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# NiAl/$Ni_3Al$ – $Al_2O_3$ COMPOSITE FORMATION BY REACTIVE BALL MILLING

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It has been presented that the bulk mechanical alloying occurring in the Ni-hydroxycarbonate–aluminium mixture can produce homogeneously refined composite of nickel aluminides with aluminium oxide. The control of mechanochemical phenomenon was carried out by phase identification of milling products as well as their structural and morphological characterization. As a result the thermoanalytical and X-ray powder diffraction measurements as well as scanning electron microscopy with backscattered electron images (BSE) and X-ray energy dispersive spectroscopy (EDS) were applied. It was found that the kinetics of mechanochemical reactions depends on the chemical nature of initial salt.

***Keywords:*** *aluminides, aluminium, high-energy ball milling, in situ reactions, mechanical alloying, nanocomposite, Ni-Al intermetallics, Ni-hydroxycarbonate*

## Introduction

Research over the last two decades has led to the emergence of intermetallics, a new class of engineering materials with numerous attractive properties, that include high oxidation and corrosion resistance as well as relatively low densities combined with their ability to retain strength and stiffness at high temperatures. Intermetallics are one of the most important group of nanostructured compounds [1–3]. Among the processing methods to synthesize 'in situ' nanophase materials, room temperature high-energy ball milling appeared to be attractive for potential large-scale economical production. Thus, the mechanical treatment allows formation of alloys, which is difficult to obtain by conventional solidification methods due to phase equilibrium constraints, as in the case of Ti–Al alloys formation [4]. Furthermore, this technique is universal for obtaining alloys with metastable structures and compositions [5].

Nickel aluminides are examples of intermetallics which typically work at elevated temperatures [6–9]. Intermetallics of the nickel–aluminium system existing in the composition region 40–75 at.% (see: phase diagram in Fig. 1) are of interest due to their properties [10], in particular $Ni_3Al$ and NiAl phases. Thus, $Ni_3Al$ phase is a structural alloy used as a strengthening phase in most superalloys. The $Ni_3Al$ – based alloys were the first intermetallic alloys fully commercialized. Such alloys have a remarkable resistance to carburizing making them an ideal choice for equipment operating in carburizing furnace [6]. However, NiAl has emerged as a possible high-temperature structural material due to its low density, high melting temperature, good thermal conductivity and excellent oxidation resistance. In factories they are used as transfer rolls, heat-treating trays, die blocks, nuts and bolts and corrosion resistance tool bits. These special features of nickel aluminides result from their structures [10–12].

The literature data shows several examples of mechanically synthesized nickel aluminides as well

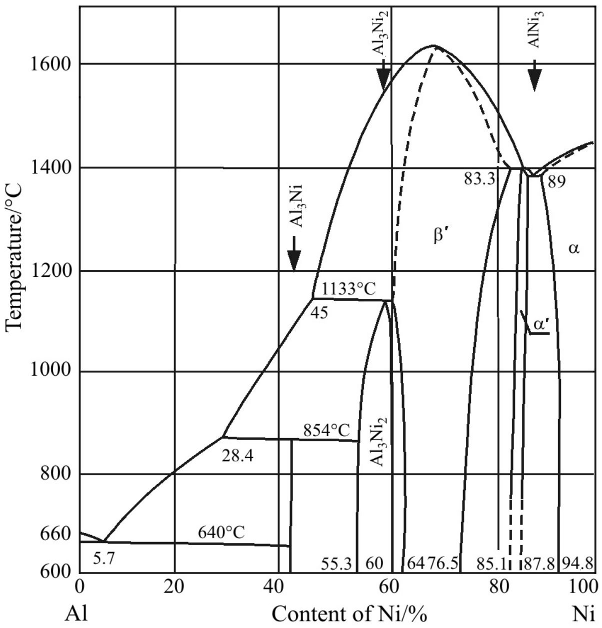

**Fig. 1** Phase diagram of Ni–Al binary system [10]

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as composites of Ni–Al intermetallics with different oxides [13–16]. Portnoy *et al*. [17] described mechanical alloying of nickel aluminides from pure metals performed in a vibratory ball mill in argon. It was shown that the product of mechanical alloying depends on the initial composition of milled mixture. Thus, milling of the mixture containing 40–61 at.% Ni brings about the formation of NiAl phase through a direct exothermic reaction without formation of any intermediate solid solution. However, alloying provided in the system with 65–85 at.% of Ni involved solid solution Ni(Al) formation characterized by nanocrystalline structure. Furthermore, it was shown that the product is always a single phase with the minimum Gibbs energy.

