MICROSTRUCTURE OF BALL-MILLED NiAl30 POWDER

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The microstructure of ball-milled NiAl30 powder prepared by a proprietary technique was studied in this paper. It appeared that the NiAl30 powder is a heterogeneous mixture of particles containing various fractions of components.

SEM and TEM observation showed that substantial part of powder particles exhibit fine lamellar microstructure resulting from severe deformation, fracture and welding in the ball milling process. Lamellar domains are formed by elemental Ni and Al as well as by ordered β-NiAl. Nanocrystalline Ni_2Al_3 was observed, too. No amorphous phase was observed in the studied microstructure.

K e y w o r d s: NiAl30 ball-milled powder, microstructure, TEM studies, intermetallic phases

MIKROŠTRUKTÚRA PRÁŠKU NiAl30 PRIPRAVENÉHO MLETÍM V GUĽOVOM MLYNE

Predmetom článku je štúdium mikroštruktúry prášku NiAl30 pripraveného mletím v guľovom mlyne. Prášok tvorí homogénna zmes častíc obsahujúcich rôzne podiely niklu a hliníka.

Pozorovania pomocou SEM a TEM ukázali, že podstatná časť práškových častíc má jemnú lamelárnu štruktúru vyvolanú opakovanými cyklami plastickej deformácie, lomov a opätovného zvárania v procese mletia. Lamely pozostávajú z tuhých roztokov na báze Ni a Al, ako aj z usporiadanej intermetalickej zlúčeniny β-NiAl. Zistila sa taktiež prítomnosť nanokryštalického Ni_2Al_3. Nepotvrdil sa výskyt žiadnych amorfných fáz v mikroštruktúre skúmaného prášku.

1. Introduction

The unusually high melting temperature of NiAl compound published in a corresponding phase diagram study attracted attention already in 1908 [1]. Later

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research identified NiAl as the B2 ordered intermetallic phase that exhibits a wide range of quite promising physical and mechanical characteristics including low density, good oxidation resistance and metal-like electrical and thermal conductivity. These have sparked interest for applications ranging from high-pressure turbine blades to buried interconnections in electronic components [2]. However the largest effort was paid to the development of alloys based on the ordered intermetallic compound NiAl for high temperature applications in advanced aerospace structures and propulsion systems [3].

NiAl can be found in various applications where resistance to oxidation and abrasion is required. These include bulk components as well as protective coatings for exposed parts. Casting technologies [4, 5], powder metallurgical routes [6] and various types of coating processes [7, 8] are used to produce the NiAl compound in a requested form.

Thermal spraying technologies form the NiAl coatings predominantly due to mutual reaction of molten elemental Al and Ni that are in an intimate contact on a powder particle scale. Initial powders are usually composite objects where the Ni core is clad by Al envelope. As these particles are melted, mutual reaction exothermic in nature takes place, what, as assumed, results in a better adherence of coating to the substrate. However, production of composite powders requires sophisticated processes what makes them relatively expensive.

High-energy ball milling of metallic powders is a well-established process for the production of stable as well as metastable crystalline and amorphous phases [9]. It might be also well recognized as alternative process for powder production for thermal spraying technologies as it brings small elemental volumes into an intimate contact on a microscopic scale in as-milled condition. This idea is further powered by the convenient powder price resulting from the less expensive technology.

NiAl30 powder is an R&D product of the Welding Institute in Bratislava. It is generally aimed for dense coatings, resistant to oxidation and abrasion produced via thermal spraying processes. Intensive studies of the powder properties as well as formation of NiAl coatings are the subject field of the running VEGA project at the IMMM SAS. This article summarizes the results of the microstructural characteristics of the as-milled initial powder. They will basically serve as an introductory reference for subsequent presentation of microstructural evolution in the process of plasma spray NiAl coating formation.

2. Experimental material and procedure

NiAl30 refers in this work to ball-milled nickel base binary powder containing 30 mass % of aluminium. It was produced by high-energy ball milling of initial high purity elemental powders of Ni (99.99 %) and Al (99.95 %) in a nitrogen atmosphere by a proprietary technique.

Initial elemental powders of gas atomized Ni with sizes below 63 μm, Al with sizes below 125 μm and finally composite NiAl30 powder with sizes below 45 μm were studied in this work.

