Thermal Analysis of NiAl30 Powder Mixture

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NiAl alloys belong to the group of modern materials for high temperature application due to their low density, excellent thermal stability and oxidation resistance. They could be used as high temperature components which are usually made of nickel superalloys, heat-resistant steel or even cobalt superalloys. Production of these alloys is relatively simple and moreover, they could be used at higher temperatures exceeding 1000 °C. However, their high melting points and poor casting properties complicate the production by melt-metallurgy process. Powder metallurgy and reactive sintering were found to be a suitable replacement for melt-metallurgy. Many phases form during reactive sintering and reaction conditions of their formation are not known or are contradictory. In this work, thermal analysis of NiAl30 (in wt. %) powder mixture was studied. Results offer the effect of heating rate on reaction temperatures, microstructure and phase composition.

Keywords: thermal analysis, NiAl system, reactive sintering, phase composition

1 Introduction

Nickel aluminides such as Ni_3Al and NiAl are the promising materials which could replace conventional nickel-based superalloys and other high-temperature structural materials in near future [1, 2]. These compounds are considered to be a modern and new generation of alloys. Their main advantages are high melting point, low densities, good thermal conductivity, high strength and good corrosion and oxidation resistance. However, they suffer from low ductility, brittle fracture, low creep strength and many problems associated with their production such as poor castability and extreme reactivity of the melts [3, 4]. For this reason, they have not been applied widely yet. They could be used in aerospace and automotive industry-combustion chambers, rotor blades and turbine disks [5, 6]. Therefore, it is necessary to balance sufficient creep strength with ductility and toughness [6]. When we compare NiAl with Ni_3Al, NiAl has much better oxidation resistance and thermal conductivity, higher melting point and lower density [7]. It is one of the reasons, why NiAl compound is more widely studied.

Powder metallurgy is a novel approach to produce intermetallics but melting is still the most used and primary production of nickel aluminides [8]. Variety of cast and wrought can be obtained relatively economically with minimal or no pores and it is possible to control resulted chemical composition [8]. Conventional melting mainly comprises air-induction melting (AIM), vacuum-induction melting (VIM), vacuum arc remelting (VAR) and commercially used Exo-Melt^{TM} process [8, 9]. The last mentioned consists in melting of nickel and aluminium and due to reaction between them, NiAl phase forms. Large heat is associated with its formation which is used to melting of Ni_3Al [9]. The biggest advantages are melting time and power reduction, control of composition and crucibles saving. Other methods usually provide products with different levels of purity and process parameters such as crucibles, melting atmosphere, furnace loading of low- and high-melting point metals significantly affect obtained alloys [8]. One of the method how avoid to all these parameters is reactive sintering process.

Reactive sintering is a method which overcomes the main problems of conventional melt metallurgy routes (poor castability and high melting points of aluminides) [4] and it is a special technology to produce high-temperature materials (10 – 15). The initial components are powders which are transformed into compacts. First of all, powder mixture is heated and intermetallics form through thermally activated chemical reactions. These reactions are strong exothermic. This technique allows to obtain homogeneous alloy with no contaminants from crucibles and also saves cost and energy [16]. However, products exhibit high porosity which is caused by Kirkendall porosity due to unbalanced diffusivities of nickel and aluminium. Reactive sintering is divided into two modes, namely plane wave propagation (PWP) and thermal explosion (TE). Reaction is initiated by rapid heating of one end of samples in PWP mode meanwhile in TE mode, the whole powder mixture is heated [17]. Reaction is able to sustain by itself because it is significantly exothermic due to formation of phases [16].

Nowadays, it is known that reaction can be initiated at 640 °C which corresponds to the eutectic point in Ni-Al system [18]. Microstructure of samples prepared by reactive sintering is mainly composed of NiAl phase with low amount of residual aluminium and pores [19]. It is also assumed that metastable Ni_2Al_3 phase forms preferentially, being followed by the formation of NiAl phase [20]. Other work [21] however shows preferential formation of $NiAl_3$ phase. Subsequently, Ni_2Al_3 phase forms and NiAl phase arises at the last stage. The initiation temperatures also differ because some publications claim that reaction started at melting point of aluminium (660 °C) [22, 23]. Moreover, [15] the effect of applied heating rate was found, showing that all reaction temperatures increase with increasing heating rate. As it can be seen, the reaction conditions, parameters and phases formation are contradictory and moreover, reaction mechanism of Ni-Al system during reactive sintering has not been studied extensively.

This work was focused on the thermal analysis of the reactions in NiAl30 powder mixture. The effect of heating rate on phase composition and microstructure was observed. The aim was to determine the sequence of the formation of Ni-Al intermetallics during reactive sintering and to determine their activation energy.