In comparison to the mechanical alloying of Ni–Al phase, self-propagating high-temperature synthesis (SHS) realized classically by thermal ignition was tested by Biswas *et al*. [18]. In general, occurrence of the SHS reaction depends on the ignition temperature, which is typical for the reactant mixture. Iltin *et al*. [19] showed that the combustion temperature of a mixture of nickel and aluminium powder is 1600–1700 K and a substantial decrease of such ignition temperature can be achieved by applying the initial mechanical activation of alloyed powders. Then the SHS reaction in the system Ni–Al starts at the temperature 800–900 K [20, 21].

Formation of nickel aluminides – aluminium oxide composite was observed recently [22] during reactive ball milling in the system of nickel oxide and aluminium. Activation process was performed in a shaker/mill apparatus with a ball/material mass ratio of 4:1. The formation of $Ni_3Al$ phase occurs according to the following reaction (1).

$$3Ni_2O_3 + 8Al \rightarrow 2Ni_3Al + 3Al_2O_3 \qquad (1)$$

'In situ' formation of composite with both phases is a consequence of an exothermic reaction process that occurs after induction time.

Another example of NiAl phase strengthened by $Y_2O_3$ and applied as a composite ODS (oxide dispersion strengthened) was performed by Grahle *et al*. [23]. In contrast to the above cases two-step preparation route was required. Initial powders of Ni and Al were blended in two proportions: Ni–13.3 mass% Al forming $Ni_3Al$ and Ni–50 mass% Al forming $Ni_2Al_3$ and $NiAl_3$ phases. This was followed by reinforcement –$Y_2O_3$ addition. The syntheses were performed using a centrifugal vibratory ball mill under vacuum. ODS–NiAl in powder form of a submicrometer and nanocrystalline sized was obtained.

Olszówka-Myalska [24] obtained a composite consisting of aluminium matrix/nickel aluminide by mechanical treatment of aluminium, nickel and aluminium oxide powders using a Fritsch mill. This metal matrix composite (MMCs) revealed a lamellar structure.

The purpose of this study was to determine the possibility of nickel aluminides formation during mechanical treatment of Ni-hydroxycarbonate – Al system. The choice of initial components was based on our previous results of $CuAl_2$–$Cu_9Al_4$/$Al_2O_3$ nanocomposite formation during several minutes in Cu-hydroxycarbonate–Al system [25–27].

## Experimental

### *Materials and apparatus*

Ni-hydroxycarbonate in a hydrated form, $Ni_2(OH)_2CO_3\cdot 3H_2O$, and aluminium powder (99.9% purity) as commercial reagents were used. The two-component (salt-metal) system, $Ni_2(OH)_2CO_3\cdot 3H_2O$–Al°, was prepared as a physical mixture at a molar ratio of NiO:Al=1:1.

A laboratory planetary mill with balls and milling container made of hardened steel was used. The mass proportion of balls to sample was of 14:1. The two milling vials were rotated at 1130 rpm. Alloying was carried out in air for several minutes at room temperature and atmospheric pressure in order to allow comparison of results of the $Cu_2(OH)_2CO_3$ –Al system under the same conditions [25–27].

### *Equipment and methods of phase identification*

X-ray powder diffraction patterns were obtained using a Philips X'Pert Diffractometer ($CuK_\alpha$) in the $2\theta$ range of 10–60°.

Thermoanalytical measurement was made in argon up to 1000°C using a SDT 2960 TA Instrument with a heating rate of 24 K $min^{-1}$.

A Hitachi S-4700 instrument (SEM) equipped with energy dispersive X-ray spectrometer was used for microstructural examination and elemental microanalysis. Atomic number contrast was observed from the polished cross-sectioned samples. Specimens were carbon-coated to obtain electrical conductivity. The BSE imaging and EDX elemental analyses were performed at an electron beam voltage of 20 kV.

## Results and discussion

### *Formation of nickel aluminides with $Al_2O_3$*

Formation of nickel aluminides in the system of Ni-hydroxycarbonate – aluminium is possible if two metallic phases are present in the milled system. Aluminium, the initial reagent component of the treated mixture should be present in sufficient amounts [28].

