

# The effect of atmosphere on reactions in Ni-Al green compacts subjected to thermal treatment in argon and air

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## Abstract

The effect of atmosphere on microstructure and formation of new phases during the reaction synthesis in Ni-Al green compacts was studied. The green bodies were prepared by uniaxial double action compression of Ni + 34 vol.% Al powders. The reactions in compacts during their heating to 660 °C and isothermal exposure for 8 h at 800 °C in air and argon atmospheres were monitored by DTA. Weight increase of oxidized samples determined by TG curves followed parabolic behaviour. This agrees with a diffusive character of thermal oxidation of metals. Heating in argon revealed the strong exothermic reaction represented by a sharp peak in DTA curve close to the melting temperature of Al. The exothermic reaction in the air takes place as well, however, it is spread over a wider temperature interval. Microstructures of samples were analysed by SEM, EDS and XRD. After 8 h of isothermal exposure at 800 °C in argon Ni<sub>3</sub>Al and NiAl intermetallic phases appeared whereas after the thermal treatment in air NiO and NiAl phases were predominantly formed. The unreacted Ni was determined after both types of treatments as well. The analysis of the compacts revealed that the applied thermal treatment in the air significantly improved the interparticle bonding providing thus the required structural integrity of Ni-Al compacts.

**Key words:** oxidation, nickel aluminides, metal matrix composites, reactive synthesis, differential thermal analysis, thermogravimetric analysis

## 1. Introduction

One of the perspective methods for preparing materials for high temperature applications and large-scale production is the reaction synthesis of powder mixtures whereby reactants are transformed to products in an exothermic reaction. The advantages of the “pressure-less” reaction synthesis (i.e., process which is not subjected to an externally applied pressure) involve the low processing temperature (in turn, low energy process), short processing time, the use of low cost equipment, and the formation of pure products [1]. The main disadvantages of this process refer to limited possibilities of reactions control after ignition temperature is exceeded. A significant amount of work

has been published on the reaction synthesis of nickel aluminides including combustive synthesis, thermal explosive and self-propagating high-temperature synthesis [1–3].

Different nickel aluminides formed by reaction synthesis depend mainly on initial relation of both powders [4]. The process described in the literature consists of cold pressing of powder mixture to produce a compact which is then heated in an inert atmosphere to the reaction temperature (usually above the eutectic temperature of 640 °C).

Reactions synthesis of aluminides from powder mixture in oxygen containing atmosphere causes some difficulties with managing reaction condition. In this case both types of reactions – oxidation of Ni and

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Al powders and aluminide formation can run simultaneously. The formed intermetallics can also oxidize, but on the surface of NiAl and Ni<sub>3</sub>Al at the temperature up to 800 °C only thin oxide layer is formed [4]. Haering and Hofmann [5] described the oxidation behaviour of Ni<sub>3</sub>Al in the temperature range 500–700 °C as complex processes at which initially both NiO and Al<sub>2</sub>O<sub>3</sub> grow through cation outward diffusion. Simultaneously, oxygen migrates into the alloy. Due to the lower growth rate of Al<sub>2</sub>O<sub>3</sub> as compared to NiO, Al<sub>2</sub>O<sub>3</sub> is covered by NiO. Dong et al. [6] sintered Ni + 50 at.% Al powder mixture in vacuum and the XRD spectrum confirms the formation of NiAl phase only. After oxidation in air at 800 °C during 160 h only very small peaks of Al<sub>2</sub>O<sub>3</sub> and Ni<sub>3</sub>Al were obtained. Selective oxidation of discontinuously deposited Ni on Al powders were studied by Vummidi et al. [7]. The weight increase of sample during oxidation to 525 °C was about 1.4 % and only NiO and Al (no metallic Ni) were detected by XRD analysis.

The oxidation reactions of pure Ni powder start at relatively low temperatures resulting in the growth of the oxide film on individual particles. The oxidation of nickel particles of various sizes in the temperature range between 250 and 350 °C can be described by diffusion-controlled mechanisms [8]. It has been shown that during the thermal oxidation of metal powders, interconnected particles tend to agglomerate and intergranular connections are often strong. In most cases the agglomeration is harmful and not desired. However, in the past this phenomenon received a special interest and several studies about the oxidation kinetics of either partially compacted metal powders or porous metallic materials appeared [9–12].