Light microscopy (LM) and microhardness measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX) were used for the structural studies. Samples for LM and SEM studies were prepared by embedding the powder in a cold-curing resin with subsequent grinding and polishing in a conventional metallographic way. The thin foil preparation of NiAl30 powder for TEM observations via the ion milling process followed the routes presented elsewhere [10].

SEM observations were performed using the JEOL 5310 electron microscope operated at the accelerating voltage of 15 kV, TEM observations were carried out at a JEOL JEM 100 C analytical electron microscope operated at 100 kV. The analyses including bright field and dark field observations with selected area electron diffraction (SAED) were employed. EDX analyses were performed using a Kevex Delta class IV spectrometer with an ultra-thin window detector (Kevex Quantum detector). Ion milling was performed using the BAL-TEC RES 010 rapid etching system.

3. Results

Initial elemental powders of Al and Ni are shown in Figs. 1 and 2. As seen, Al powder contains not only individual more or less spherical particles, but also clusters or irregular arrangements formed by several particles. Initial Ni powder

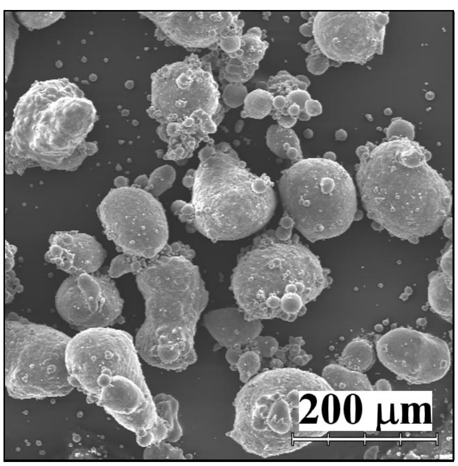

Fig. 1. Secondary electron micrograph of the initial Al powder (SEM).

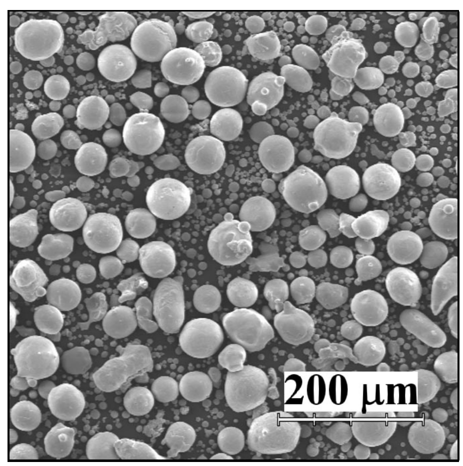

Fig. 2. Secondary electron micrograph of initial Ni powder (SEM).

exhibits smooth surface morphology and mostly spherical shape. Some irregular shapes resulting from the mutual particle collisions during the gas atomization also appear.

On the contrary, ball-milled NiAl30 powder shown in Fig. 3 is formed by sharply edged particles of irregular shape. As the particles were sieved to 45 μm, they appear smaller when compared with the initial elemental powders.

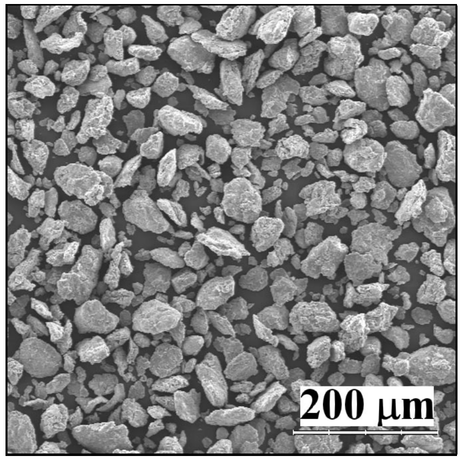

Fig. 3. Secondary electron micrograph of as-milled NiAl30 powder (SEM).

