

Fabrication, Structure and Consolidation of NiAl–Al₂O₃ Mechanically Alloyed Nanocomposite Powders

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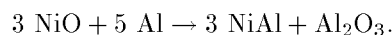
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Reactive milling of NiO + Al powder mixture resulted in the formation of NiAl–Al₂O₃ nanocomposite powders, with a crystallite size of about 20 nm. The Hall–Williamson analysis revealed that NiAl showed an orientation dependent crystallite size after short processing time and orientation dependent internal strain after long milling time. Both anisotropies were removed by heating the powders in the differential scanning calorimetry. Calorimetric studies showed one exothermic effect attributed to the reduction reaction of NiO and endothermic one associated with melting of Al. Two methods were applied for powders compaction: resistance sintering and pulse electric discharge. In both cases the densities of about 90% of the theoretical value were achieved. A significant increase in average NiAl crystallites size in compacted samples was observed, up to several hundreds of nanometers.

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1. Introduction

It has been reported that mechanical alloying (MA) can be used to induce a variety of solid-state chemical reactions. These reactions have been described in the literature as mechanosynthesis or mechanochemical synthesis and usually a metal oxide is reduced by more reactive metal [1, 2]. MA technique can be also used to synthesize compounds and nanocomposites using the mechanochemical reactions. For example the reduction reaction of nickel oxide by aluminium can give us an intermetallic matrix composite (IMC)



IMCs are produced by metallurgical methods, rapid solidification, reactive sintering [3] and also by MA. IMCs reinforced with ceramic phases, which can further improve some properties, like creep resistance or wear resistance, are widely investigated.

The purpose of this work was to study *in situ* formation of NiAl–Al₂O₃ composite powders and to examine their structure. An attempt of powders consolidation has been undertaken as well.

2. Experimental details

The powders of NiO and Al, with a purity better than 99.9% and particle sizes below 40 μm , were used for the milling processes. The powders were mixed to give the starting composition 3 NiO + 5 Al, in order to give the final products 3NiAl + Al₂O₃, with about 40 vol.% fraction of alumina. The MA processes were performed in a Fritsch P5 Pulverisette planetary ball mill equipped with hardened steel vials and balls. The ball-to-powder weight ratio was 10:1. All powder handling was performed in a glove bag under an argon atmosphere. The X-ray investigations (XRD) were performed on a Philips PW 1830 diffractometer using Cu K_{α} ($\lambda = 0.15418$ nm) radiation. The values of lattice parameter were calculated with an accuracy of ± 0.001 nm, applying the $\cos^2 \theta / \sin \theta$ function. XRD was also used to determine the average internal strain and crystallite size, based on a Hall–Williamson analysis of peak broadening [4]. In this approach the broadening of the diffraction lines is plotted versus $\sin \theta$ (θ is Bragg's angle). From the intercept at $\sin \theta = 0$ the average crystallite size and from the slope the internal strain can be derived. Differential scanning calorimetry (DSC) measurements were carried out in a Perkin Elmer DSC 7 unit within the temperature range of 50–700°C, applying the heating rate of 20°C/min.

A resistance sintering method was applied to consolidate the powders. In this process a low voltage and high current were applied through the powder compact. The powder compact was heated directly by the applied current, a high heating rate and, consequently, a very short sintering time, can be achieved. The compact was contained in an insulated cavity of a ceramic die set and compressed simultaneously. The pressure (about 30 MPa) acting on the sintered powder caused a rapid consolidation of the powder. The sintering process was executed in a protective atmosphere of pure argon. During the sintering process the current was kept at about 800 A, sintering time 1 and 3 min was used. The temperature was kept constant at 1200°C. It was measured by Pt–PtRh thermocouple. The sintered specimens of cylindrical shape (6 mm diameter and about 7 mm height) were produced.