**Table 1** The phases which can be formed during mechanical alloying of $Ni_2(OH)_2CO_3 \cdot 3H_2O$-Al system

| Compound | Elemental concentration/ % (m/m) – calculated | | | | | ANF value | BSE grey tone levels |
|---|---|---|---|---|---|---|---|
| | Ni | Al | O | C | H | | |
| Ni | 100 | 0 | 0 | 0 | 0 | 28.0 | v. bright |
| $Ni_3Al$ | 86.7 | 13.3 | 0 | 0 | 0 | 26.6 | |
| $Ni_3Al_5$ | 78.4 | 21.6 | 0 | 0 | 0 | 24.8 | |
| NiO | 78.6 | 0 | 21.4 | 0 | 0 | 23.7 | |
| NiAl | 68.6 | 31.4 | 0 | 0 | 0 | 23.3 | |
| $Ni_2Al_3$ | 59.3 | 40.7 | 0 | 0 | 0 | 21.9 | ↓↑ |
| $NiAl_3$ | 42.1 | 57.9 | 0 | 0 | 0 | 19.3 | |
| $Ni_2(OH)_2CO_3$ | 55.5 | 0 | 37.8 | 5.4 | 0.9 | 18.9 | |
| $Ni_2(OH)_2CO_3 \cdot 3H_2O$ | 44.2 | 0 | 48.2 | 4.5 | 3.0 | 16.5 | |
| Al | 0 | 100 | 0 | 0 | 0 | 13.0 | |
| $Al_2O_3$ | 0 | 52.9 | 47.1 | 0 | 0 | 10.6 | v.dark |

Nickel forms as a result of two reactions: mechanical decomposition of hydroxysalts–Eq. (1), and aluminothermic reduction of nickel oxide –Eq.(2).

$$Ni_2(OH)_2CO_3 \rightarrow 2NiO+CO_2+H_2O \quad (1)$$

$$3NiO+2Al \rightarrow 3Ni+Al_2O_3 \quad (2)$$

$$x\text{Ni}+\text{Al} \rightarrow \text{Ni}_x\text{Al} \text{ (where } x=1 \text{ or } 3). \quad (3)$$

These two metals may then combine to intermetallic phases of NiAl and $Ni_3Al$ –Eq.(3) forming nickel aluminides with alumina composite in the treated system.

Reaction (2) is a typical self-propagating high temperature synthesis (SHS) with ignition occurring after the critical time of mechanical activation. During this time treated materials reach 'an active state' through creation of structural defects and formation of ‘fresh surfaces’. Then, the temperature in the milling vials increases abruptly indicating the occurrence of the SHS reaction.

### *XRD analysis*

The X-ray powder diffraction patterns shown in Fig. 2 indicate formation of the qualitative phase composition of the mechanically activated mixtures of Ni-hydroxycarbonate with aluminium. The presence of intermetallic phases was confirmed. It may suggest that few minutes of milling are sufficient for the initiation of alloy formation in the studied system. NiAl and $Ni_3Al$ phases are detectable in a broad peak in the range of 2θ (42–45°). The low intensity of this peak indicates the weak crystallinity of phases undergoing mechanical action. The lack of the peaks for Ni-hydroxycarbonate indicates full decomposition of the salt during milling or its amorphous form. It can be assumed that $Al_2O_3$ appeared in low crystalline form.

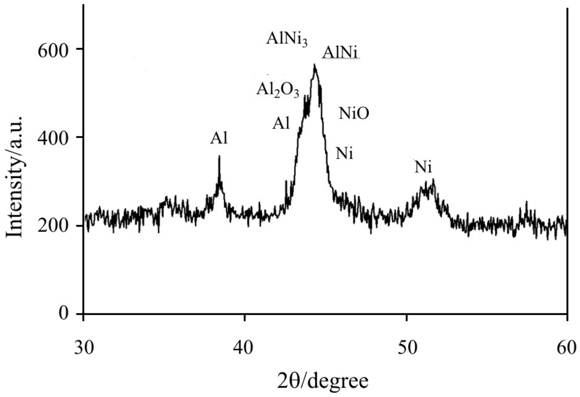

**Fig. 2** X-ray diffraction patterns of $Ni_2(OH)_2CO_3 \cdot 3H_2O$–Al mixture after mechanical alloying for several minutes

### *Thermal analysis*

Thermoanalytical measurement appeared to be versatile for phase characteristics of milling products. The course of TG–DTA curves in Fig. 3 confirmed the presence of Ni-hydroxycarbonate in milling products because of the thermal decomposition of mechanically undecomposed part of $Ni_2(OH)_2CO_3$ up to 350°C.

The decomposition degree of salt in mixture of $Ni_2(OH)_2CO_3$–Al after 15 min of milling was equal 80%. It is important to note that at the time of milling Cu-hydroxycarbonate decomposes completely [25–27]. However, the milling of $Ni_2(OH)_2CO_3$ without addition of Al results in only 8% of decomposition [28], in contrast to $Cu_2(OH)_2CO_3$, which decomposes in about 65%. The possible difficulty in activation of Ni-salt is the presence of crystalline water since water can stabilize the structure of compound. Active reagent such as aluminium facilitates the dehydration as well as its decomposition to oxide.