Ni + Al reactions are exothermic in nature and often quite intense. Typically, as the volume of sample grows, the extent of reaction grows extensively. This leads to detrimental effects like cracking or even disintegration of green powder compacts, melting of crucibles, etc. Therefore, means with the potential of limiting the intensity of mutual reaction is highly desired. The aim of this work was to study the effect of atmosphere on the course of reaction synthesis in Ni + Al system.

## 2. Experimental material and methods

Commercially available Ni powder with particle size < 75 µm (purity 99.5 %) and Al powder 1050 with particle size < 45 µm (purity 99.7 %) were used in this study. Both types of powders were turbula mixed for 30 min in air to give an Ni + Al mixture with 34 vol.% Al. Ni-Al green compacts with the diameter of 30 mm and the height of 8 mm were prepared at room temperature by an uniaxial double action compression method applying the pressure of 500 MPa.

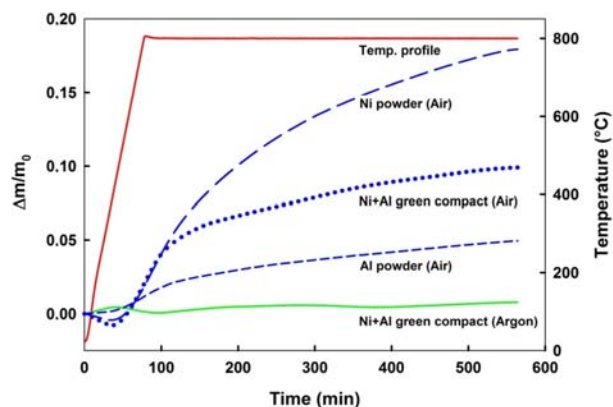


Fig. 1. Time dependent temperature profile and mass change recorded during the heating and isothermal exposure of Ni and Al powders in air as well as Ni-Al green compacts in air and argon atmospheres.

STA device Linseis LV75VS was employed for the thermal treatment of Ni and Al powders as well as Ni-Al green compacts either in air or in protective Ar atmosphere. Thermal treatment consisted of heating at the rate of 10 K min<sup>-1</sup>, up to the temperature of 800 °C followed by isothermal exposure for 8 h. Concurrently, the thermogravimetric (TG) measurements and differential thermal analysis (DTA) were performed using the powder samples with total weight of 150 mg. The alumina powder standard was used for a method validation.

The structure and chemical composition of samples were studied by scanning electron microscopy (SEM) using JSM Jeol 6610 microscope. Energy dispersive X-ray spectroscopy (EDX) was used for chemical analysis using X-Max detector (Oxford Instruments). XRD measurements were performed in Bragg-Brentano geometry using Cr K $\alpha$  radiation on a Bruker D8 Advance equipped with a linear detector and incident beam shaping aperture due to limited sample size. The lattice parameters were calculated from the angular positions of all available X-ray diffraction peaks by linear extrapolation, using least squares fitting (Cullity and Stock, 2001) as well as by total pattern analysis using Bruker TOPAS software (Bruker, 2005) with the accuracy better than  $\pm 0.0003$  nm.

## 3. Results

### 3.1. TG and DTA measurements

Time dependent TG curves recorded during the heating and isothermal exposure of Ni and Al powders in air as well as Ni-Al green compacts in air and argon atmospheres are compared in Fig. 1.

The highest mass increase was recorded for Ni powder (approx. 20 %) followed by Ni-Al green com-

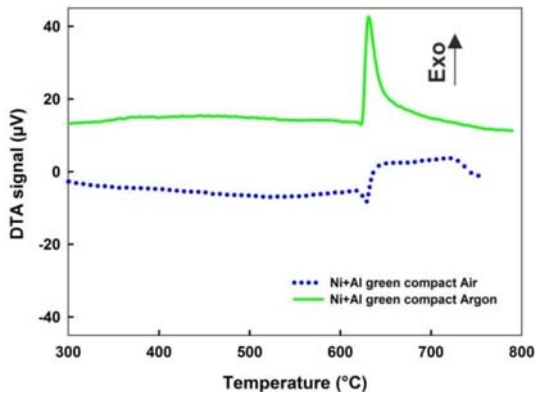


Fig. 2. DTA curves revealing the different course of reaction during heating of Ni-Al green compacts in argon and air.

compact (approx. 10 %) and Al powder (approx. 5 %) in air. The mass increase in argon was negligible.

