It was assumed that the crystallite size and strain line profile are both

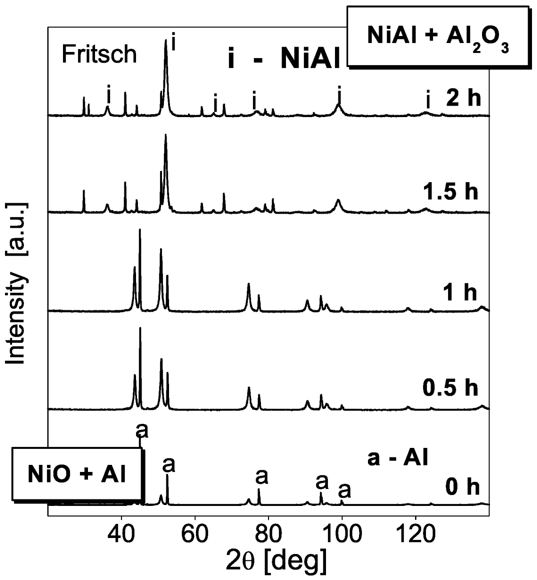

Figure 1 XRD patterns collected after increasing milling times of NiO + Al powder mixture.

presumed to be Cauchy and the appropriate equation for the separation of crystallite size and strain takes the following form:

$$\beta(2\theta)\cos\theta_0 = K\lambda/D + 4e\sin\theta_0,$$

where θ_0 is the position of analyzed peak maximum, λ the X-ray wave length, D the crystallite size and e the maximum strain.The constant K can be set equal to unity. All available reflections may be used to construct a linear plot of $\beta(2\theta)\cos\theta_0$ against $\sin\theta_0$. From the ordinate intercept λ/D and slope $4e$, the crystallite size D and strain e may be determined. This method was first proposed by Williamson and Hall [8] and is usually referred as the "Williamson-Hall method".

2.4. Methods of powder compaction

Two methods of powder compaction were applied. In the first method, a high-pressure toroid-cell press was used for hot-pressing consolidation of the reactive milled final product. The pressure applied was 7.7 GPa and the temperatures were in the range 700–1000°C. The samples were hold at the maximum pressure and selected temperatures for 5–10 min. The second method of powders densification was explosive compaction. In this method the powders were preliminary uniaxially cold pressed and then compacted by a plane wave generated during the detonation of the explosive material. The pressure and temperature achieved in this method were 4.4 GPa and 400°C, respectively.

3. Results and discussion

Fig. 1 shows an example of the XRD patterns collected after increasing milling times. For milling times up to 1.25 h no phase transformations were observed. Even the broadening of the diffraction lines of NiO and Al, usually observed for mechanically alloyed powders, is not significant. The reduction reaction of NiO takes place between 1.25 and 1.5 h of milling and a new XRD pattern consists of the diffraction lines of NiAl and alumina, which are formed "*in situ*", directly during the MA process. It is worthwhile to notice, that this phase transformation was accompanied by an increase of the temperature of the vial, in other words at least partially a combustion-type of the reaction took place. Unfortunately the temperature measurement of the vial was not performed. Fig. 2 shows the XRD pattern of the sample subjected to prolonged ball milling up to 40 h. The diffraction lines of NiAl are marked by arrows (s—superstructure lines), remaining peaks belong to alumina. Significant broadening of the diffraction lines of both phases is observed, testifying decrease of crystallite size and increase of lattice strain. The results of Williamson-Hall analysis of crystallite size and lattice strain calculations are collected in Table I. Prolongation of milling leads to the decreasing of crystallite size down to 10–20 nm and, at the same time, considerably increasing of lattice strain up to 0.9%. Heating the sample in the DSC results in significant increase

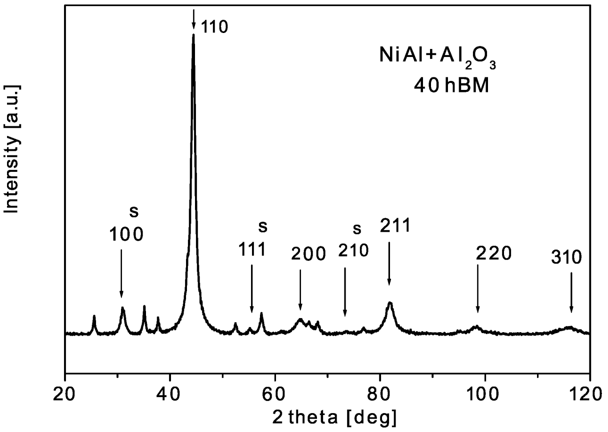

Figure 2 XRD pattern of NiAl + Al_2O_3 sample subjected to ball milling up to 40 h.