2 Experimental

Powder mixture was prepared by blending of nickel powder (purity 99.99 wt. %, particle size < 150 µm) with aluminium powder (99.62 %, 44 µm). Resulted chemical composition was NiAl30 (in wt. %) which corresponded to NiAl phase [24]. Uniaxial cold pressing of powder mixture followed and cylindrical green bodies with diameter of 10 mm and weight of 3 g were obtained. LabTest5.250Sp1-VM universal loading machine was used and compaction carried out at a pressure of 450 MPa for 5 minutes. The differential thermal analysis (DTA) of compressed samples was performed using SETSYS Evolution-1750 device by heating from laboratory temperature to approximately 930 °C in the argon protective atmosphere. Heating rate was 10 and 30 $°C\cdot min^{-1}$. From the obtained curves, enthalpies were calculated. Subsequently, reaction temperatures were determined according to heating curve. Samples were then annealed for one minute at temperatures of peak maximum determined by DTA and heating rates were applied same as in the case of DTA. Samples were in quartz ampoules during heating and they were cooled in water after exposure. The aim was to determine phase composition at appropriate temperatures. Prepared materials were ground by sandpapers P80-P2500, polished using colloidal suspension Eposil F mixed with hydrogen peroxide (volume 1:6) and etched by Kroll´s reagent (5 ml HNO_3, 10 ml HF, 85 ml H_2O). Microstructure was studied by scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max 20 mm^2 SDD EDS analyzer for identification of the chemical composition of the individual phases. Phase composition was determined by X-ray diffraction and evaluated using PANalytical X´pert Pro software package with PDF2 database.

3 Results

DTA heating curves are shown in Fig. 1. As it can be seen, heating rate has the significant effect on the course of reaction. There are two exothermic peaks during heating at 10 $°C\cdot min^{-1}$ meanwhile only one peak appeared during heating at 30 $°C\cdot min^{-1}$. These peaks represent the formation of phases. All temperatures associated with double peak were lower than melting point of aluminium. Work [17, 21] also observed two peaks during heating but one peak was associated with melting of aluminium [17]. This means that phases formed due to the solid-state reaction. The onset temperature of first peak was 551 °C with the maximum of 568 °C and offset temperature 576 °C. Reaction was the least exothermic (enthalpy was -289 $J\cdot g^{-1}$ ~ -25 $kJ\cdot mol^{-1}$). Only NiAl phase was found during EDS analysis and study of phase composition Fig. 2 a and Tab. 1. Matrix of obtained microstructure was composed of NiAl phase and pores (Fig. 2 a). Second peak represents reaction during which only NiAl phase formed again (Fig. 2 b, Tab. 1). This reaction was much more exothermic and enthalpy of this reaction was determined to -463 $J\cdot g^{-1}$ ~ -40 $kJ\cdot mol^{-1}$. Reaction started at 635 °C and finished at 645 °C. Maximum of reaction (654 °C) did not exceed the melting point of aluminium but NiAl phase formed after the reaction between solid nickel and liquid aluminium. The presence of liquid aluminium was caused by the eutectic transformation. Temperatures found at second peak were close to the eutectic temperatures (640 °C) which caused melting of aluminium and it is mainly typical for Al-rich system or in mechanically activated system [17, 18, 21]. Although, no endothermic peak confirming this eutectic reaction was observed during heating work [22] showed that endothermic process happened at the same time. Then, expected endothermic effect is hidden and counterbalanced [22]. The melting point of aluminium is 660 °C, nickel melts at 1455 °C and the melting point of stoichiometric NiAl phase is approximately 1638 °C. The adiabatic temperature (the maximum temperature which could be achieved during reactive sintering, usually 1647 °C [25]) was not reached during heating and that means NiAl phase was not liquid. Thus, this phase could not react with nickel to form other phases. However, melt can form because it coexists with aluminium at lower temperatures as it can be seen in diagram Ni-Al [24]. It can be also seen that porosity was higher (Figs. 2 a, b) when the temperature of reaction increased though there is the presence of liquid phase. Kirkendall porosity had to dominate due to unbalanced diffusivities of nickel and aluminium.

Heating rate of 30 $°C\cdot min^{-1}$ caused that only one peak was observed and its position corresponded to first peak found during heating by 10 $°C\cdot min^{-1}$(Fig. 1). This peak was significantly more exothermic with enthalpy -1238 $J\cdot g^{-1}$ ~ -106 $kJ\cdot mol^{-1}$. Reaction started at 539 °C and finished at 573 °C. These temperatures were, therefore, lower than in the case of heating by 10 $°C\cdot min^{-1}$ meanwhile maximum of temperature was higher (588 °C). Work [22] also detected only one exothermic peak with onset temperature 660 °C. So, they assume that the liquid-solid reaction and they claim that melting of aluminium is necessary to form the nickel aluminides. However, our measurements show that NiAl phase could form due to reaction between aluminium and nickel in solid form (Fig. 2 c). Further, same authors observed the formation of other intermetallics, e. g. Ni_3Al, Ni_2Al_3 and Ni_5Al_3 during slow cooling. Very fast quenching prevents the formation of other phases and single phase alloy could be obtained. All measured enthalpies were similar to values calculated for formation of NiAl phase published in [17, 26].