To establish the kinetics of the oxidation process TG curves were fitted to a parabolic equation. The evolution of the square of the normalized weight gain over time was fitted by linear curve for all powder

samples (for Ni powder sample  $R^2 = 0.980$ , for Al powder sample  $R^2 = 0.951$ , and for Ni-Al powder sample  $R^2 = 0.966$ ). This clearly indicates that in all cases the weight gain clearly follows a parabolic behaviour, which agrees with a diffusive process occurring during the thermal oxidation.

The DTA curves recorded during the heating period of the thermal treatment are compared in Fig. 2. Both curves indicate the endothermic reaction with the onset at 618°C. The endothermic reaction is to be related to the melting of Al powders in the compact. However, the reaction in argon proceeds immediately with strong exothermic reaction represented by a sharp peak (625°C). The exothermic reaction in the air takes place as well, however, with some delay. Although the onset of the exothermic reaction is at 628°C, the reaction in this case is not restricted to particular temperature but is spread over a wider temperature interval.

### 3.2. Microstructural and XRD analysis

Microstructure of samples treated in argon and air

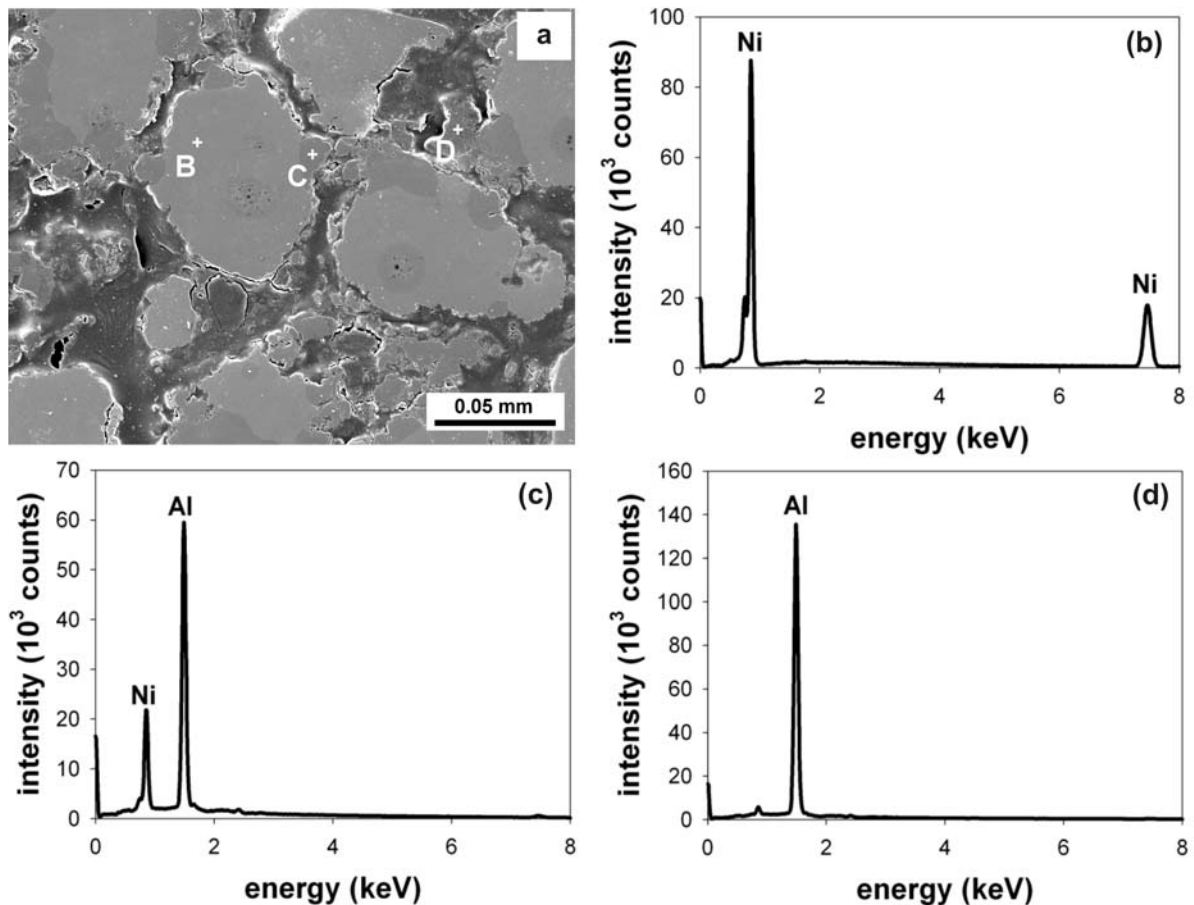


Fig. 3. Secondary electron micrograph of the microstructure of Ni-Al green compact as heated to 660°C in argon (a), EDX spectra corresponding to Ni in B (b), NiAl<sub>3</sub> in C (c) and Al in D (d).