The powders were sintered by a pulse electric discharge method as well. In this method the powder to be sintered is heated in a resistive way using periodically applied high current electric impulses. A 200 μF capacitor battery discharged from a voltage of maximum 10 kV generated the impulses. The capacitor battery, used as

the source of electric energy, generates periodically current impulses of duration of several tens of microseconds and magnitude of hundreds of kA. Thanks to the very short time during which the heating current flows through the powder, compared to the intervals between the consecutive impulses (1–5 s), the sintering process proceeds in a quasi-adiabatic way and the average temperature of the heated material during the process does not exceed several tens of degrees. The studied powders were sintered in an argon atmosphere in a graphite die of an 8 mm inner diameter.

3. Results and discussion

Figure 1 shows the XRD patterns collected after increasing milling times. For processing times up to 1.25 h no phase transformations were observed. The reduction reaction of NiO takes place between 1.25 and 1.5 h of milling and a new XRD pattern, consisting of the diffraction lines of NiAl and alumina, appears. Both phases are formed *in situ*, directly during the MA process. The milling process was prolonged up to 40 h and resulted in a further broadening of the diffraction lines only, testifying the microstructure refinement and/or increase in internal strain. The value of lattice parameter of NiAl was calculated as 0.2885 nm and remained unchanged after prolonged milling as well as after compaction of the powders.

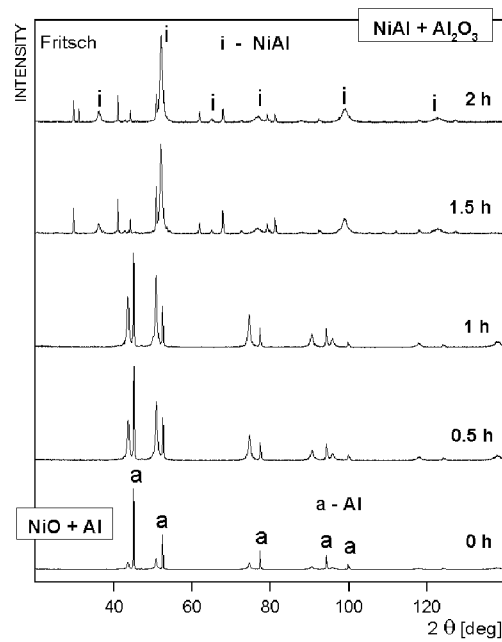


Fig. 1. XRD patterns of NiO + Al powder mixture after milling for increasing times.

The results of the Hall–Williamson analysis performed for NiAl intermetallic compound are collected in the Table. For milling time 1.5 h the mean crystallite size D is orientation dependent, while the internal strain $\langle\epsilon^2\rangle^{1/2}$ remains almost the same in both directions. On the contrary, after 40 h of processing there is a considerable increase in the internal strain for (100)–(200) direction and, at the same time, some strain decrease in (110)–(220) direction. The above changes in the internal strain levels are accompanied by changes of crystallite sizes. A considerable refinement is observed after 40 h of milling for (110)–(220) direction, from 70 nm down to 10 nm. Simultaneously, the average crystallite size in (100)–(200) direction remains almost the same. The variation in diffraction peak broadening with reflection can be explained in terms of the correlation of internal strain with elastic anisotropy of the lattice [5].

TABLE
Calculated crystallite size D and lattice strain $\langle\epsilon\rangle^{1/2}$ for NiAl compound after various processing.

Processing	$D_{100-200}$ [nm]	$\langle\epsilon\rangle_{100-200}^{1/2}$ [%]	$D_{110-220}$ [nm]	$\langle\epsilon\rangle_{110-220}^{1/2}$ [%]
1 h 30 min MA	15	0.59	70	0.57
40 h MA	18	0.88	10	0.34
40 h MA + DSC	$D = 125$ nm, $\langle\epsilon\rangle^{1/2} = 0.35\%$			

Heating the sample results in a considerable increase in mean crystallite size of NiAl up to 125 nm and a decrease in lattice strain down to 0.35%. Simultaneously, both anisotropies have been removed. Figure 2 shows the Hall–Williamson plot for the sample after 40 h of milling and subsequent heating in the DSC up to 700°C.

