The application of a modern Powder Metallurgy route, mechanical alloying, to powdered nanocrystalline NiAl obtaining is investigated. The compound synthesis from components via reactive mechanical alloying occurred in ~6 hours, while for crystal grains refining to ~10 nm the subsequent mechanical disordering process had to be extended to 36–48 hours.

Key words: nanocrystalline materials, intermetallics, nanocrystalline nickel aluminide.

1. INTRODUCTION

Intermetallic compounds, especially aluminides, have emerged as materials with very attractive properties for applications at high temperatures and/or severe oxidation and/or corrosion conditions. They became serious candidates for superalloys replacing in structural components [1] and have already been applied as protective coatings, of a higher corrosion resistance, even on superalloys [2]. Among them, NiAl, is of a high interest due to its favorable property/cost ratio [3].

However, as in the case of other intermetallics, NiAl applications are still limited, among others, by the high brightness and low ductility exhibited at ambient temperature, determined by the high order and low symmetry of its crystal lattice (only 3 slip systems), and by the low grain boundary cohesive force [3].

The methods to overcome these drawbacks have in view to activate a greater number of slip systems and make slip easier. The most attempts were made, up to day, to realize these by alloying with elements able to modify the NiAl slip systems (Fe, Cr, Mn, V, Ti, Nb, Zr), and to increase the grain boundary cohesive strength (B) [3]. But, alloying proved to reduce, to a certain extent, the NiAl corrosion resistance [4]. The compound obtaining in a nanocrystalline state seems to be more favorable as it introduces a great disorder into the crystal
lattice without the aid of other elements. However, only particular aspects of this method have been published, in spite of the large interest manifested today for nanomaterials [5].

The present paper has as purpose even to fill this gap.

2. FUNDAMENTAL CONSIDERATIONS

Nanocrystalline materials exhibit unique mechanical properties, different from those of conventional coarse-grained polycrystalline ones. This is determined especially by the effects of the broad grain boundaries, whose volume fraction rapidly grows with the grain refinement. The randomly distributed atoms from grain boundaries act as obstacles for dislocation slip and, at the same time, open up several specific deformation mechanisms that usually are not significant in coarse-grained polycrystalline materials: diffusional grain boundary creep, triple junction diffusional creep, rotational grain boundaries blocks movement and grain boundaries sliding [6]. As a result, the grain refinement causes switching between conventional slip deformation to these mechanisms. Their high effectiveness and crystal grains refinement determines extensive deformation rates, \( \frac{d\varepsilon}{dt} \), of nanocrystalline materials, as results from expression:

\[
\frac{d\varepsilon}{dt} = \frac{\sigma \cdot \Omega}{d^2} \cdot k \cdot T \cdot \left( B_1 \cdot D_v + B_2 \cdot \Delta D_b / d \right)
\]

(1)

where \( \sigma \) is the applied stress, \( \Omega \) – the atomic volume, \( d \) – the grain size, \( k \) – the Boltzmann constant, \( T \) – the temperature, \( D_v \) and \( D_b \) – the volume and grain boundary diffusion coefficients respectively, \( \Delta \) – the grain boundary width, \( B_1 \) and \( B_2 \) – constants [7]. At ambient temperature, \( D_v = 0 \), resulting:

\[
\frac{d\varepsilon}{dt} = \frac{\sigma \cdot C \cdot \Delta D_b / d^3 \cdot k \cdot T}{d^2}
\]

(2)

where \( D_b \) and \( \Delta \), as has been stated above, are much higher while \( d \) is much smaller than of common materials, determining much higher values of \( d\varepsilon/dt \).

A certain yield strength increasing results too from the Hall-Pech relation:

\[
\sigma_y = \sigma_0 + k_{HF} \cdot d^{-1/2}
\]

(3)

where \( \sigma_0 \) is the yield strength of a perfect single crystal and \( k_{HF} \) a constant, even if this relation is not entirely valid in nanomaterials [7].

However, nanocrystalline NiAl in a bulk form is difficult to be directly produced [1]. It can be quite easily obtained as a powder, instead, by Powder Metallurgy (P/M) routes. From this very reactive powder, bulk nanocrystalline material can be obtained too by P/M routes [8].

There are several methods for NiAl nanocrystalline powder producing [1]. From the practical point of view, the most favorable seem to be those involving
the compound reactive synthesis, as follows: i) bulk NiAl compound of normal crystal grains synthesis by SHS and its crystal grains refining through Mechanical Disordering (MD) by the high energy ball milling; ii) direct nanocrystalline NiAl obtaining by a combined Reactive Mechanical Alloying (RMA) and MD. Even if the first method has been applied with good results [9] as SHS is very advantageous from the energetic point of view, the second one seems to be even more efficient as it joins together the two mentioned steps into only one process – Mechanical Alloying (MA). Its application to powdered nanocrystalline NiAl producing is studied in this paper.

In the nanocrystalline materials obtaining by Mechanical Alloying, due to the extensive deformation, the internal energy of the particle lattice increases and, consequently, their reactivity increases leading to the ignition temperature of the possible reactions between the system constituents, $T_{ig} \gamma$, decreasing (curve a, Fig. 1). At the same time, the system temperature increases due to the collision energy partial transformation in heat (curves b and c). Pure alloys/solid solutions of an extended solubility limit are obtained by the true MA if components does not react together, or if the reached temperature is too less for a possible reaction ignition (curve c). Intermetallics/other compounds are formed if components reacts each-other {Reactive MA (RMA)} or with the milling atmosphere {Reactive Milling (RM)} – if $T_{ig} \gamma$ is reached (curve b). Amorphous/nanocrystalline materials are obtained by MD for an enough long MA [8].