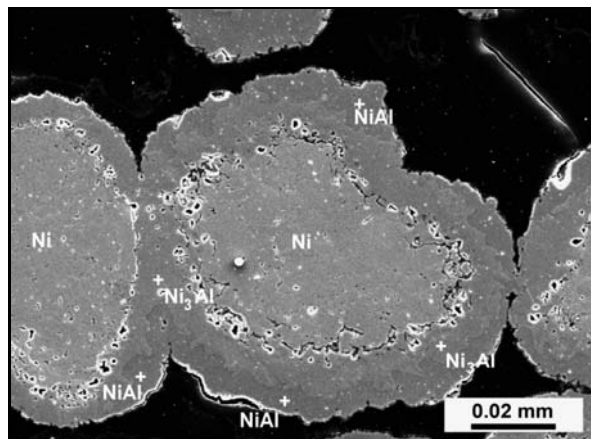


Fig. 4. Secondary electron micrograph of the microstructure of Ni-Al green compact as isothermally exposed for 8 h at 800 °C in argon.

has been analysed. In order to elucidate the factors responsible for the different course of the exothermic reactions the thermal treatment for some samples was interrupted at the temperature of 660 °C, i.e., immediately after reaching the exothermic peak. These microstructures were subsequently compared with those subjected to the whole thermal treatment, i.e., after 8 h of isothermal exposure at 800 °C.

Typical porous microstructure of the Ni-Al green compact as heated to 660 °C in argon is presented in Fig. 3. Due to the poor integrity of the sample, it had to be vacuum embedded into epoxy resin. Therefore the pores are not empty, but mostly filled.

The microstructure is formed by large Ni powders and intermetallic phases randomly distributed at the surface of Ni particles. The distribution is not homogeneous what reflects the fact that the mutual Ni – Al reaction took place preferably in locations where molten Al had been in contact with Ni particles. EDX + XRD analysis confirmed that the dominant intermetallic phase had been NiAl<sub>3</sub>. Pure Al had been recognized only rarely, indicating that the diffusion of Ni in molten Al was quite rapid. The diffusion of Al into solid Ni was not recognized.

The microstructure of Ni-Al green compact as exposed for 8 h at 800 °C in argon is different as shown in Fig. 4. It appeared that all aluminium had reacted and relatively thick intermetallic layer had been formed surrounding the Ni particles. XRD analysis (Fig. 5) confirmed that NiAl<sub>3</sub> phase did not appear any more. It was replaced by higher Ni content phases, particularly Ni<sub>3</sub>Al followed by NiAl. The composition of phases slightly differs in Al content decreasing towards the Ni particle. There are numerous small cracks and pores at the Ni-Ni<sub>3</sub>Al interface. They are formed due to redistribution of Ni taking part in the formation of Ni rich aluminides. NiAl phase with different Al contents was determined. The lattice parameter of NiAl

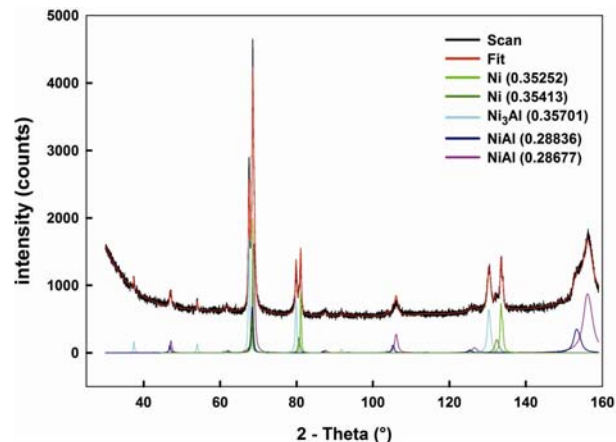


Fig. 5. XRD analysis of the structure of Ni-Al green compact as isothermally exposed for 8 h at 800 °C in argon with measured lattice parameters of phases in nm (in brackets).

is 0.2887 nm. Since this intermetallic compound can exist over a range of compositions, the parameter of this intermetallic compound has been shown to be strongly dependent on the stoichiometry within this wide single-phase region [13]. A maximum in the lattice parameter occurs at the stoichiometric composition. On the Ni-rich side, an increase in density and decrease in lattice parameter with increasing Ni content has been observed since Ni atoms are smaller than Al.