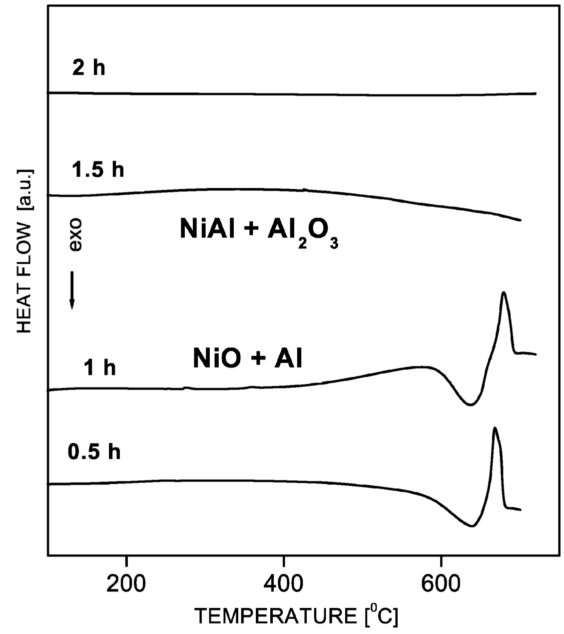

Figure 3 DSC curves of the samples after increasing processing time.

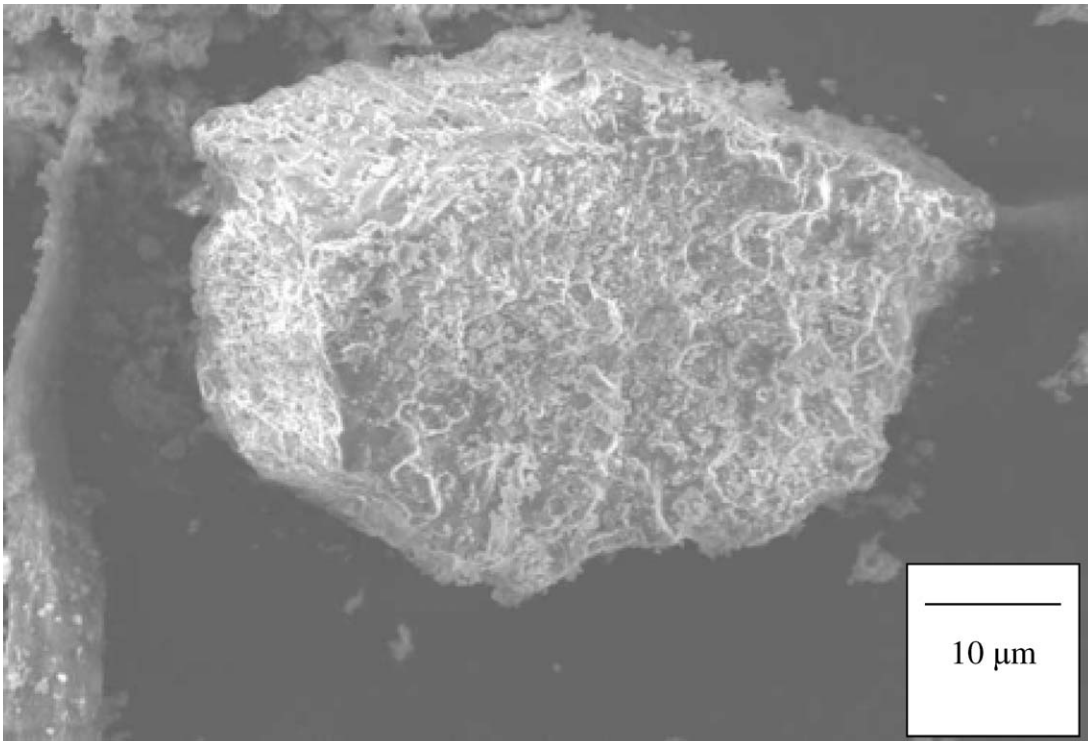

Figure 4 SEM micrograph of the single powder particle after 1.5 h of milling.

