A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 57 2012 Issue 3
DOI: 10.2478/v10172-012-0075-7

D. KALIŃSKI*, M. CHMIELEWSKI*, K. PIETRZAK*, K. CHORĘGIEWICZ*

AN INFLUENCE OF MECHANICAL MIXING AND HOT-PRESSING ON PROPERTIES OF NiAl/Al_2O_3 COMPOSITE

WPŁYW MECHANICZNEGO MIESZANIA ORAZ PARAMETRÓW SPIEKANIA POD CIŚNIENIEM NA WŁAŚCIWOŚCI KOMPOZYTU NiAl/ Al_2O_3

Intermetallic phases of the Ni-Al type belong to the group of modern constructional materials which have numerous advantageous properties such as high melting temperature, low density, high resistance to high-temperature oxidation (to about 1200°C), high mechanical strength, high fatigue strength, and high tensile and compressive strength (also at elevated temperatures). Intermetallic compounds have however also drawbacks in that they are quite brittle at room temperature which makes their mechanical processing very difficult and restricts their application range. These drawbacks can be obviated by modifying their chemical composition. Improving the properties of NiAl-based materials can be achieved by creating the composite with the matrix made of an intermetallic phase NiAl reinforced with ceramic (Al_2O_3) particles.

This paper is concerned with the mechanical and physical properties (bending strength, fracture toughness, hardness, and Young modulus) and also the microstructure of NiAl/Al_2O_3 composite. The composite materials were produced by the hot-pressed method using the NiAl/20%Al_2O_3 (vol.%) powder mixtures. The composite thus produced had a high density of about 99% of the theoretical value and a high bending strength. The bending strength of the NiAl/20vol.%Al_2O_3 composite was higher by about 80% (635 MPa) than that of the pure NiAl phase (345 MPa). The experiments included also the examination of the effect of the rotational speed of the mill and the duration of the mixing process upon the size and distribution of grains, the microstructure, and phase composition of the composite powder mixtures obtained.

Keywords: intermetallics, composite materials, mechanical mixing, hot pressing, mechanical properties

Fazy międzymetaliczne typu Ni-Al należą do grupy nowoczesnych materiałów konstrukcyjnych, charakteryzujących się m.in: wysoką temperaturą topnienia, niską gęstością, wysoką odpornością na utlenianie w wysokich temperaturach (do około 1200°C), wysokim modułem sprężystości- stabilnym ze wzrostem temperatury, wysoką wytrzymałością, wysoką odpornością na ścieranie, wysoką wytrzymałością zmęczeniową, wysoką wytrzymałością na rozciąganie i ściskanie (również w wysokich temperaturach). Związki międzymetaliczne mają jednak wady, są dość kruche w temperaturze pokojowej – co znacznie utrudnia m.in. ich obróbkę mechaniczną i zawęża zakres zastosowań. Jednym ze sposobów wyeliminowania tych wad jest modyfikacja ich składu chemicznego. Poprawę właściwości materiałów na bazie NiAl można osiągnąć m.in. poprzez wytworzenie kompozytu na osnowie NiAl umocnionego cząsteczkami Al_2O_3.

W artykule zaprezentowano wyniki prac dotyczących opracowania warunków procesu mechanicznego mieszania mieszanin proszków związek międzymetaliczny (NiAl) – ceramika (Al_2O_3), a następnie ich spiekania. Przyjęte parametry mieszania i spiekania pozwoliły otrzymać kompozyt charakteryzujący się odpowiednią gęstością, bliską teoretycznej (99.9%) oraz wysoką wytrzymałością. Wytrzymałość na zginanie kompozytu NiAl/20%obj.Al_2O_3 była o 80% (635 MPa) wyższa od wytrzymałości czystej fazy NiAl (345 MPa).

1. Introduction

Intermetallic phases of the Ni-Al type belong to the group of modern constructional materials with low density and advantageous properties. They are e.g. characterized by a high melting temperature, good resistance to oxidation at high temperatures (to about 1200°C), high value of the Young modulus stable with increasing temperature, high mechanical, fatigue, tensile and compressive strengths (also at high temperatures), and good frictional wear resistance [1-12].

This unparalleled combination of unique physico-chemical and mechanical properties offers great applicative possibilities for these materials. They are widely used in technologically developed countries in the automobile, aircraft, spacecraft, metallurgical, chemical and power generation industries.