The analysis of the microstructure of the Ni-Al green compact (Fig. 6) as heated to 660 °C in air confirmed that two reactions, i.e., oxidation of Ni as well as Ni – Al mutual reaction had taken place. The EDX analysis revealed that locations with higher Al content appeared more frequently than if heated in argon. This indicates that nickel oxide hinders the formation of intermetallic phases. In some Ni particles with well developed Ni oxide envelope the formation of nickel aluminides was significantly suppressed. The phase composition is quite diverse including besides Ni mainly NiO, Ni<sub>3</sub>Al, Ni<sub>5</sub>Al<sub>3</sub>, Ni<sub>2</sub>Al<sub>3</sub>, NiAl<sub>3</sub>.

The analysis of the microstructure of Ni-Al green compact (Fig. 7) as exposed for 8 h at 800 °C in air revealed that Ni particles were covered with NiO layer that was thicker and more continuous than in previous sample heated to 660 °C. Besides NiO, the prevailing intermetallic phase as confirmed by XRD analysis is NiAl (Fig. 8). The structural integrity of the sample as heated to 660 °C in air was not sufficient. However, after the isothermal exposure for 8 h at 800 °C the integrity improved substantially and the preform had gained the necessary manipulative strength.

#### 4. Discussion of results

Depending on particular conditions, nickel and alu-

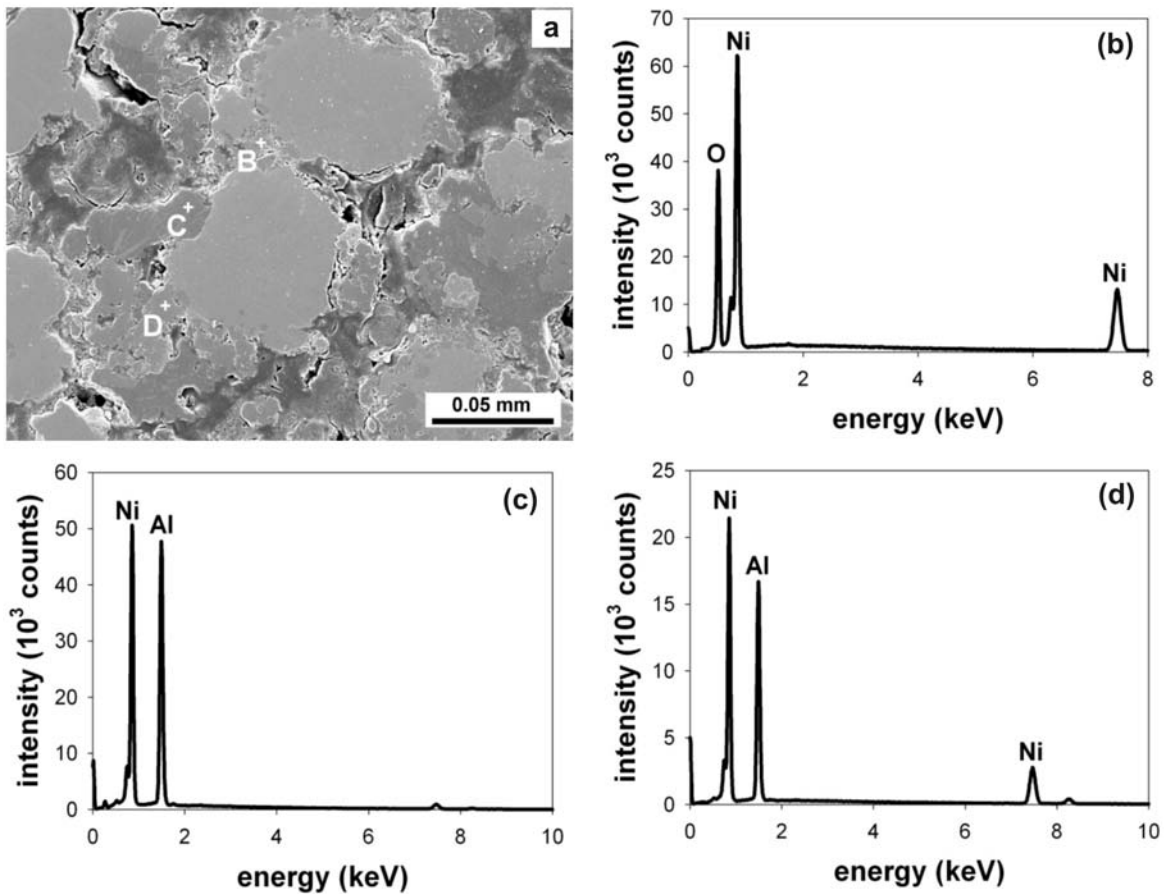


Fig. 6. Secondary electron micrograph of the microstructure of Ni-Al green compact as heated to 660°C in air (a), EDX spectra corresponding to NiO in B (b), Ni<sub>2</sub>Al<sub>3</sub> in C (c) and NiAl in D (d).

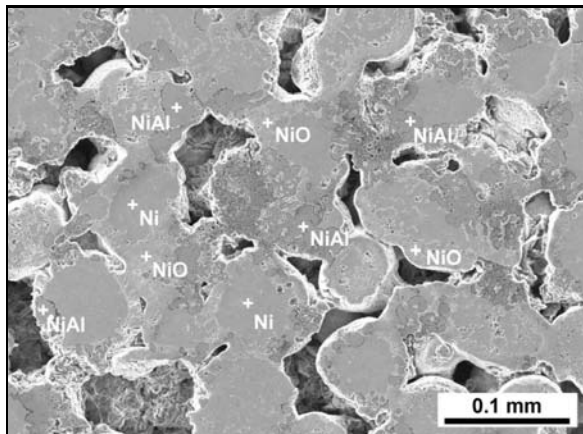


Fig. 7. Secondary electron micrograph of the microstructure of Ni-Al green compact as isothermally exposed for 8 h at 800°C in air.

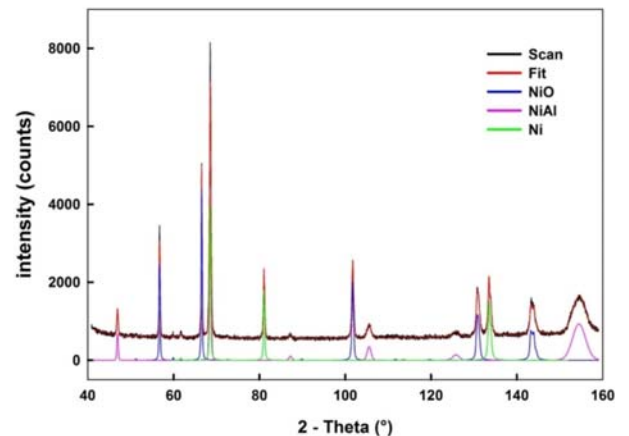


Fig. 8. XRD analysis of the structure of Ni-Al green compact as isothermally exposed for 8 h at 800°C in air.