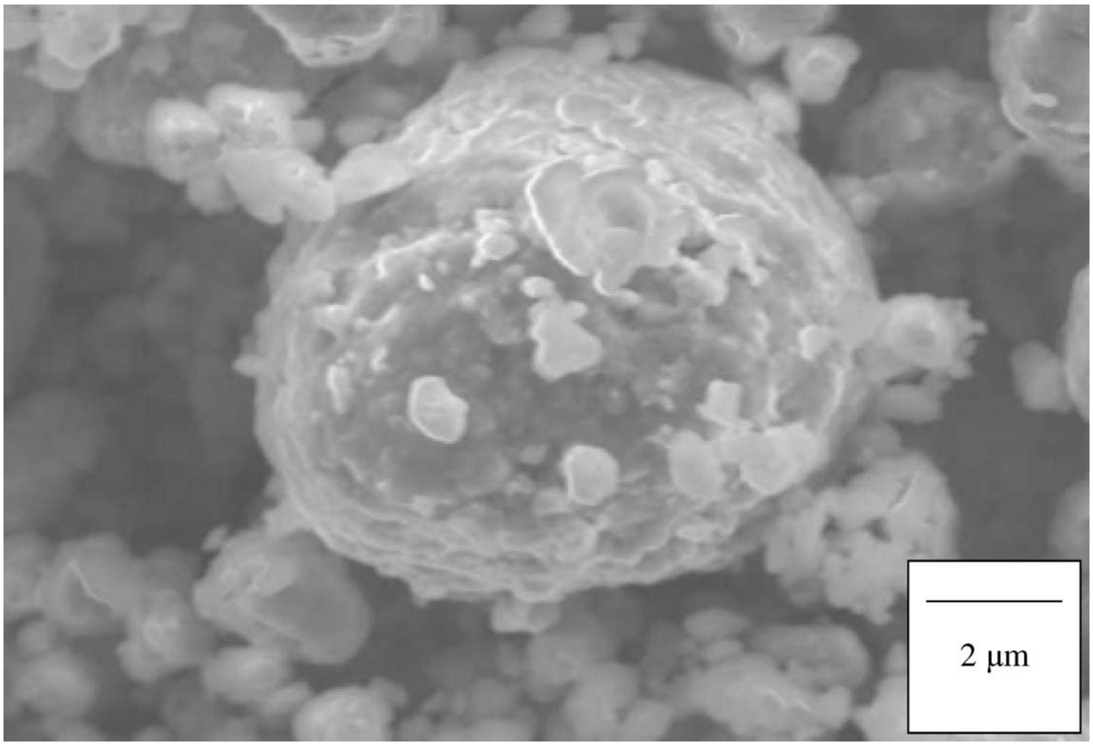

Figure 5 SEM micrograph of the single powder particle after 40 h of milling.

TABLE I Crystallite size *D* and lattice strain *e* for the samples after various processing time and heat treatment

Sample processing	*D* (nm)	*e* (%)
Just after the reaction (1.5 h BM)	40–50	0.40
After prolonged milling (40 h BM)	10–20	0.90
Prolonged milling + DSC annealing	80–100	0.35

of crystallite size up to 100 nm and simultaneously the strain drops down to 0.35%.

DSC curves recorded for the samples after increasing processing time are shown in Fig. 3. For milling times shorter than required for the reduction reaction of NiO, endothermic effect attributed to the melting of Al at 660°C is observed. After the formation of

NiAl + Al_2O_3 composite, there is no reaction at the DSC curves.

The calculated values of lattice parameter of NiAl after 1.5 h (i.e. just after the reaction) and 40 h of milling were essentially the same as the equilibrium one for ordered NiAl intermetallic compound (0.288 nm).