**Table 2** Results of the EDX microanalysis for area (Fig. 4) of mechanically alloyed $Ni_2(OH)_2CO_3{\cdot}3H_2O$–Al mixture

| Fig. 4, point | Elemental concentration/ % (m/m) - measured | | | | ANF value |
|---|---|---|---|---|---|
| | Ni | Al | O | (Fe) | |
| a | 73.90 | 21.27 | 4.03 | (0.79) | 24.0 |
| b | 62.78 | 33.08 | 2.91 | (1.23) | 22.4 |

**Table 3** Results of the EDX microanalysis for area (Fig.6) of mechanically alloyed $Ni_2(OH)_2CO_3{\cdot}3H_2O$-Al mixture

| Fig. 6, point | Elemental concentration/ % (m/m) - measured | | | | ANF value |
|---|---|---|---|---|---|
| | Ni | Al | O | (Fe) | |
| a | 31.46 | 38.80 | 24.86 | (4.87) | 17.1 |
| b | 50.93 | 29.60 | 16.47 | (2.99) | 20.2 |

Furthermore, one can observe the strong exothermic effect at the temperature of about 620°C corresponding to the high-heat emission that results from aluminothermic reaction between NiO and Al initiated thermally during the experiment.

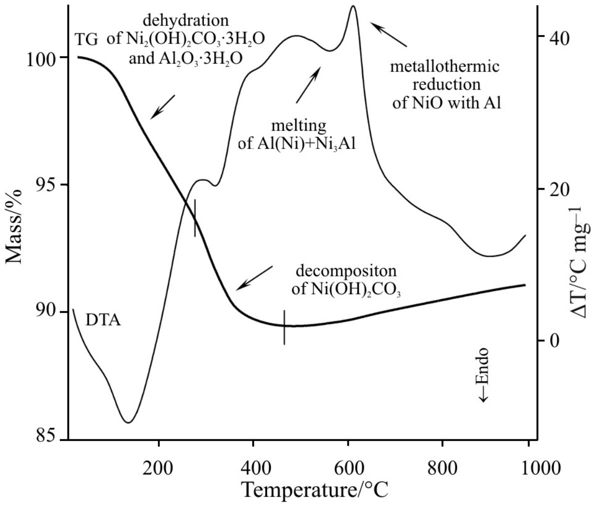

**Fig. 3** TG – DTA curves of $Ni_2(OH)_2CO_3{\cdot}3H_2O$-Al mixture (in inert atmosphere) after mechanical alloying for several minutes

## *SEM analysis*

Scanning electron microscopy (SEM) with the backscattered electron (BSE) imaging and quantitative energy dispersive X-ray microanalysis (EDS) of Ni, Al, O and C were used for analysis of the composition and microstructure of composite formed during mechanical alloying of the $Ni_2(OH)_2CO_3{\cdot}3H_2O$–Al system.

The BSE images being sensitive to changes in the mean atomic number (ANF) of the sample indicate variations in grey levels associaed with different phases. The probable phases present in the composite with their ANF values are shown in Table 1. The brightest areas include phases characterised by the highest ANF values as seen in nickel and $Ni_3Al$ phases while the darker contain phases with lower ANF as indicated by Al and $Al_2O_3$. Therefore, the simultaneous information obtained from the BSE signals and EDS elemental microanalysis can be used for estimation and localization of the phases observed on the scanning electron microscopy.

The typical microstructure of the mechanically alloyed of $Ni_2(OH)_2CO_3{\cdot}3H_2O$–Al system for 15 min is shown in Fig. 4. The variation of grey tone levels indicates the strong differentiation in phases present in the activated mixture. The correlation between BSE image and the results of EDS analysis of point a – indicates possible presence of nickel in this area while in the point b – NiAl intermetallics. The results of EDS analysis are shown in Table 2.

In contrast to the multiphase character of area in Fig. 4, the microphotograph in Fig. 5 shows only one phase, Ni-hydroxycarbonate. The large grain of such phases reveals the presence of large fractures, probably formed during the collisions with milling balls.