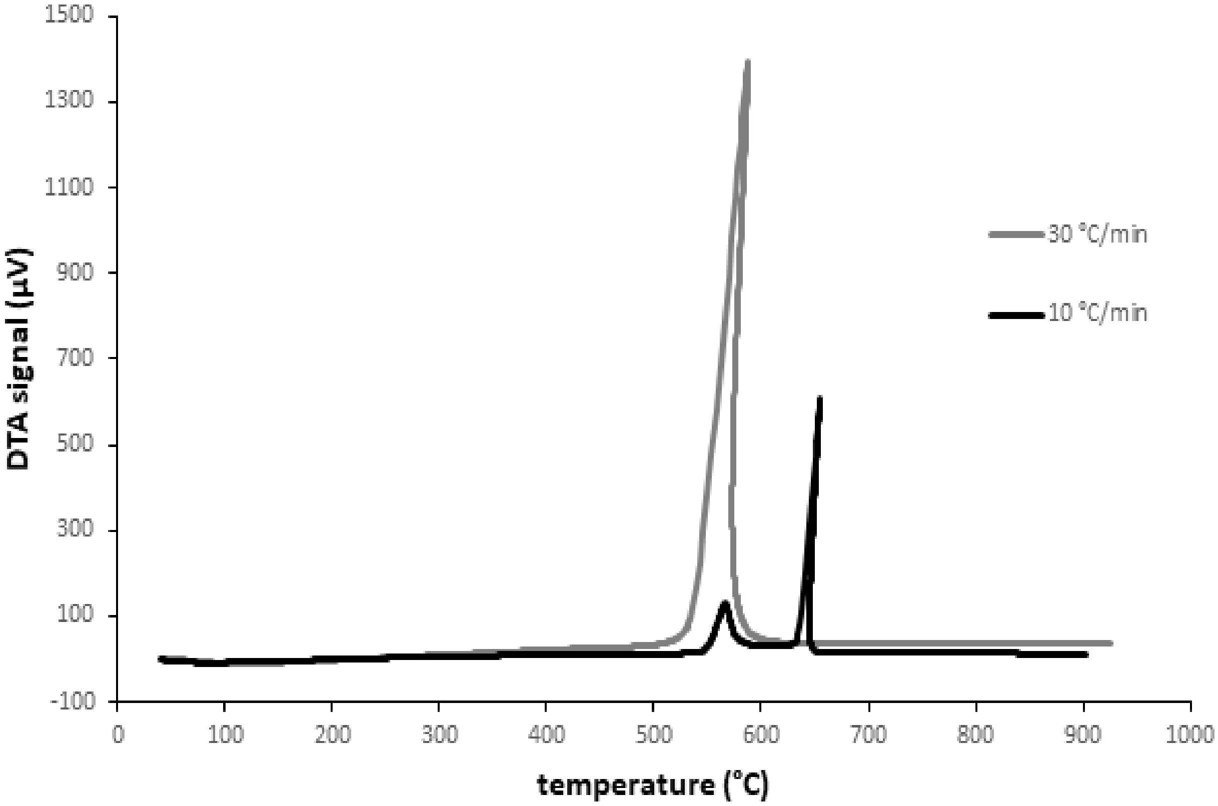
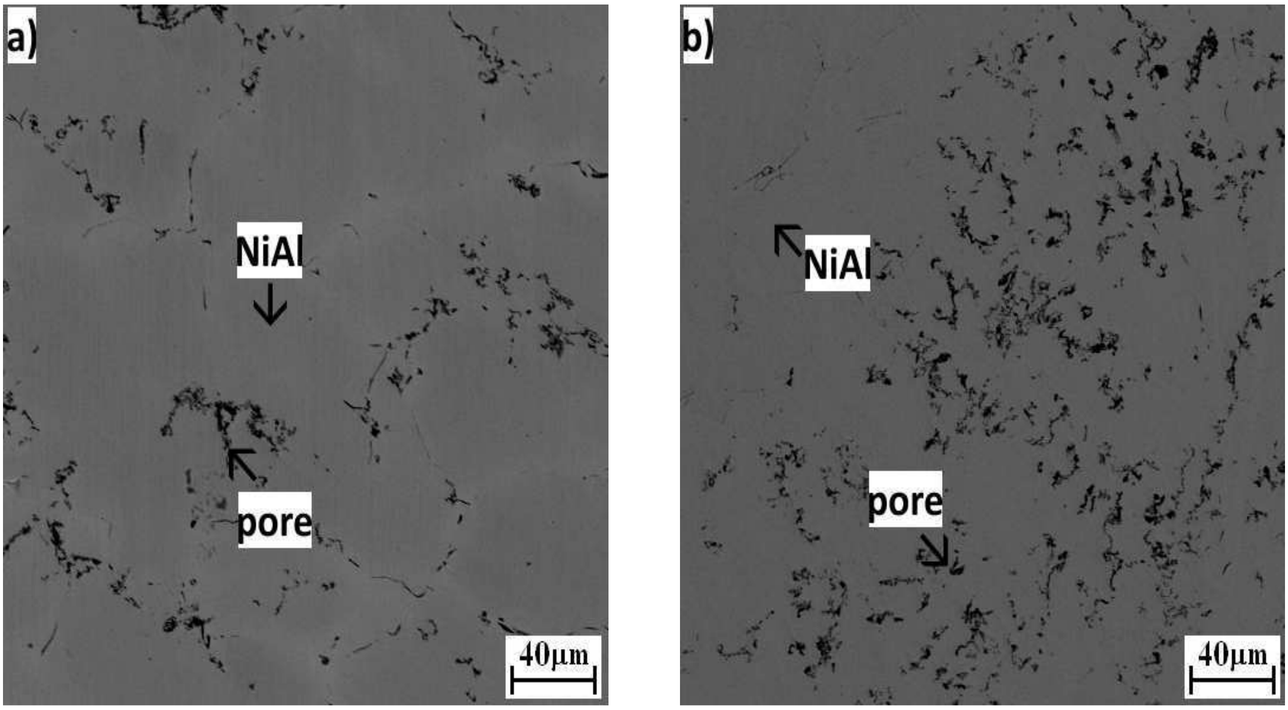