Figs 4 and 5 show SEM micrographs of the single powder particles after 1.5 and 40 h of milling, respectively. For short processing times, but sufficient for the displacement reaction and formation of NiAl, as shown in XRD studies, the particles exhibit a polyhedron morphology and average size of several tens of micrometers. Prolonging of milling up to 40 h results in considerable refinement of the powders down to about 5 μm and, simultaneously, in change of morphology from polyhedron into spherulitic one.

Performed detailed analysis of average particles size and their distribution shows that just after the displacement reaction a broad distribution of particle size is observed (from 1 to 100 μm), with an average value of 20 μm (Fig. 6). Long term milling, however, leads to a very narrow particle size distribution, giving an average value of 4–5 μm (Fig. 7).

TEM observations confirm the nanocrystalline nature of the composite. Fig. 8 shows a bright field micrographs of the powder sample after 40 h of ball milling. Highly deformed nanograins in the range below 50 nm are clearly visible.

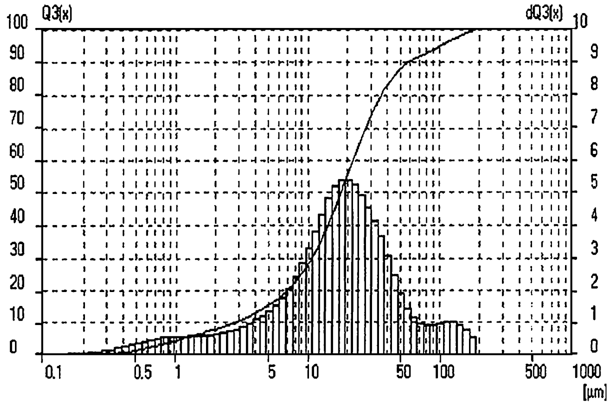

Figure 6 The distribution of particles size after 1.5 h of processing (after the displacement reaction).

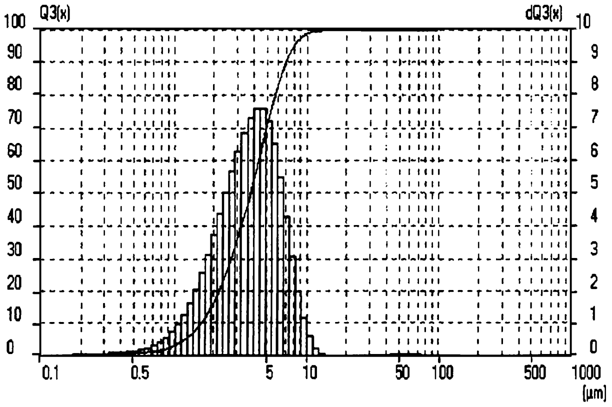

Figure 7 The distribution of particles size after 40 h of processing (after the prolonged milling).

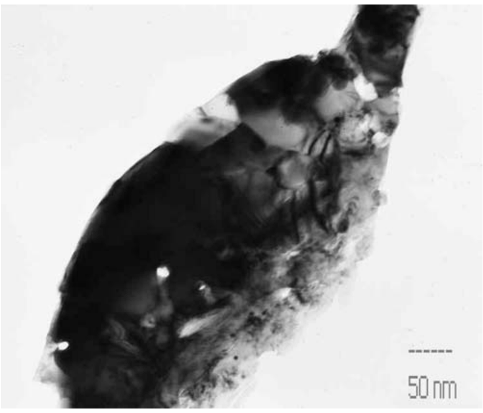

Figure 8 TEM bright field micrographs of the sample after 40 h of processing.