* INSTITUTE OF ELECTRONIC MATERIALS TECHNOLOGY, 01-919 WARSZAWA, 133 WOLCZYNSKA STR., POLAND

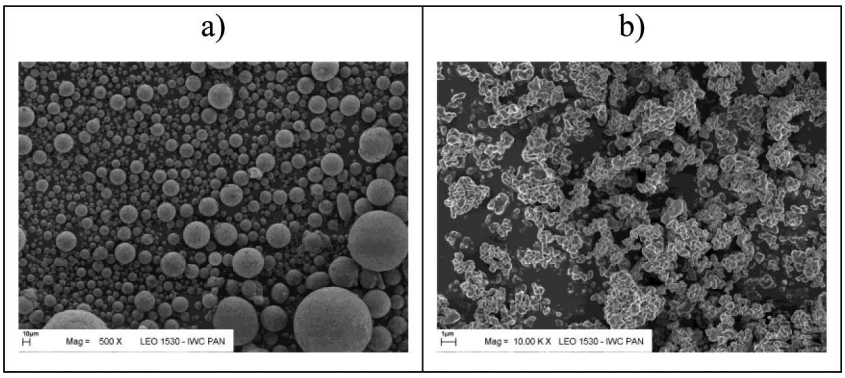

Fig. 1. SEM photographs of the powders: (a) NiAl, (b) Al_2O_3

Intermetallic compounds have however drawbacks in that at room temperature they are brittle and thus difficult to machine, whereas at high temperatures they are susceptible to creep. These disadvantageous properties restrict their application range but can be improved by modifying the composition of the compound or by subjecting it to appropriate plastic and/or heat treatments.

Our preliminary investigations and technological experiments, and also the available literature reports indicate that it is possible to produce materials which show the advantageous properties of the intermetallic phases but are free from their drawbacks. Such materials may be e.g. composites built of an intermetallic matrix which is reinforced with ceramics. This paper presents the results obtained in our experiments with establishing the optimum parameters of the mechanical mixing of intermetallic/ceramic powder mixtures and of their further sintering. We expected that the sintered composites thus obtained will have better properties than pure intermetallic phases.

2. Starting materials

The materials used in the experiments were nickel aluminide powder (delivered by the Goodfellow Company) and an aluminum oxide powder (NewMet Koch). Fig.1 shows SEM photographs of these powders.

The grain size of the starting powders was examined in a Clemex tv image analyzing system. The grain size distributions were analyzed using the Feret diameter (d). Based on the results obtained, the average Feret diameters d_{avg} were determined to be d_{NiAl} = 3.71 μm (for NiAl) and d_{Al2O3} = 2.28 μm (for Al_2O_3). The spread of the grain sizes of the powders was relatively small, being 1-5 μm in Al_2O_3 and 1-10 μm in NiAl.

The powders were mixed in a Pulverisette 6 planetary mill (with a 250 ml container) in an air atmosphere. The container lining and the mill balls were made of tungsten carbide doped with cobalt.

The chemical composition of the powder mixtures prepared for technological experiments was 80%NiAl/20%Al_2O_3 (in vol.%), and was selected so that the properties of the composite differ appreciably from those of pure NiAl but its advantageous properties are preserved.

In order to find how the mixing speed and duration affected the microstructure and properties of the powder mixtures we performed two series of experiments that differ by the mixing process parameters:
series 1 – rotational speed ω_1 =100 rpm, BPR coefficient 5:1, time 1-8 h, and
series 2 – rotational speed ω_2 =200 rpm, BPR coefficient 5:1, time 1-8 h, where
BPR – ball-to-powder weight ratio

Since, at the rotational speed of 200 rev/min, the container was heated to a high temperature, the mixing operation was conducted in the two time cycles (t_1-mixing time, t_2-pause, t_3- cooling):

– at the rotational speed ω_1 = 100 rpm for t_1 = 15 min then pause for t_2 = 2 min, and
– at the rotating speed ω_2 = 200 rpm in the 3 cycles: t_1 = 5 min/t_2 = 2 min, t_1 = 5 min/ t_2 = 2 min, t_1 = 5 min/ t_3 =30 min

The powder mixtures thus prepared were subjected to microstructural examinations, and their grain size distribution and phase composition were analyzed.

3. Results of mixing process

The effect of the mixing parameters on the microstructure, grain size, grain size distribution and possible phase changes that could take place during the process was examined. Just as was the case with the starting powders, the grain size distributions in the powder mixtures were analyzed using a Clemex tv image analyzing system.