Fig. 1 *DTA heating curve obtained at 10 and 30 °C·min^{-1}*



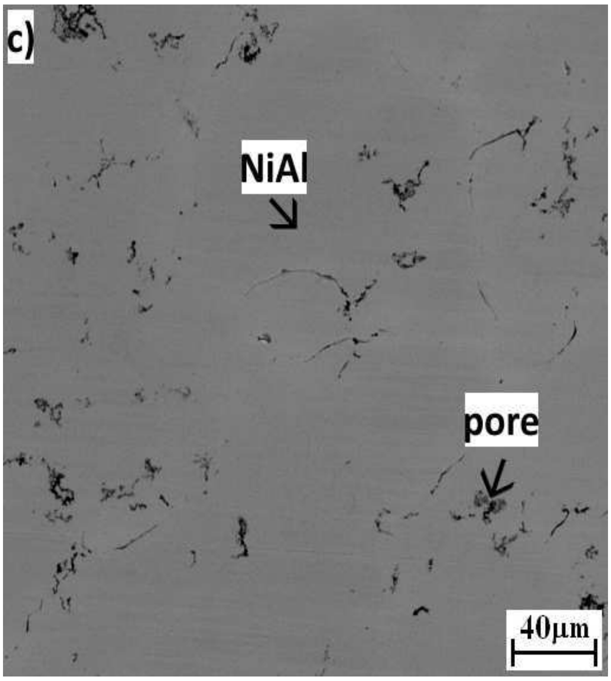


Fig. 2 *Microstructure of NiAl30 obtained annealing at a) 568 °C, b) 654 °C, c) 588 °C for 1 min*

Tab. 1 *Phase composition*

Temperature	Phase composition
568 °C	NiAl
654 °C	NiAl
588 °C	NiAl

In all cases, only NiAl phase was detected although no temperatures did not exceed 650 °C. This temperature is important because it was showed that Ni_2Al_3 and $NiAl_3$ phases form predominantly below this temperature [21, 27]. Moreover, Ni_2Al_3 phase forms preferentially in Ni-rich system [21]. Our experiments differ from others by time at reaction temperature and cooling. Temperatures were too high for formation of Ni_2Al_3 phase because this phase has to form below 540 °C and subsequently, transformed into NiAl phase. The formation of NiAl phase is thus caused by thermal explosion which released the heat sufficient for its formation.

Because only NiAl phase formed, we were able to determine activation energy. This activation energy was calculated from Kissinger equation and was 125 $kJ \cdot mol^{-1}$ which is approximately same value found in work [28].

4 Conclusion

According to the obtained results, it was found that only NiAl phase formed at studied heating rate. Various heating rates caused the formation of NiAl phase due to solid-state reaction at lower temperatures and due to eutectic reaction at higher temperatures. Enthalpy of its formation increased with increasing heating rate. Activation energy was determined to be 125 $kJ \cdot mol^{-1}$. Further, it was revealed that porosity was much higher at higher temperature despite of the presence of liquid phase. Moreover, fast quenching in water does not allow for other phases.

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