minium mutually react giving rise to a wide family of nickel aluminides. All these reactions exhibit negative Gibbs free energy of formation and therefore are feasible. Those with higher energy should run preferentially, however, the course of reactions is determined also by additional factors. Among them the diffusion

of atoms into reaction zone should play a key role. However, this can be affected by newly formed phases and the thickness of reaction layer. Current work confirms that the effect of atmosphere on reactions in Ni-Al green compacts is also quite important.

As revealed by TG measurements, there was nearly

no mass change for Ni-Al compact treated in argon. However, significant oxidation was recorded when the thermal treatment was applied in air. After the starting oxidation in air a slight weight loss in all samples was observed. This likely corresponds to the removal of organic matter as well as absorbed water and gases [14, 15]. As the temperature increased with time up to the range between 300–400°C, the mass gain due to the oxidation of particles was observed. Above this temperature, oxidation prevailed and the weight rapidly increased. As reported in Song et al. [14] the total mass gain of Ni powder sample is about 26 %. At this level is the thickness of NiO layer so high that the diffusion of oxygen to Ni atoms is practically interrupted.

The oxidation of Ni powders after isothermal exposure for 8 h at 800°C was approaching 20 %. This indicates that the applied treatment was not enough for total conversion of Ni powders.

In the case of Ni-Al green compact, the mass gain is only about half of that recorded for pure Ni powder. This has obviously to do with the decrease of free surface in the pressed body. Moreover, oxygen has no access to closed pores. The formation of closed porosity is further facilitated by the formation of nickel aluminides. In spite of these the ongoing mass increase confirms that the particles were not completely sealed by impermeable barrier layer.