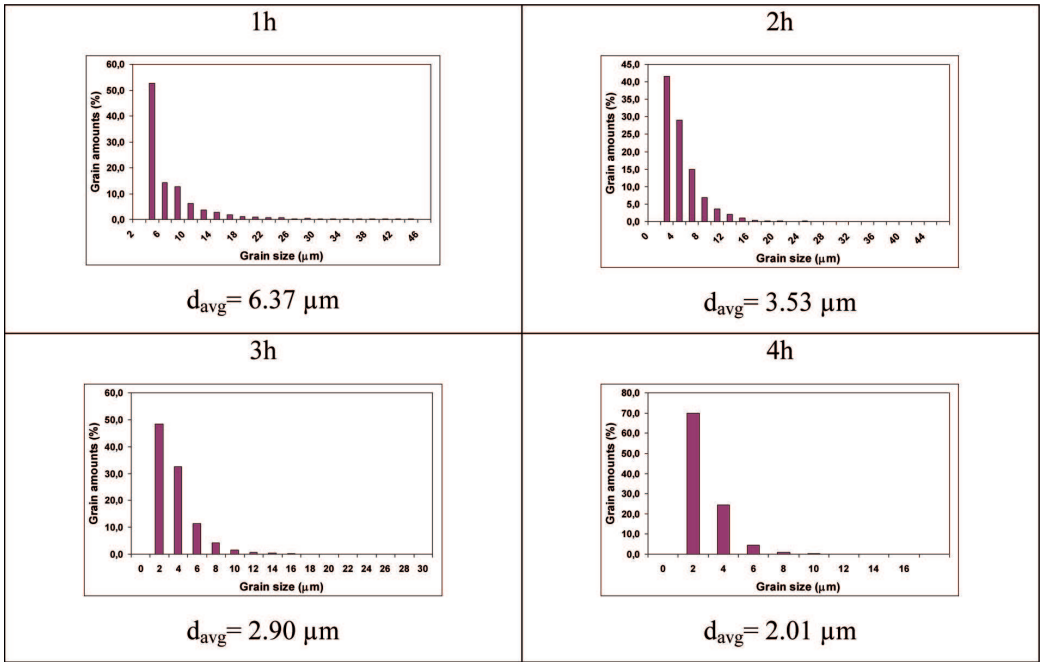

Fig. 2. Grain sized distributions in the NiAl/20vol.%Al_2O_3 powder mixture depending on the mixing time; mixing speed ω =200 rpm

It has been found that with increasing mixing time and duration, the average grain size decreases. At ω_2 (200 rpm), the average grain size decreases from d_{avg} =6.37 μm after 1h of mixing to d_{avg} = 2.0 1 μm after 4h (Fig.2), whereas at ω_1 (100 rpm), it decreases in a decidedly smaller degree (d_{avg} =10.04 μm after 1h decreases to d_{avg} = 8.34 μm after 4h).

The morphology and phase composition of the powder mixture is shown in Fig.3. It should be noted that the morphology varies with mixing time and speed. A prolongation of the mixing time as well as an increase of the mixing speed result in the NiAl grain shape being changed (in the starting state they are spherical) and the grains being refined (Fig.3b). This is crucial when the powder mixture is first subjected to axial or isostatic pressing so as to obtain pieces with a specified shape and then it is sintered, since the spherical grain shapes make, in a great measure, these technological operations

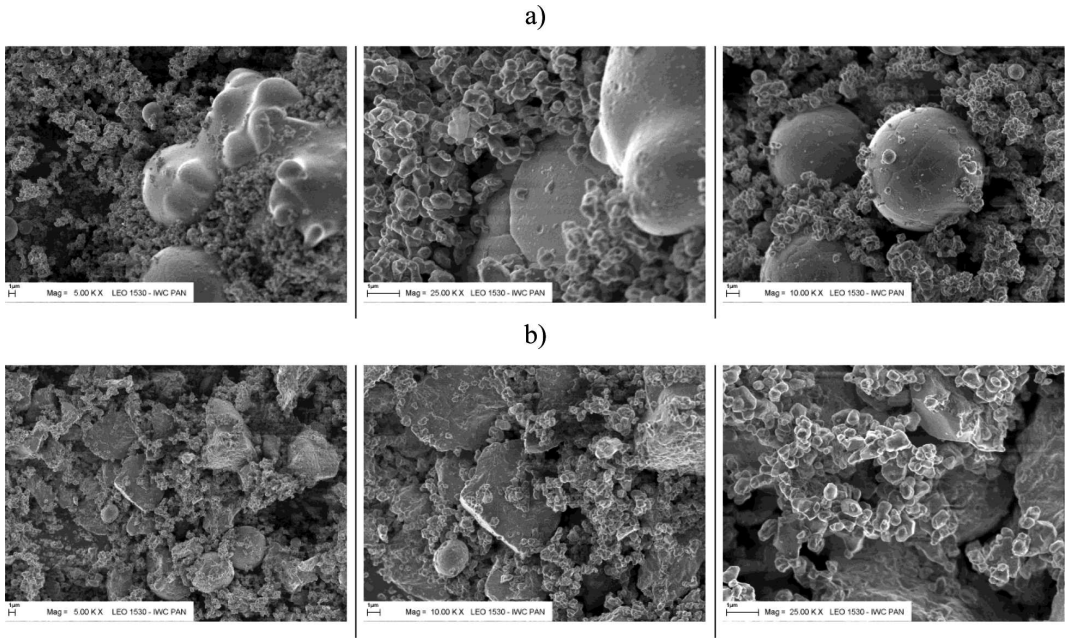

Fig. 3. Morphology of the NiAl/20vol.%Al_2O_3 composite powder mixtures produced by the mechanical mixing as a function of the mixing speed: (a) ω_1 =100 rpm, (b) ω_2 = 200 rpm, t= 4 h

difficult. We can also see in Fig.3b that the harder ceramic phase has been forced into the NiAl phase. On the other hand, when mixing for 4h at the lower rotational speed ω_1 (100 rpm), the morphology shows no appreciable changes. The NiAl grains have still the spherical shape, they are not refined, and there is almost no the harder ceramic phase forced into the NiAl phase (Fig.3a).