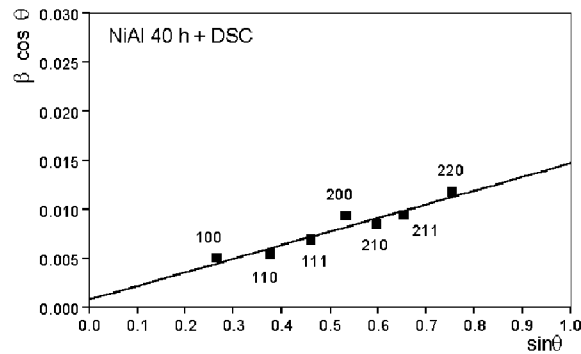


Fig. 2. The Hall–Williamson plot for NiAl intermetallic compound after 40 h of processing and subsequent heating in the DSC up to 700°C.

DSC studies of short time milled samples (before the reaction takes place) reveal one exothermic effect, which can be attributed to the reduction of nickel oxide, and endothermic one, associated with melting of aluminium. The DSC curves are presented in Fig. 3.

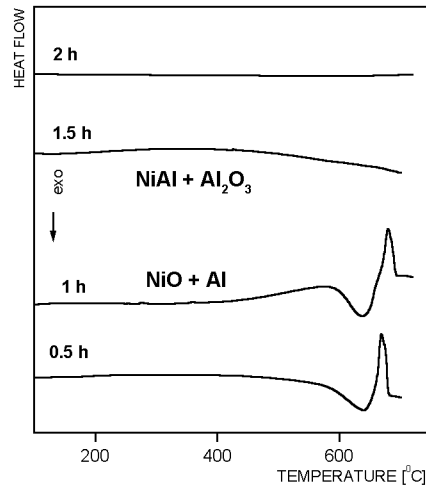


Fig. 3. DSC curves recorded after various milling times for NiO + Al powder mixture.

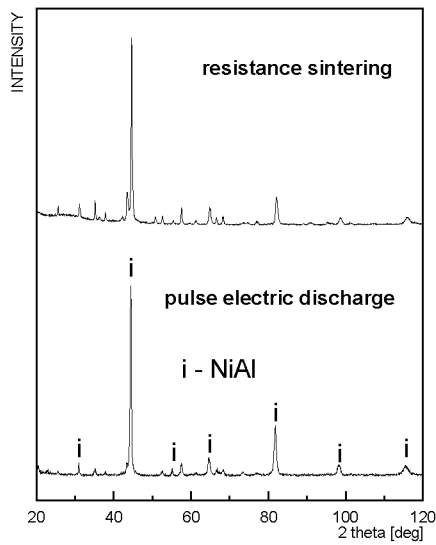


Fig. 4. XRD patterns for NiAl + Al₂O₃ composite after consolidation.

For both methods of powders compaction, i.e. resistance sintering and pulse electric discharge, the densities of about 90% of the theoretical value have been achieved. The obtained diffraction patterns for the compacted samples (Fig. 4) are qualitatively similar to those taken after 2 hours milling synthesis (Fig. 1). In both cases there are no phase transformations due to the consolidation processes, however, a significant increase in average NiAl crystallite size is observed, up to several hundreds of nm.

4. Conclusions

The use of mechanical alloying/reactive milling as a processing tool for nanocrystalline intermetallic matrix composites is very promising and effective. However, further studies, including densification methods (hot isostatic pressing, cold isostatic pressing followed by pressureless sintering, shockwave compaction, spark plasma sintering, microwave sintering) are necessary to get a fully dense material with preserved nanocrystalline structure. These studies allow us to understand and optimize the correlations between processing, structure, and properties.

Acknowledgment

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References

- [1] P.G. McCormick, *Mater. Trans. Jpn. Inst. Metals* **36**, 161 (1995).
- [2] P. Matteazzi, G. Le Caer, *Mater. Sci. Eng. A* **156**, 229 (1992).
- [3] L. Froyen, in: *Proc. Int. Conf. Light Alloys and Composites, May 1999, Zakopane, Poland*, Eds. J. Dutkiewicz, S. Pietrowski, Lodart, Łódź 1999, p. 15.
- [4] G.K. Williamson, W.H. Hall, *Acta Met.* **1**, 22 (1953).
- [5] D.G. Morris, A. Benghalem, *Mater. Sci. Forum* **179-181**, 11 (1995).