As reported in Suwanwatana et al. [8], the oxidation of nickel particles of various sizes starts at low temperature, e.g., in the temperature range between 250 and 350°C, and can be described by diffusion-controlled mechanisms. The growth of an oxide film on a metal by thermal oxidation is usually discussed as the transport of ions across the oxide film under the combined effect of concentration gradients and electric fields. This leads to a parabolic kinetics with the growth of the oxide layer. Oxidation of nickel is generally accepted to be governed by a diffusion mechanism through the oxide layer formed on the nickel particle. The thicker the oxide layer grows, the lower the oxidation rate becomes. Based on the assumption of a diffusive process, long thermal treatments are needed to ensure a uniform oxidation layer of the nickel [16].

Present results further confirm that the applied atmosphere, i.e., argon or air can significantly affect the course of Ni-Al reactions. It has been shown that an extensive reaction takes place already upon heating in inert atmosphere. This reaction starts with Al melting and then proceeds with intense exothermic reaction taking place in narrow temperature range. This reaction results mostly into formation of intermetallic NiAl<sub>3</sub>. Subsequent isothermal exposure at 800°C leads to the development of various Ni aluminides converting the Al rich NiAl<sub>3</sub> into Ni rich NiAl and Ni<sub>3</sub>Al phases. This indicates that the system is moving towards equilibrium decreasing the concentration gradients.

On the other hand, the thermal treatment in air resulted in different course of reaction. The DTA curve shown in Fig. 2 reveals that the exothermic reaction is spread into wider temperature range. This is due to the presence of Ni oxide formed during the heating. The microstructural observations confirmed the presence of NiO already after reaching the first exothermic peak. The oxide layer at the surface of Ni powders obviously hinders the mutual Ni-Al reaction. Therefore, various aluminides appear in the structure, however, with inhomogeneous distribution. The process of aluminide formation is governed by the local chemistry, local temperature and particularly is affected by the presence of Ni oxide layers.

Considering the fact that solid-state inter-diffusion should always be considered when dealing with the Ni-Al system at temperatures higher than 400°C and at low heating rates 10 K min<sup>-1</sup>, we assume that under current thermal treatment conditions the solid-state inter-diffusion reaction took place. This hypothesis was further supported by the model study of Farber et al. [17]. They stated that the early stage of Ni-Al reaction was very important since it determined the reaction path and the kinetics of the synthesis process. If thermal explosion occurs in the course of Al-rich intermetallics growth such as NiAl<sub>3</sub> or Ni<sub>2</sub>Al<sub>3</sub>, it will result in the rapid formation of NiAl as the final product. However, if thermal explosion has not been triggered at the stage of Al-rich aluminides formation, it will not take place at the further synthesis stages and the growth of NiAl and Ni<sub>3</sub>Al will proceed via controlled solid state reactions [14, 15].

Ni-Al porous green compacts as shown in this work can be converted into metallic/intermetallic or metallic/oxide/intermetallic bodies. These can be further used for as preforms for composites prepared by e.g. liquid metal infiltration. The crucial precondition here is some degree of mechanical integrity that would help to survive the rather severe process of infiltration.

This integrity can be achieved by applying appropriate thermal treatment converting the initial mechanical bondings into metallic/covalent interparticle ones. However, this treatment is in Ni-Al system accompanied by extensive exothermic reaction that can typically damage the preform. The appropriate thermal treatment in air can decrease the extent of this reaction into reasonable limits.

## 5. Conclusions

The effect of atmosphere on reactions in Ni + 34 vol.% Al green compacts subjected to heating and isothermal exposure for 8 h at 800°C was analysed in this work. Obtained results can be summarized as follows:

- Ni-Al green compact heated to the temperature of 660°C in argon was formed by unreacted Ni and

NiAl<sub>3</sub> exhibiting low integrity.

– Heating in air confirmed both – oxidation of Ni particle as well as Ni-Al mutual reaction. In oxidized sample besides unreacted Ni quite diverse NiO, Ni<sub>3</sub>Al, Ni<sub>5</sub>Al<sub>3</sub>, Ni<sub>2</sub>Al<sub>3</sub>, NiAl<sub>3</sub> phases were determined.

– Weight increase after isothermal exposure for 8 h at 800°C was about 20 % for Ni, 10 % for Ni-Al green compact and 5 % for Al. TG curves of oxidized samples followed parabolic behaviour, which agrees with a diffusive process of thermal oxidation of metals.