As-milled powder can be characterized as a heterogeneous mixture of particles containing various fractions of components. Particles with only one component can be also found although this is not a frequently appearing event. The substantial part of powder particles exhibit polyphase, mostly fine lamellar structure resulting from severe deformation in the ball milling process. The results of microhardness measurements presented in the Table 1 reflect the degree of homogeneity determined in the initial as well as in as-milled powders. The typical lamellar structure of the NiAl30 particles can be seen in SEM micro-

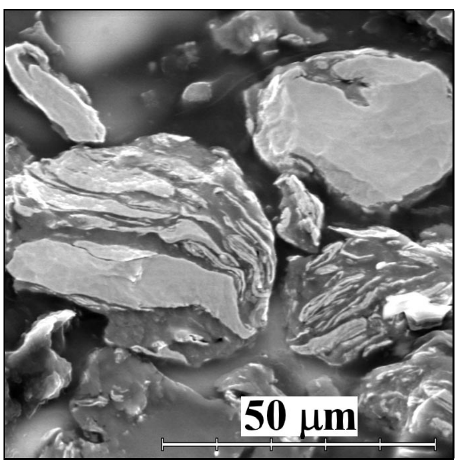

Fig. 4. Secondary electron micrograph of the cross-section of NiAl30 powder (SEM).

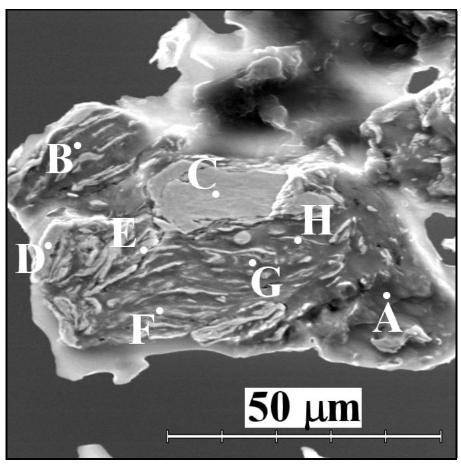

Fig. 5. Microstructure of NiAl30 powder as observed in the particle cross-section (SEM).

graphs shown in Figs. 4 and 5. EDX point analysis revealed that darkly appearing regions refer to aluminium whereas lighter regions refer to nickel locations. As can be seen in the Table 2, regions with nearly pure elemental compositions can be found, however, concentrations with varying contents of Al and Ni were also

Table 1. Hardness of initial Al, Ni and as-milled NiAl30 powders

Powder	Hardness HV 0.02	Standard deviation
Al	36.6	1.6
Ni	200.2	13.8
NiAl30	197.3	54.3

Table 2. EDX analysis of chemical composition in the powder particle shown in Fig. 6

Element	Position of point analysis							
	A	B	C	D	E	F	G	H
Al [mass %]	100.0	99.7	0.4	1.3	21.5	62.1	52.0	31.6
Ni [mass %]	0.0	0.3	99.6	98.7	78.5	17.9	48.0	68.4

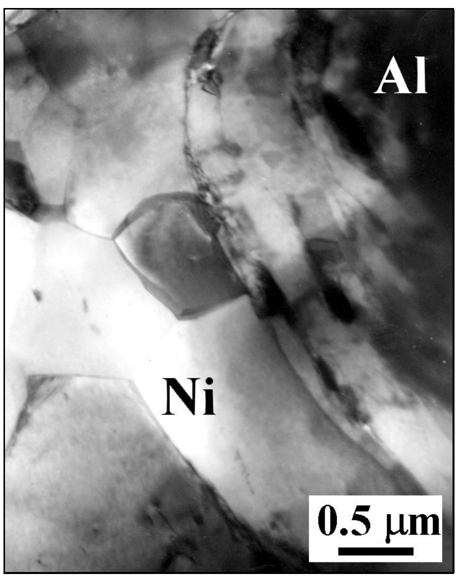

Fig. 6. Interlayer boundary region in the microstructure of as-milled NiAl30 powder (TEM, BF image).

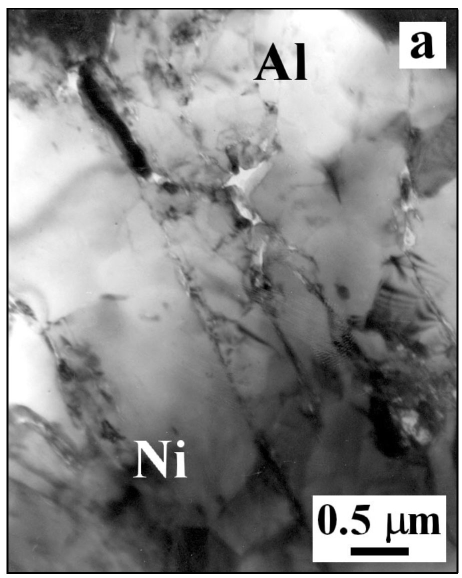

Fig. 7a. Interlayer boundary region in the microstructure of as-milled NiAl30 powder (TEM, BF image).