The further prolongation of the mixing time to 8h did not result in appreciable changes in the morphology and composition of the powder mixtures.

The changes of the morphology of the powder mixtures have an important influence upon the microstructure and, thus, on the physical and mechanical properties of the composite materials produced of them. The results of our experiments, presented later in the paper, confirm this observation.

XRD examination of the powder mixtures did not reveal any new phases, irrespective of the mixing time and speed. All the composite powder mixtures only contain the NiAl and Al_2O_3 phases.

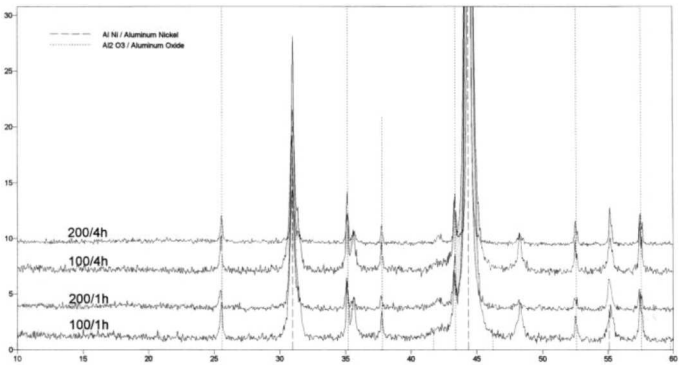

Fig. 4. Phase analysis of the powder mixtures depending on the time and speed of the mixing operation of the NiAl/20vol.%Al_2O_3 (ω_1 =100 rpm, ω_2 = 200 rpm, t = 1 & 4 h)

4. Technological experiments

The powder mixtures were pressure sintered in an ASTRO HP50-7010 press in an argon protective atmosphere. The sintering process parameters were:

- Sintering temperature T_S = 1200-1400°C
- Sintering time t_S = 30-60 min
- Pressure P ~ 30 MPa

The sintered materials thus produced were subjected to examinations of their mechanical and physical properties (density, bending strength, fracture toughness, Young's modulus, and hardness) and their microstructure was analyzed.

The density was determined using the hydrostatic method. The bending strength, fracture toughness, and Yong's modulus were examined in a ZWICK 1446 strength machine at a support spacing of 40 mm and a head travel speed of 1.0 mm/min. The samples intended for the bending strength and fracture toughness tests were sized at 5×5×50 mm, and the head load was 1kN (bending strength) and 10 kN (fracture toughness).

The fracture toughness was also tested by three-point bending. The samples were notched beams sized at 5×5×50 mm. The notch was made in the two stages: the samples were first notched to a depth of 0.9 mm using a wheel 0.2 mm wide and, then, deepened to about 1.1 mm (the total depth of the notch) with a wheel 0.023 mm wide. The straining rate, i.e. the head travel speed was 1.0 mm/min

The measurements of the Young's modulus by the bending test (samples in the form of beams sized at 5×1×50 mm, support spacing – 40 mm) consisted of recording the load-induced deflection of the beam. The load P ranged from 5 to 20 N.

The hardness of the composites was determined in a Vickers hardness-meter under a load of 10 kG applied for 10 s. Each sample was tested 5 times (five measurements).

The microstructural of the sintered composites was analyzed in an optical microscope and a scanning electron microscope. The surface element distribution was determined by EDS, and the phase composition was examined using the XRD examination.

5. Examination of some selected properties of the hot-pressed NiAl/20vol.%Al_2O_3 composite

Table 1 gives the measured values of the density of the composite sintered at: T_s = 1200°C, t_s = 60 min, and P ~ 30 MPa.

TABLE 1
Density of the hot-pressed NiAl-based material. Sintering process parameters: T_s = 1200°C, t_s = 60 min, P ~ 30 MPa

Material	Density of the composite constituents [g/cm^3]		Theoretical density [g/cm^3]	Measured density [g/cm^3]		Relative density [%]	
	NiAl	Al_2O_3		ω_1*	ω_2*	ω_1*	ω_2*
NiAl	5.91	–	5.91	5,55		93.9	
NiAl/20vol.% Al_2O_3	5.91	3.97	5.52	4.94	5.03	89.5	91.1

*) Mixing speed: ω_1 = 100 rpm, ω_2 = 200 rpm, mixing time t= 4h

The porosity of the composite greatly varied depending on whether the powders were mixed at 100 rpm (ω_1) or at 200 rpm (ω_2): in the former case the porosity was 10% and in the latter it was even as low as 2%.