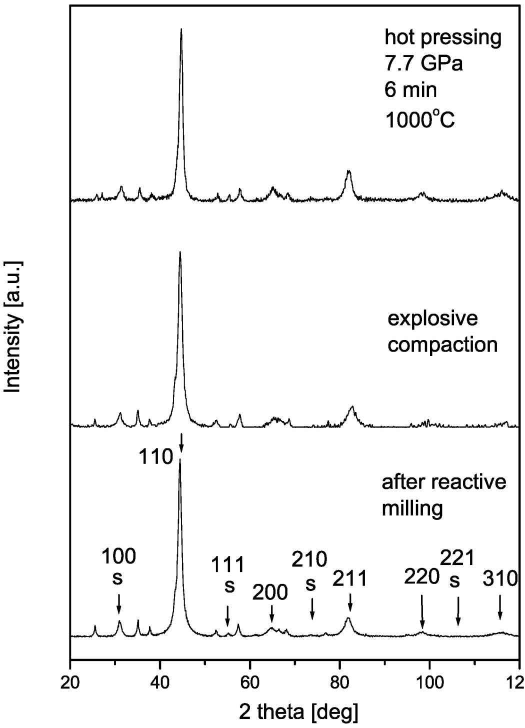

Figure 9 XRD patterns of the samples after 40 h of milling, explosive compaction and hot pressing.

The XRD patterns registered for the samples after explosive compaction and hot pressing are presented in Fig. 9. For comparison the pattern of the powders before consolidation (ball milled for 40 h only) is included as well. There are no significant differences between all these patterns, suggesting that both powder consolidation methods allow preservation of nanostructure of the composite, obtained as a result of long term milling. Indeed, the Williamson-Hall analysis reveals that crystallite size of NiAl for both samples is in the range of several tens of nanometers (Table II). Moreover, the

TABLE II Crystallite size *D*, lattice strain *e*, density ρ and microhardness of NiAl-Al_2O_3 composite after explosive compaction and hot pressing

Sample processing	*D* (nm)	*e* (%)	ρ(%)	HV0.1
Explosive compaction	20–30	0.40	92–95	1100
Hot pressing, 7.7 GPa, 1000°C, 6 min	30–40	0.40	98–99	1400

applied compaction methods do not cause an increase of lattice strain, which remains at the level comparable to the one observed for the powders just after the displacement reaction or annealed in the DSC.

The hot pressing technique allows obtaining excellent densities of the compacts, reaching 99% of the theoretical density. As a consequence, also the measured microhardness value was in this case very high, approaching 13 GPa. Explosive compaction method resulted in lower density obtained. Further studies and some modifications of this method are needed to improve the properties of the composite, simultaneously preserving its nanostructure.

4. Conclusions

It has been shown that reactive milling of powder mixture of nickel oxide and aluminium corresponding to the stoichiometric reaction $3NiO + 5Al$ resulted in the formation of intermetallic matrix composite $NiAl$-Al_2O_3, with about 28 wt% of alumina. Under the applied milling conditions, 1.5 h of processing was necessary to achieve the reaction. Prolongation of the milling process allowed obtaining the microstructure with nanosize range of crystallites of both phases, as showed XRD measurements and TEM observations. The refinement of microstructure was accompanied with an increase of lattice strain as a result of ball milling. The particles size and morphology changed from several tens of micrometers and polyhedron shape observed immediately after the reaction took place, to several micrometers and spherulitic shape after long-term milling.

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References

1. R. DAROLIA, J. J. LEWANDOWSKI, C. T. LIU, P. L. MARTIN, D. B. MIRACLE and M. V. NATHAL, "Structural Intermetallics" (TMS, Warrendale, PA, 1993).
2. C. T. LIU, *J. Nucl. Mater.* **85/86** (1979) 907.
3. J. A. GRAVES, R. R. BOWMAN and J. J. LEWANDOWSKI, in Intermetallic Matrix Composites III, Mat. Res. Soc. Symp. Proc. (Pittsburgh, PA, 1994) Vol. 350.
4. D. B. MIRACLE and M. G. MENDIRATTA, in "Intermetallic Composites in Intermetallic Compounds" edited by J. H. Westbrook and R. L. Fleischer (Wiley, Chichester, 1994) Vol. 2, p. 287.
5. J. S. BENJAMIN, *Metall. Trans.* **1** (1970) 2943.
6. L. TAKACS, *Progr. Mater. Sci.* **47** (2002) 355.
7. P. C. BRENNAN, W. H. KAO and J. M. YANG, *Mater. Sci. Eng.* A **153** (1992) 635.
8. G. K. WILLIAMSON and W. H. HALL, *Acta Metal.* **1** (1953) 22.

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