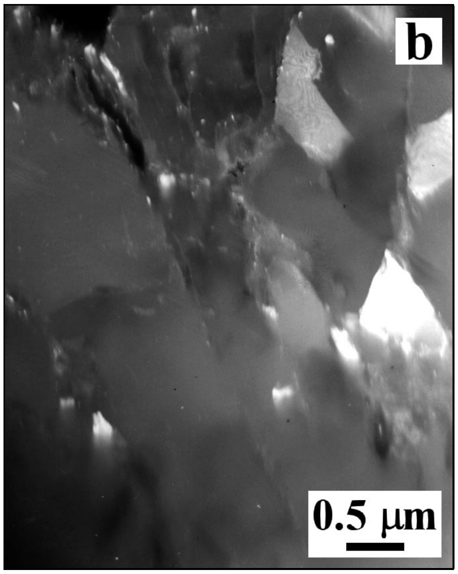

Fig. 7b. Dark field image formed using $(\bar{1}11)$ reflection of Al.

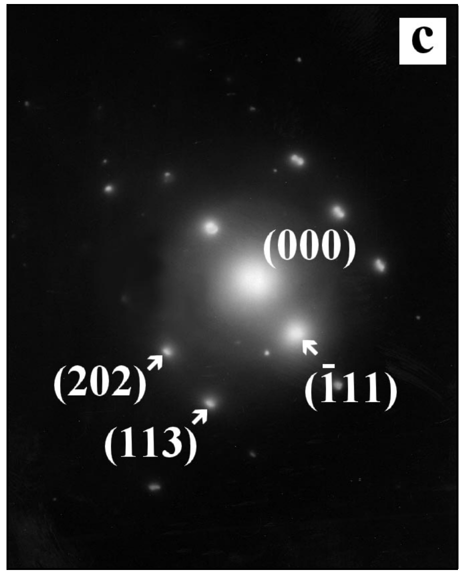

Fig. 7c. SAED pattern corresponding to $[\overline{12}1]$ zone of Al.

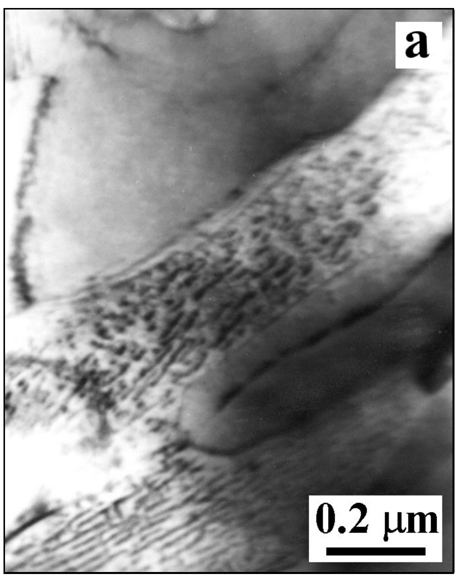

Fig. 8a. β-NiAl phase with mottled appearance in the microstructure of NiAl30 powder (TEM, BF image).

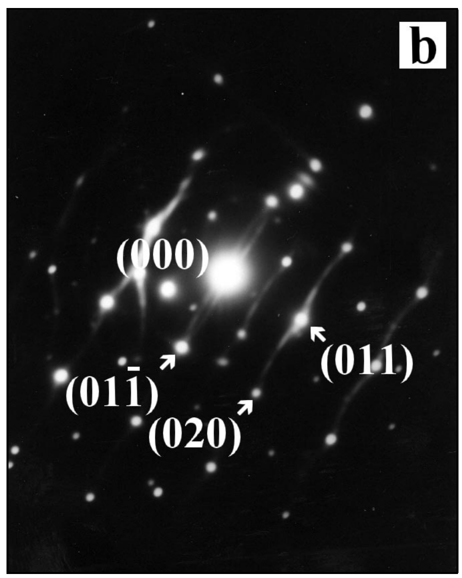

Fig. 8b. SAED pattern corresponding to [100] zone of β-NiAl.