These differences in the density and the resulting porosity can be attributed to e.g. the considerable differences in the morphology of the two powder mixtures which in turn are due to the differences in the mixing parameters. As already mentioned, both a prolongation of the mixing operation and an increase of the mixing speed give a change of the shapes of the NiAl grains and their refinement. Hence we can conclude that this form of the powder mixture ensures its better consolidation which may be due to the increased specific surface area of the powder and its greater surface energy.

Table 2 gives the results of measurements of the mechanical strength and hardness of the composite made of powder mixtures prepared at different rotational speeds. We can see that, here too, the mixing parameters strongly affect the mechanical properties of the composites. The highest bending strength (327 MPa) was achieved in the NiAl/20%Al_2O_3 composite sintered of the powder mixture prepared at 200 rpm (ω_2). Its strength was however only slightly higher than that of the pure NiAl phase (325 MPa – Table 2).

The HV_{10} hardness of this composite was 2.45 GPa which was lower than that of the pure NiAl phase by 10%. The composite sintered of the powder mixture prepared at the lower speed ω_1 (100 rpm) had the bending strength and hardness decidedly lower than the pure NiAl phase, namely 200 MPa and 2.17 GPa, respectively. This can be explained by the poor density of this composite.

TABLE 2

Bending strength σ_c and hardness of the hot-pressed NiAl-based material; parameters of the sintering process were T_s =1200°C, t_s = 60 min, P ~ 30 MPa

Material	Bending strength σ_c (MPa)		Hardness HV_{10} (GPa)	
	ω_1*	ω_2*	ω_1*	ω_2*
NiAl	325.0		2.76	
NiAl/20vol.%Al_2O_3	200.0	327.0	2.17	2.45

*) ω_1 = 100 rpm, ω_2 = 200 rpm – mixing speed, mixing time t= 4h

The sintered pure NiAl and NiAl/20vol.%Al_2O_3 composite were examined in an optical microscope (Figs. 5-6), the surface distribution of the elements was analyzed by EDS (Figs. 7) and their phase composition was determined by XRD examination. When comparing the images shown in Figs. 6a and 6b, we can see clear differences between the structures of the composite depending on the rotational speed ω at which the constituent powders were mixed. The microstructure of the composite prepared from the powder mixture mixed at the greater speed of 200 rev/min (ω_2) is more homogeneous, better consolidated, and more strongly refined (Fig.6b). This is confirmed by the surface distributions of the elements (Fig.7b). The phase analysis did not reveal any new phases formed during the sintering process.

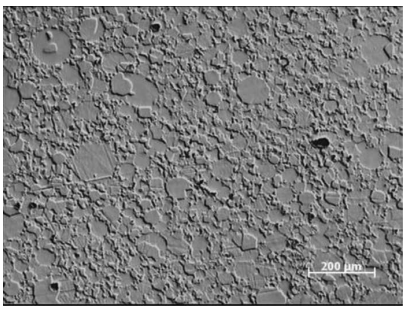

Fig. 5. Microstructure of hot-pressed NiAl intermetallic compound; Sintering process parameters: T_s =1200°C, t_s = 60 min, P~30 MPa

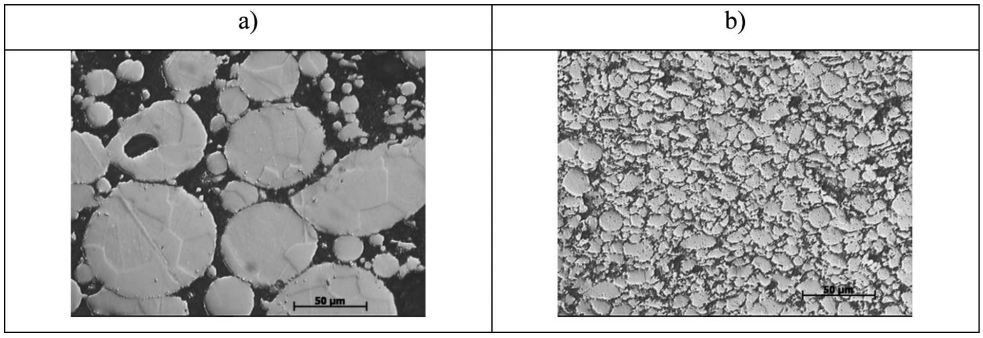

Fig. 6. Microstructure of hot-pressed NiAl/20vol.%Al_2O_3 composite; constituent powders mixed at (a) ω_1 = 100 rpm, (b) ω_2 = 200 rpm for t = 4 h and then sintered at T_s =1200°C for t = 60 min under P~30 MPa