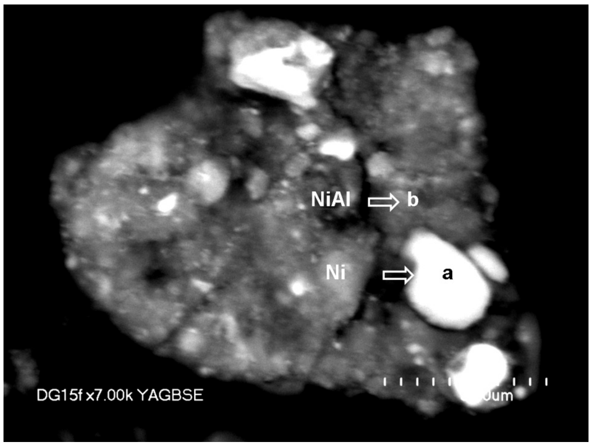

**Fig. 4** SEM microphotographs of mechanically alloyed $Ni_2(OH)_2CO_3{\cdot}3H_2O$-Al mixture shows a – Ni and b – NiAl

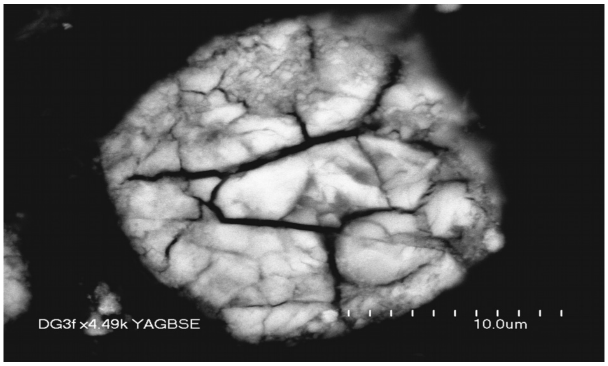

**Fig. 5** SEM microphotographs of mechanically alloyed $Ni_2(OH)_2CO_3{\cdot}3H_2O$–Al mixture shows the grain of $Ni_2(OH)_2CO_3{\cdot}3H_2O$

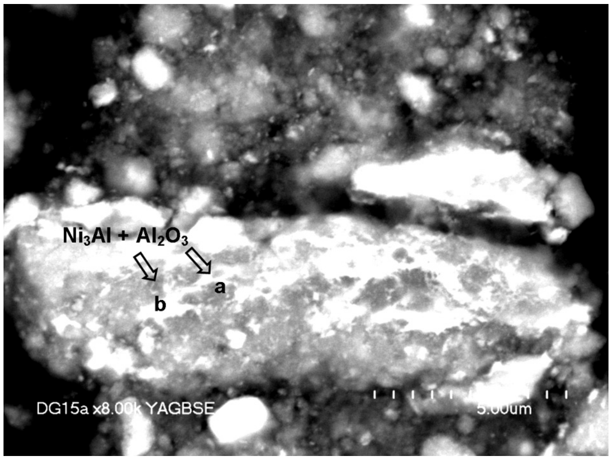

**Fig. 6** SEM microphotographs of mechanically alloyed $Ni_2(OH)_2CO_3{\cdot}3H_2O$–Al mixture shows the beginning of lamellar structure of NiAl/$Ni_3Al$ – $Al_2O_3$ composite formation. The darker network corresponds to higher amount of $Al_2O_3$, the brighter one – to higher content of intermetallics

The microstructure of the composite shown in Fig.6 is typical for only few regions. As we can see materials reveal higher value of homogeneity than those in Fig. 5. From the EDS analysis and BSE images one can assume that the areas marked a) and b) indicate presence of the mixture of $Ni_3Al$ and $Al_2O_3$. The darker grey tone level of point a) is the result of higher content of $Al_2O_3$. Typical for this microphotograph is a very bright grey tone level of many places, which are surrounded by darker network. This indicates the lamellar morphology of composite of intermetallic phase with aluminium oxide.

## Conclusions

Mechanical alloying of the Ni-hydroxycarbonate-aluminium mixture involves formation of a nanocomposite composed of intermetallic phases – NiAl and $Ni_3Al$ and aluminium oxide. Such phases are the result of mechanical decomposition of Ni-salt, aluminothermic reduction of Ni-oxide and mechanical alloying of Al with Ni. Therefore, the mechanism of the intermetallics formation is the same as described earlier in the case of the copper hydroxycarbonate–aluminium system [25–27]. However, the kinetics of mechanochemical reactions described above under the same milling conditions differs in comparison to the $Cu_2(OH)_2CO_3$–Al system. After few minutes of mechanical treatment the Ni–Al intermetallics formation is only initiated because the mechanical decomposition of salt is not complete and both Ni and Al are not fully synthesized.

- Summing up, the kinetics limitations are influenced by :
- difficulties with $Ni_2(OH)_2CO_3$ decomposition due to the hydrated form of this salt;
- aluminothermic reduction of NiO is more difficult to achieve than that of CuO due to its higher enthalpy formation [29] as well as the dilution effect of the reactants, NiO and Al, because of the low decomposition degree of salt.

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