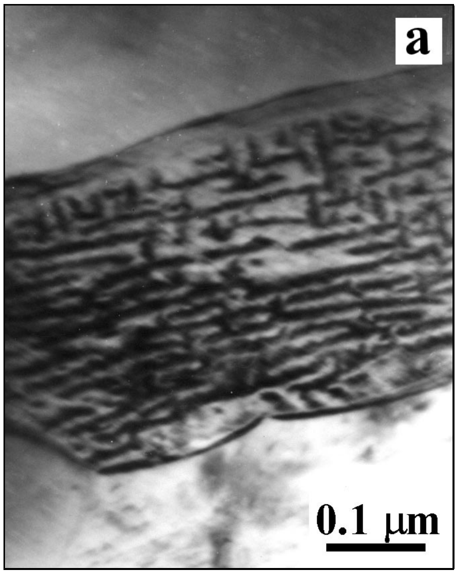

Fig. 9a. β-NiAl in the microstructure of NiAl30 powder (TEM, BF image).

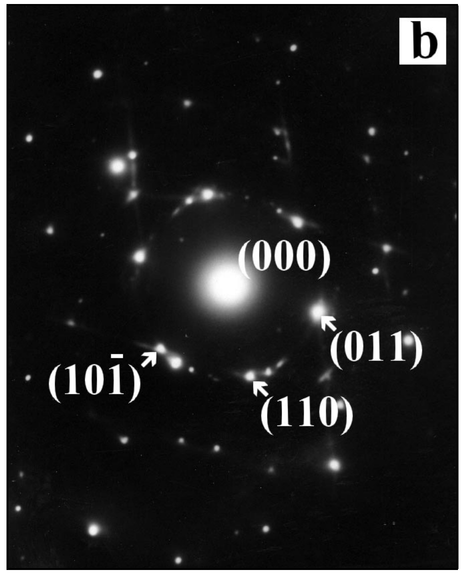

Fig. 9b. SAED pattern corresponding to [1$\bar{1}$1] zone of β-NiAl.

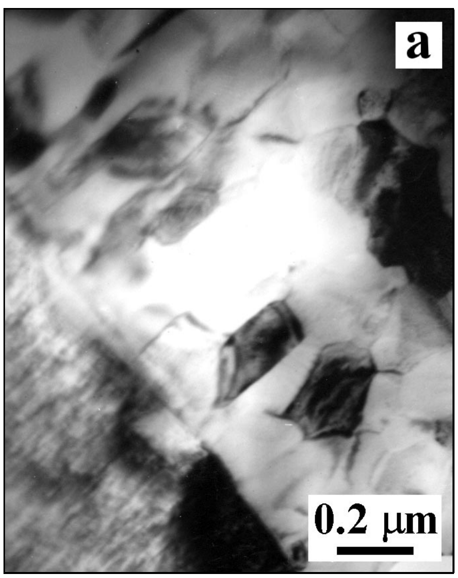

Fig. 10a. Fine grained β-NiAl in the microstructure of NiAl30 powder (TEM, BF image).

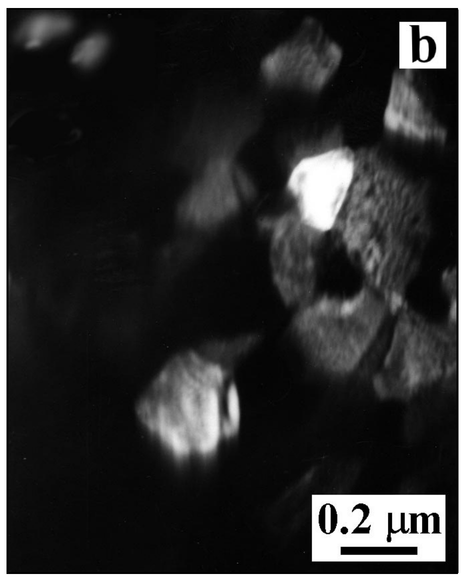

Fig. 10b. Dark field image formed using the (101) reflection of β-NiAl.