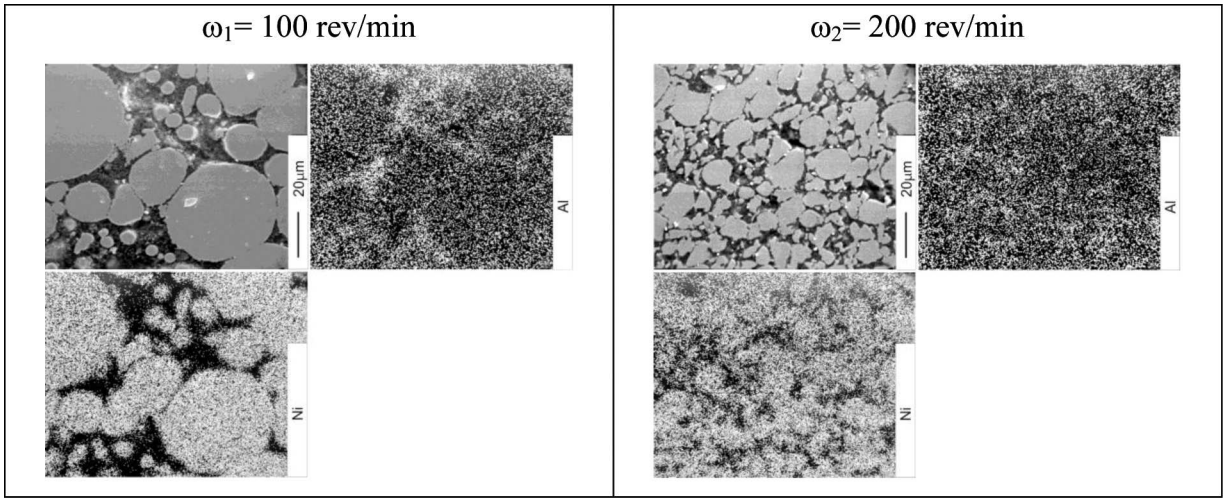

Fig. 7. Surface distributions of Ni and Al in the hot-pressed NiAl/20vol.%Al_2O_3 composite; powders mixed at a rotational speed of 100 rpm (ω_1) and 200 rpm (ω_2) for 4h and then sintered at T_s =1200°C for t_s = 60 min under P~30 MPa

A decisive increase of the density and thus the mechanical strength and hardness of the composite was achieved by optimizing the parameters of the sintering process, in particular by increasing the sintering temperature by 150 to 200°C. Sintering at the optimized parameters, namely T_s =1400°C, t_s = 30 min, P ~ 30 MPa yielded a composite with high density – on average about 99% of the theoretical value (Table 3).

TABLE 3

Density of the hot-pressed NiAl-based material sintered at: T_s =1400°C, t_s =30 min, P ~ 30 MPa. Mixing process parameters: ω = 200 rpm, t = 4h

Material	Density of the composite constituents [g/cm^3]		Theoretical density [g/cm^3]	Measured density [g/cm^3]	Relative density [%]
	NiAl	Al_2O_3			
NiAl	5.91	–	5.91	5.88	99.5
NiAl/20vol.% Al_2O_3	5.91	3.97	5.52	5.51	99.9

The measured values of the bending strength, fracture toughness, Young modulus and hardness of the composite sintered under the optimized sintering conditions (T_s =1400°C, t_s =30 min, P ~ 30 MPa) are given in Table 4.

A comparison of the results given in Tables 4 shows that the bending strength of the NiAl/20vol.%Al_2O_3 composite (635 MPa) is higher by 80% than that of the pure NiAl phase (345 MPa). The fracture toughness of the two materials differs however only slightly (Table 4), and the Young's modulus of the composite is slightly higher than that of the pure NiAl phase but considerably lower than the value calculated from the mixing rule (Voigt's model – 223 GPa, Reuss's model – 208 GPa). The hardness of the composite exceeds that of NiAl by about 30%.

TABLE 4

Properties of the hot-pressed NiAl-based material sintered at: T_s =1400°C, t_s = 30 min, P ~ 30 MPa. Mixing process parameters: ω = 200 rpm, t = 4h

Material	Bending strength σ_c [MPa]	K_{IC} [MPa·m$^{1/2}$]	Young modulus [GPa]	Hardness HV_{10} [GPa]
NiAl	345.6±53.8	7.2±0.4	188	3.08±0.1
NiAl/20vol.% Al_2O_3	635.2±43.7	6.6±0.2	191.9	4.29±0.5

Figure 8 shows the microstructure of the sintered pure NiAl and NiAl/20vol.%Al_2O_3 composites. The images confirm that the sintering degree of the NiAl/20vol.%Al_2O_3 composite is high and its grain size is smaller than that in pure NiAl. We can also see small pores in the microstructure image but they are not due to the incomplete sintering of the composite but have been formed during polishing its metallographic cross-sections with the use of a diamond powder.