![Fig. 1. – Ignition and particle temperature variation vs. MA time [8].](image)

M/P processing of nanocrystalline compounds starting from components implies RMA and MD. For RMA, the components should react each-other and, therefore, the value of Standard Gibbs Free Energy of formation / reaction, $\Delta G_{f/r}^0$, should be negative [10].

### 3. EXPERIMENTAL PROCEDURE

To establish the NiAl thermodynamic both possibility of synthesis and stability, the $\Delta G_{f/r}^0$ values for the possible reactions/compounds formation in
the Ni-Al system have been calculated and plotted vs. temperature up to their melting points, with a step of 100 [K], using the known formula:

\[
\Delta G_{f,r,T} = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_p \cdot dT - T \cdot \left( \Delta S_{298}^0 + \int_{298}^{T} \Delta C_p / T \cdot dT \right)
\]

where \( \Delta H_{298}^0 / \Delta S_{298}^0 \) are the enthalpy/entropy of compound formation and \( \Delta C_p \) - heat capacity change of reactants to products, all taken from the literature [10].

For NiAl elaboration, atomized aluminum powder and carbonyl nickel of purities of 99.5 [%wt.], respectively 99.85 [%], and a particle size of (–71 ÷ +63), respectively –15 [μm] were used. A Ni-Al powder mixture of 1:1 atomic ratio was realized by blending for 3 hours in a Turbulla blender. The (RMA+MD) process was performed in a planetary ball mill, with the absolute rotation speed of 90 rot/min and the vial one of 150 rot/min. The ball/powder ratio was 10:1 and that of vial volume occupancy of ~1/3. At selected times, a sample of powder was taken off from the vial and analyzed by SEM and XRD for the morphological evolution of powder particles observation, phase identification and grain size calculation.

4. RESULTS AND DISCUSSION

The variation with temperature of the calculated values of \( \Delta G_{f}^0 \) of the possible reactions between components is presented in Fig. 2. As can be seen, the NiAl direct formation does not have the lowest value of \( \Delta G_{f}^0 \) among the Ni aluminides. However, as it was started from Ni-Al powder mixture of 1:1 stoichiometric ratio, the formed intermediates (NiAl₃, Ni₂Al₃ and Ni₃Al), further react with the excess of Al/Ni forming NiAl, the corresponding reactions having too negative values of \( \Delta G_{f}^0 \). So, for a NiAl stoichiometric composition, always NiAl results as the final product.

XRD analysis confirmed this thermodynamic prediction. It has shown that, for 6 h RMA time, the distinct peaks of Ni and Al from XRD pattern disappeared and a new phase formed, identified as being, as it was expected, NiAl. For the lack of space, here is given only the XRD pattern for 48 h MA time (Fig. 3), representative for diffraction lines broadening determined by the crystal grains refinement at enough long MA times [11]. The same NiAl diffraction lines can be distinguished on it, some of them quite completely flattened due to the broadening effect.

The powder particles morphological evolution during RMA and MD is presented in SEM images from Fig. 4. As can be seen, initially (Fig. 4a), the powder mixture consists, corresponding to the used powders, of quite large
atomized Al particles and much smaller Ni carbonyl ones. After 1 hour of milling (b), a beginning of Al particles flattening and a better homogenization can be observed, while for 2 milling hours (c) a pronounced particles coarsening by cold welding and flattening by plastic deformation occurred. For 3 hours of milling, a
complete Al flattening and Ni penetration into the as formed thin foils – forming an intimate mixture – is highlighted in micrograph d. Only several small, isolated, Ni particles can be still observed at a higher magnification (e). After 6 h of milling instead (f), the SEM image clearly shows a conglomerate of very small particles, indicating the formation of a new phase. This is in good agreement with the above-mentioned result of the XRD analysis, indicating the NiAl formation after a 6 hour RMA time. For MA time increasing up to 12 h, during MD these conglomerates are progressively divided in smaller ones (<20 [µm]), in which even finer particles of a crystalline shape can be observed.
For the crystal grain size evolution with MA (RMA+MD) time, their dimensions have been calculated by the Sherrer’s formula [11] using the broadening of the diffraction lines at their half maximum values (FWHM), determined by the diffractometer facilities. As standard has been adopted the value of the line broad corresponding to the obtained NiAl at 6 hours of milling, in an annealed state (600°C, 60 min). Only peaks of Ni (111) and Al (200) for 0 to 3 hours MA and of NiAl (110) for 6 to 48 hours MA, having quite the same diffraction angle, have been considered for this purpose (Fig. 5). As can be seen, really, as MA time increases their notable broadening occurs. The variation of the calculated crystal sizes vs. (RMA+MD) time is presented in Fig. 6. The discontinuity in crystal grains decreasing at 6 ÷ 8 hours of MA is, certainly, determined by the NiAl formation. For longer MA times, only a MD process occurred leading to a further grains refinement but much slowly, the final grain size being of ~10 [nm].

4. CONCLUSIONS

Powdered nanocrystalline intermetallics in general and NiAl in special can be successfully and in advantageous both technical and economical conditions
processed by MA starting from powdered components. For a reasonable MA
time, depending upon the processing conditions, the compound synthesis occurs
by RMA and its crystal grains are subsequently refined by MD to nanometric
sizes.

REFERENCES
2. Y. Zhang *et. al.*, Synthesis and cyclic oxidation behavior of a NiAl coating on a Ni-base
9. M. Lucaci *et. al.*, Self propagation high temperature synthesis of NiAl intermetallic compound,