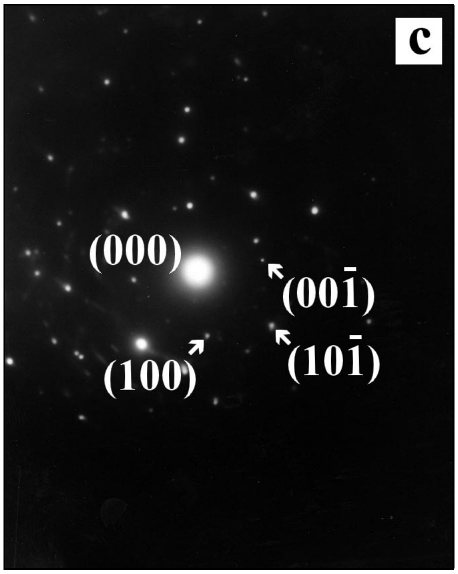

Fig. 10c. SAED pattern corresponding to [010] zone of β-NiAl.

observed. These are determined mostly in those regions where the lamellar structure is very fine and it cannot be distinguished whether they come from two overlapping elemental phases or indicate the presence of some intermediate phase.

The TEM studies revealed that the powder microstructure is very fine, mostly composed of more or less deformed bands or lamellar domains of aluminium and nickel. The interlamellar boundary region is mostly sharp with no visible reaction zone. Aluminium regions seem to be more severely deformed and mostly contain numerous grains with fine dispersoids. These are most probably oxides. They were too fine and it was not possible to achieve a regular diffraction pattern to identify their actual structure. Typical examples are shown in Figs. 6 and 7. However in some locations phases with mottled appearance were also observed and the corresponding electron diffraction patterns could have been indexed in terms of B2 β-NiAl structure. They were often incorporated inside powder particles adjacent to elemental regions. Typical examples are shown in Figs. 8 and 9.

The β-NiAl is ordered as manifested by superlattice reflections. It was observed also with fine-grained morphology as shown in Fig. 10. It also occupied a distinct part of the powder neighboring with some elemental region. The interface is also in this case quite straight with the absence of any reaction zone.

Finally, very fine-grained region giving electron diffraction ring patterns was observed in one particle. These patterns could have been identified in terms of trigonal Ni_2Al_3. Typical example is shown in Fig. 11.

The electron diffraction analysis confirmed the absence of any amorphous phase in the as-milled NiAl30 powder.

4. Discussion of results

High-energy ball milling, of metallic powders, sometimes referred to as mechanical milling, was developed in the late 1960s and early 1970s [11, 12, 13]. The initial efforts were aimed towards the development of dispersion strengthened Ni-base superalloys. As the repeated deformation, melting and fracture of milled

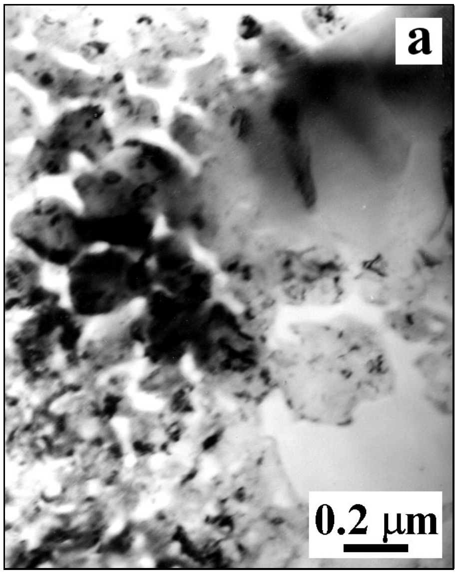

Fig. 11a. Nanocrystalline Ni_2Al_3 in the microstructure of NiAl30 powder (TEM, BF image).

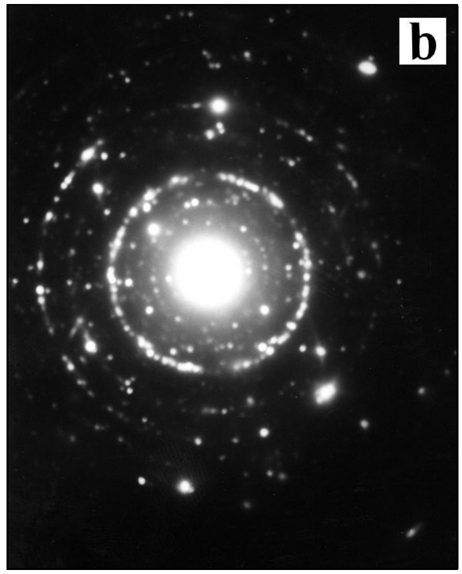

Fig. 11b. SAED ring pattern corresponding to random orientation of Ni_2Al_3.

powders had resulted in homogeneous composite microstructures, the promising potential of a new powder-processing route appeared.