The composite has a homogeneous and compact structure and the ceramic phase is distributed relatively uniformly on the entire cross-section of the sample. This is confirmed by the element surface distributions examined by EDS (Fig. 9).

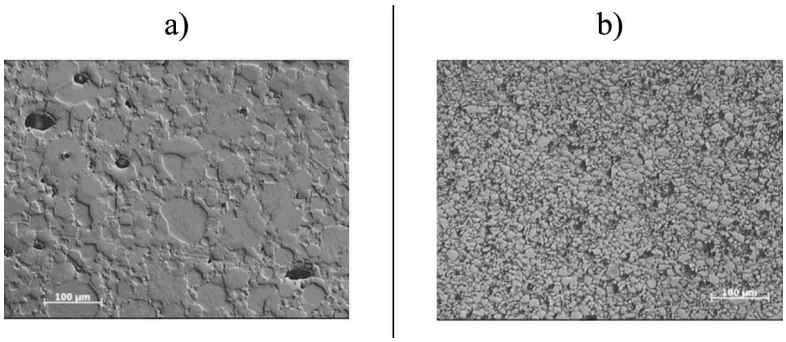

Fig. 8. Microstructure of the hot-pressed NiAl intermetallic compound (a) NiAl/20vol.%Al_2O_3 composite (b) sintered at T_s = 1400°C, t_s = 30 min, P ~ 30 MPa. Mixing process parameters: ω = 200 rpm, t = 4h

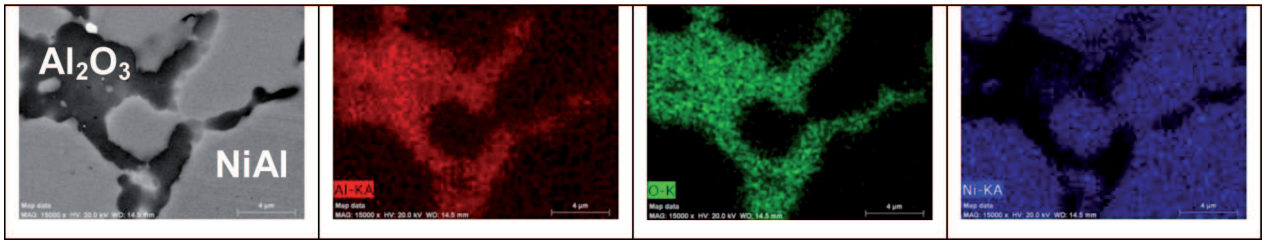

Fig. 9. Surface distributions of the elements in the hot-pressed NiAl/20vol.%Al_2O_3 sintered at: T_s = 1400°C, t_s = 30 min, P ~ 30 MPa. Mixing process parameters: ω = 200 rpm, t = 4h

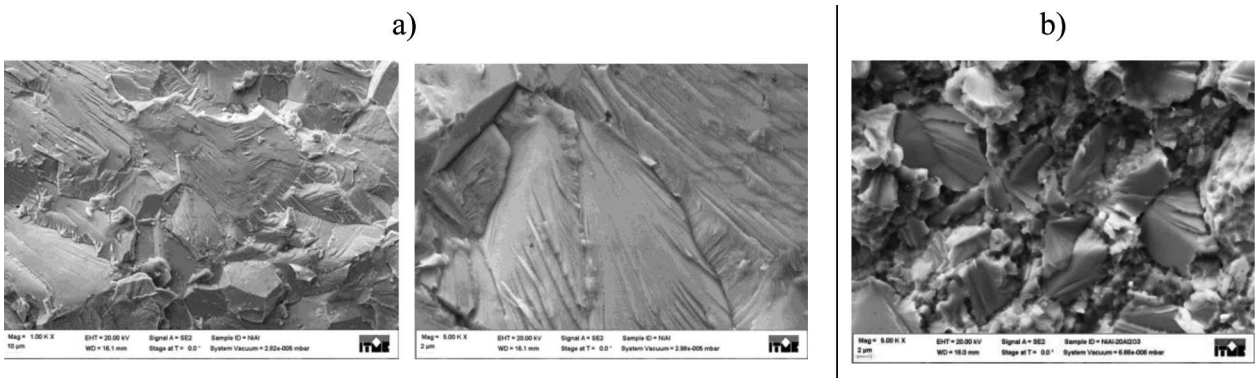

Fig. 10. Exemplary microstructures of a fracture in (a) NiAl, and (b) NiAl/20vol.%Al_2O_3 sintered at T_s = 1400°C, t_s = 30 min, P ~ 30 MPa. Mixing process parameters: ω = 200 rpm, t = 4h

The addition of the ceramic phase and the refinement of the NiAl phase (during the mixing operation) have an essential effect on the course of failure of the composite.