– Heating green compact for 8 h at 800°C in argon leads to intense Ni-Al exothermic reaction (close to the melting temperature of Al) giving rise to Ni<sub>3</sub>Al and NiAl aluminides, whereas heating in air results in moderate reaction spread over a wider temperature interval (of about 630–720°C), forming predominantly NiO and NiAl phases.

– The applied thermal treatment in air significantly improved the interparticle bonding providing thus the required structural integrity for Ni-Al compacts; these can be further used for additional processing, e.g., liquid metal infiltration.

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### References

- [1] Morsi, K.: Mater. Sci. Eng. A, 299, 2001, p. 1. [doi:10.1016/S0921-5093\(00\)01407-6](https://doi.org/10.1016/S0921-5093(00)01407-6)
- [2] Beltran, A. M., Brown, E. E., Chambers, W. L., Chang, D. S., Coust Jr., W. H.: Super Alloys II. New York, Wiley 1987.
- [3] Stoloff, N. S., Sikka, V. K.: Physical Metallurgy and Processing of Intermetallic Compounds. London, Chapman and Hall 1996.
- [4] Kresse, G. S. M., Napetschnig, E., Shishkin, M., Kohler, L., Varga, P.: Science, 308, 2005, p. 1440. [doi:10.1126/science.1107783](https://doi.org/10.1126/science.1107783)
- [5] Haering, M., Hoffmann, S.: Appl. Surf. Sci., 125, 1998, p. 99. [doi:10.1016/S0169-4332\(97\)00403-0](https://doi.org/10.1016/S0169-4332(97)00403-0)
- [6] Dong, H. X., Jiang, Y., He, Y. H., Zou, J., Xu, N. P., Huang, B. Y., Liu, C. T., Liaw, P. K.: Mater. Chem. Phys., 122, 2010, p. 417. [doi:10.1016/j.matchemphys.2010.03.017](https://doi.org/10.1016/j.matchemphys.2010.03.017)
- [7] Vummidi, S. L., Aly, Y., Schoenitz, M., Dreizin, E. L.: J. Propul. Power, 26, 2010, p. 454. [doi:10.2514/1.47092](https://doi.org/10.2514/1.47092)
- [8] Suwanwatana, W., Yarlagadda, S., Gillespie, J. W.: J. Mater. Sci., 38, 2003, p. 565. [doi:10.1023/A:1021854026668](https://doi.org/10.1023/A:1021854026668)
- [9] Słoczyńska, K., Werber, T.: Arch. Hutn., 13, 1956, p. 323.
- [10] Denisenko, E. T.: Poroshkovaya Metallurgiya, 7, 1956, p. 4.
- [11] Fedortchenko, I. M., Lyapunov, A. P., Shorochod, W. V.: Powder Metall., 12, 1963, p. 27.
- [12] Werber, T.: Solid State Ionics, 42, 1990, p. 205. [doi:10.1016/0167-2738\(90\)90009-G](https://doi.org/10.1016/0167-2738(90)90009-G)
- [13] Taylor, A., Doyle, N. J.: J. Appl. Crystallogr., 5, 1972, p. 201. [doi:10.1107/S0021889872009203](https://doi.org/10.1107/S0021889872009203)
- [14] Song, P., Wen, D., Guo, Z. X., Korakianitis, T.: Phys. Chem. Chem. Phys., 10, 2008, p. 5057. [doi:10.1039/B800672E](https://doi.org/10.1039/B800672E)
- [15] Uchikoshi, T., Sakka, Y., Yoshitake, M., Yoshihara, K.: Nanostruct. Mater., 4, 1994, p. 199. [doi:10.1016/0965-9773\(94\)90078-7](https://doi.org/10.1016/0965-9773(94)90078-7)
- [16] Cabanas-Polo, S., Bermejo, R., Ferrari, B., Sanchez-Herencia, A.: J. Corros. Sci., 55, 2012, p. 172. [doi:10.1016/j.corsci.2011.10.016](https://doi.org/10.1016/j.corsci.2011.10.016)
- [17] Farber, L., Gotman, I., Gutmanas, E. Y.: Defect Diffus. Forum, 147, 1997, p. 643. [doi:10.4028/www.scientific.net/DDF.143-147.643](https://doi.org/10.4028/www.scientific.net/DDF.143-147.643)