The high-energy ball milling of ductile materials initially leads to powder mixing and concurrent deformation, fracture and welding of powder particles. These result in the formation of large flake-shaped particles and composite particles containing layers of the alloy components [14]. Accordingly to general classification of the process [13], the initial stage is followed by period of welding predominance and the period of equiaxed particle formation. Then the welding with random orientation starts and the process is completed by steady state processing.

The key aim of the ball milling in the process of powder preparation for thermal spraying applications is the achievement of intimate contact of elemental constituents on fine, best of all, microstructural scale. The formation of intermetallic phases is not decisive particularly in the case of β-NiAl, where the melting temperature of the intermetallic compound is far above the melting temperatures of elemental constituents, Ni and Al. Therefore, in this case the process of ball milling is to be interrupted at a point where the homogeneous distribution of elemental constituents is already achieved but the extensive formation of intermetallic phases is not yet fully developed. The microstructural observations in this work confirmed the finely spaced multilayer structure of NiAl30 powder. The thickness of lamellar elemental domains was quite often close to 1 μm range what should create suitable preconditions for mutual reaction of Ni and Al constituents in the process of thermal spray coating formation. A significant variability in the morphology and hardness of the analysed particles can be related to the statistical nature of the ball milling process.

The results of EDX analysis showed that both regions with pure elemental compositions as well as locations with varying contents of Al and Ni could be found in the powder microstructure. The fundamental problem here was the question whether these locations are occupied by finely dispersed elemental constituents appearing simultaneously in the excited volume of the sample or they already represent the newly formed intermetallic phases.

The TEM observations undoubtedly confirmed that the microstructure is really formed by finely spaced lamellar domains with sharp interfaces without any reaction zone. These lamellar domains are formed by both elemental constituents – Ni and Al as well as by intermetallic compounds, predominantly β-NiAl. Atomic concentrations for NiAl30 powder correspond to $Ni_{54}Al_{46}$ and so the formation of equiatomic NiAl with respect to its wide phase field in the binary diagram is not surprising at all. The presence of Ni_2Al_3 intermetallic compound was also confirmed. However as it was only in one location, its formation could be well acknowledged as a local event.

The solid state reactions induced by high-energy ball milling of Al/Ni elemental mixtures have been studied in numerous papers [15–24]. It appeared that the results are determined by the type of mill, energy input, overall composition of blend and time of milling.

For similar elemental blends, abrupt formation of NiAl phase through direct rapid exothermic solid state reaction without formation of intermediate solid solutions was observed in some works [18, 22]. This reaction takes place only when Al and Ni reach critical nanocrystalline sizes [18].

On the other hand, when $Ni_{50}Al_{50}$ powder is milled continuously for time in excess of 120 min, gradual NiAl formation was observed in [23]. It is supposed that during continuous milling, each particle, after reaching a critical lamellar thickness appropriate for the steady-state conditions, undergoes a reaction when ignited by a collision. Gradual character of this reaction is the result of explosions in individual grains leading to thermal equilibration.

The unique character of these reactions differs substantially from the gradual solid-state layer diffusion mechanism. In a layer diffusion mechanism, the initial reaction occurs in a thin interfacial region and the composition of the initially formed phase depends on thermodynamic and kinetic considerations, but not on the overall composition. Thus $NiAl_3$ is the first phase to form upon thermal annealing of thin film Al-Ni couples [24]. $NiAl_3$ appears as the first phase also upon thermal annealing of $Al_{50}Ni_{50}$ composites prepared by ball milling [25]. $NiAl_3$ is then followed by Ni_2Al_3 and finally by NiAl. This sequence was not observed by the formation of intermetallic phases due to high-energy ball milling where the direct formation of NiAl is often reported. Quite exceptionally some remarks about Ni_2Al_3 formation can be found but these are related mostly to blends with less Ni content [17, 24].

It appears that the overall picture of the mechanism of new phase formation in the ball milling process has not been completed yet. Moreover, as far as the details of the preparation route of the investigated powder are not known, the obtained results cannot be related to the presented theories. Anyway, we can conclude that the investigated powder was prepared by a process advancing the gradual character of the NiAl formation. The process was interrupted prior to formation of extensive reaction leading to massive formation of NiAl. The larger part of the powder volumes is thus formed by Ni and Al base solid solutions in intimate contact on microstructural scale, what gives good preconditions for further gains by exothermic reaction in the process of thermal spray coating deposition.