This can be seen in Fig.10 which shows the microstructures of fractures of pure NiAl and the NiAl-based composite after the bending test. Failure in the pure NiAl phase (Fig.10a) runs characteristically in one direction through the NiAl grains, whereas in the composite material (Fig.10b) the ceramic grains force the crack to wind its way which greatly elongates its path and thereby increases the strength of the composite.

6. Conclusions

The effect of the technological parameters on the properties of the constituent powders and of the NiAl/20vol.%Al_2O_3 composite sintered under pressure from a mixture of these powders was examined and the parameters were optimized. The experiments have shown that the physical and mechanical properties (such as e.g., density, resulting porosity, bending strength, and hardness) of the composite closely depend on the parameters of both the mixing and sintering processes. From the point of view of the uniformity of the distribution of the ceramic reinforcement (Al_2O_3) within the NiAl matrix, the most advantageous mixing parameters were found

to be: the rotational speed ω =200 rpm, mixing time t = 4 h, the ball-to-powder weight ratio (BPR) of 5:1 and the mill ball size of 10mm.

After an appropriate mixing time, the higher rotational mixing speed (two speeds were examined) resulted in the NiAl grains changing their shapes (initially spherical) and being more refined. In addition, the harder ceramic phase was forced into the NiAl phase. This form of the powder mixtures appeared to enable them to be better consolidated during the sintering under pressure.

With the powder mixtures prepared at the higher speed ω_2 (200 rpm), the composites had a higher relative density (and hence lower porosity), better bending strength, and higher hardness. Their structure was homogeneous, well refined, and more compact.

The decisive improvement of the bending strength and hardness of the composite was achieved after optimization of the sintering process, in particular by increasing the sintering temperature. The NiAl/20vol.%Al_2O_3 composite sintered at the optimum process parameters established during the experiments (T_s = 1400°C, t_s = 30 min, P ~ 30 MPa) had a high density near the theoretical value (99.9%), and its bending strength (635 MPa) exceeded the strength of the pure NiAl phase (345 MPa) by 80%. This increase of the bending strength can be explained by an important change in the course of the failure process. In pure NiAl, the failure proceeds in one direction through the grains, whereas in the composite, the ceramic grains force it to wind its way, which elongates the cracking path and thereby increases the bending strength of the composite.

Acknowledgements

The results presented in this paper have been obtained within the project "KomCerMet" (contract no. POIG.01.03.01-14-013/08-00 with the Polish Ministry of Science and Higher Education) in the framework of the Operational Programme Innovative Economy 2007-2013.

Received: 20 February 2012.

REFERENCES

[1] K. Morsi, Review: reaction synthesis processing of Ni-Al intermetallic materials Materials Science and Engineering **A299**, 1-15 (2001).

[2] R. Darolia, Ductility and fracture toughness issues related to implementation of NiAl for gas turbine applications Intermetallics **8**, 1321-1327 (2000).

[3] K. Matsuura, T. Kitamutra, M. Kudoh, Microstructure and mechanical properties of NiAl ntermetallic compound synthesized by reactive sintering under pressure. Journal of Materials Processing Technology **63**, 293-302 (1997).

[4] K. Uenishi, K.F. Kobayashi, Processing of intermetallic compounds for structural applications at high temperaturea Intermetallics **4**, 95-101 (1996).

[5] J. Mei, P. Xiao, Joining metals to zirconia for high temperature applications Scripta Materialia **40**, 5, 587-594 (1999).

[6] A. Kitaoka, K. Hirota, M. Yoshinaka, Y. Miyamoto, O. Yamaguchi, Toughening and Strengthening of NiAl with Al2O3 by the Addition of ZrO_2(3Y), J. Am. Ceram. Soc. **83**[5], 1311-1313 (2000).

[7] C.T. Liu, E.P. George, V.K. Sikka, S.C. Deevi, in: N.S. Stoloff, R.H. Jones (Eds.), Processing and Design Issues in High Temperature Materials, The Mineral, Metals and Materials Society 139-155 (1997).

[8] M.R. Ghomashchi, Al_2O_3 reinforced Al/Ni intermetallic matrix composite by reactive sintering J. of Mater. Sciance **30**, 2849-2854 (1995).

[9] K. Morsi, T. Fujii, H. McShane, M. McLean, Control of heat generation during reaction synthesis Scripta Materialia **40**, 3, 359-364 (1999).

[10] S. Gialanell, L. Lutterotti, A. Molinari, J. Kazior, T. Pieczonka, Reaction-sintering of intermetallic allos of the Ni-Al-Mo system Intermetallic **8**, 279-286 (2000).

[11] Engineered Materials Reference Book, ASM International, 1999.

[12] T. Chmielewski, D. Golański, New method of in-situ fabrication of protective coatings based on Fe-Al intermetallics compounds, Proceedings of the Institution of Mechanical Engineers Part B – Journal of Engineering Manufacture **225(B4)**, 611-616 (2011).