5. Conclusions

The microstructure of ball-milled NiAl30 powder was studied in this paper.

It appeared that the NiAl30 powder is a heterogeneous mixture of particles containing various fractions of components.

Substantial part of powder particles exhibits fine lamellar microstructure resulting from severe deformation, fracture and welding in the ball milling process.

It was shown that lamellar domains are formed by elemental Ni and Al as well as by ordered β-NiAl. Nanocrystalline Ni_2Al_3 was observed, too.

No amorphous phase was observed in the microstructure of as-milled NiAl30 powder.

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REFERENCES

[1] GWYER, A. G. C.: Z. anorg. Chem., *57,* 1908, p. 113.
[2] NOEBE, R. D.—BOWMAN, R. R.—NATHAL, M. V.: International Materials Reviews, *38,* 1993, p. 193.
[3] MIRACLE, D. B.: Acta metall. Mater., *41,* 1993, p. 649.
[4] LAPIN, J.: Kovove Mater., *40,* 2002, p. 209.
[5] LAPIN, J.—PELACHOVÁ, T.—BAJANA, O.: Intermetallics, *8,* 2000, p. 1417.
[6] WHITTENBERGER, J. D.—GRAHLE, P.—ARZT, E.—BEHR, R.: Powder Processing of NiAl for Elevated Temperature Strength. In: High-Temperature Ordered

Intermetallic Alloys VII. Eds.: Koch, C. C., Liu, C. T., Stoloff, N. S., Wanner, A. Vol. 460. Pittsburg, Material Research Society 1997, p. 487.
[7] SAMPATH, S.—McCUNE, R.: MRS Bulletin, *25,* 2000, p. 12.
[8] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.: Kovove Mater., *39,* 2001, p. 316.
[9] KUSCHKE, W. M.—KELLER, R. M.—GRAHLE, P.—MASON, R.—ARZT, E.: Z. Metallkd., *86,* 1995, p. 804.
[10] IŽDINSKÝ, K.—IVAN, J.—ZEMÁNKOVÁ, M.—KOLENČIAK, V.: Kovove Mater., *35,* 1997, p. 188.
[11] BENJAMIN, J. S.: Metall. Trans., *1,* 1970, p. 2943.
[12] BENJAMIN, J. S.: Scientific American, *234,* 1976, p. 40.
[13] BENJAMIN, J. S.—VOLIN, T. E.: Metall. Trans., *5,* 1974, p. 1929.
[14] AIKIN, B. J. M.—COURTNEY, T. H.: Metall. Trans., *24A,* 1993, p. 647.
[15] IVANOV, E. U.: Tverdofaznyje reakcii pri mechanicheskom splavlenii metallov. In: Mechanochimicheskij Sintez v Neorganicheskoj Chimii. Novosibirsk, Nauka 1991.
[16] HWANG, S. J.: Mater. Sci. Forum, *7,* 2000, p. 1.
[17] CARDELLINI, F.—MAZZONE, G.—MONTONE, A.—VITTORI ANTISARI, M.: Acta Metall. Mater., *42,* 1994, p. 2445.
[18] PABI, S. K.—MURTY, B. S.: Mater. Sci. Eng., *A 214,* 1996, p. 146.
[19] SURINACH, S.—MALAGELADA, J.—BARO, M. D.: Mater. Sci. Eng., *A 168,* 1993, p. 161.
[20] HWANG, S. J.: Mater. Sci. Forum, *6,* 1999, p. 581.
[21] ALBITER, A.—BEDOLLA, E.—PEREZ, R.: Mater. Sci. Eng., *A 328,* 2002, p. 80.
[22] PORTNOY, V. K.—BLINOV, A. M.—TOMILIN, I. A.—KUZNETSOV, V. N.—KULIK, T.: J. Alloys and Comp., *336,* 2002, p. 196.
[23] ATZMON, M.: Phys. Rev. Lett., *64,* 1990, p. 487.
[24] CORENO-ALONSO, O.—CABANAS-MORENO, J. G.—CRUZ-RIVERA, J. J.: Mater. Sci. Forum, *7,* 2000, p. 290.
[25] COLGAN, E. G.—NASTASI, M.—MAYER, J. W.: J. Appl. Phys., *58,* 1985, p. 4125.

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