

Combustion synthesis of Al-Ni compounds in microwave reactor

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Abstract

Investigations of intermetallic compounds of Al - Ni system produced on the base of combustion synthesis method are presented. It was aimed to obtain homogeneous chemical constitution and porous structure used to locally reinforce castings. Production method of perform with microwave heating was elaborated. Special heating chamber with strongly focused field and possibility of exact control process was constructed. Various stoichiometric ratio samples corresponding to compounds from binary diagram were synthesized. Basing on the temperature profiles dynamics of process was analyzed, typical combustion temperatures and possible compounds were determined. Microscopic investigations with chemical analysis EDS showed considerable differences in chemical constitution and morphology of phases. Sample made from mixture of powders with composition of Al:Ni = 3:1 revealed relatively uniform porosities but considerable differences in chemical composition. With increase of Ni content the synthesis underwent at higher temperatures, with progress of reaction the melting of transient phases led to uniform chemical composition of product. Unfortunately as a result of structure fusion coagulation and closing of pores occurred excluding received structure for further attempts to infiltrate with squeeze casting method.

Keywords: Intermetallic, Al-Ni, SHS, Preform

1. Introduction

Nickel aluminides and alloys based on such compounds are materials of growing technological importance. Their beneficial attributes are corrosion and oxidation resistance, thermal stability, relative low cost, good strength at high temperature and low density.

An economic route for manufacturing of these materials are combustion synthesis (CS) and self-propagation high temperature synthesis (SHS). Depending on starting composition, stoichiometric ratio and thermodynamic conditions several intermetallics are possible. The Al-Ni system contains some important for application phases: Al_3Ni , Al_3Ni_2 , AlNi , and AlNi_3 (Fig.1). Most of the experimental and theoretical studies on

combustion processes have been focused on the mechanism of reaction especially determination of intermetallic sequence occurring during synthesis. When substrates are heated to ignition temperature very slowly pre-combustion products may appear. Usually between substrates, on Al surface cuboidal Al_3Ni crystals form, which coexist with eutectic $\text{Al}(\text{Ni})\text{-Al}_3\text{Ni}$. At this time on the Ni side slowly growing Al_3Ni_2 consumes Ni and eutectic [1-3]. In [4] using time-resolved X-ray diffraction technique (TRXRD) first AlNi was detected preceding formation of Al_3Ni , Al_3Ni_2 and Al_3Ni_5 . Moreover at high rate of heating it is very difficult to reach equilibrium and homogeneous composition. Thermodynamically transient compounds do not influence on extracted heat but dissipation of heat to environment and entire sample may slow down reaction completely [5]. Additionally pre-combustion compounds separate metallic Al and Ni forming

diffusion barrier [6]. Generally ignition starts when aluminum melts and engulfs solid Ni particles. Diffusion across the intermediate layer leads to the saturated melt from which may crystallize AlNi.

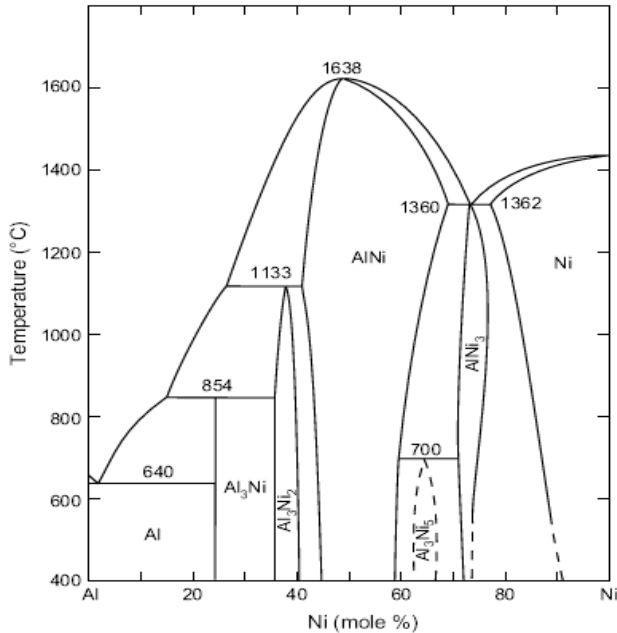


Fig. 1. Phase diagram of Al-Ni system [7]

Heat extracted from exothermic reaction during the high temperature synthesis influences on process parameters and properties of products. For nickel aluminides enthalpy formation are as follows: Al₃Ni -150,6; Al₃Ni₂ -282,4; NiAl -118,4; Ni₃Al -153,1 kJ/mol [8,9]. The general formula for enthalpy of the SHS reaction initiated at T_{ig} (usually melting temperature of aluminum) is as follows:

$$-(\Delta H_s + \Delta H_p) = \Delta H_{ig} \quad (1)$$

The enthalpy of reaction at the ignition temperature, ΔH_{ig}, as a amount of heat available under adiabatic conditions is divided to heat the adjacent layer from T₀ to T_{ig}, and absorbed by the product (ΔH_p) to T_c temperature. Preheating substrates and increasing T₀ to T_{ig} will decrease (ΔH_s) to zero and all of the heat will be absorbed by the product, resulting in higher adiabatic temperature. In practice combustion synthesis is usually conducted under non-adiabatic conditions and heat dissipates from the reaction front to the environment. Therefore the heat loss (ΔQ) decreasing combustion temperature disturbs wave stability or even halts the propagation of the combustion front.

On the base of thermodynamic theory enthalpy of fusion at T_{ig}:

$$\Delta H_{ig} = \Delta H_{298} + \int_{298}^{T_{ig}} [C_p(\text{product}) - C_s(\text{substrate})] dT \quad (2)$$

When reaction between nickel and aluminum elements to Al_xNi_{1-x} intermetallic is expressed as:



and the maximum combustion temperature T_c, and the enthalpy of reaction from equation (1) and (2) will be compared, the following formula for Al-Ni compounds is as follows:

$$-\int_{298}^{T_{ig}} C_p(xAl + (1-x)Ni) dT - y\Delta H_{Al-l} - \int_{T_{ig}}^{T_c} C_p(Al_xNi_{1-x}) dT - \Delta Q = \Delta H_{(298)} + \int_{298}^{T_{ig}} [C_p(Al_xNi_{1-x}) - C_p(xAl + (1-x)Ni)] dT - y\Delta H_{Al-l} \quad (4)$$

Where C_p(xAl+(1-x)Ni), C_p(Al_xNi_{1-x}), is the heat capacity of solid reactants and product respectively, y is the fraction of molten aluminum, ΔH_{Al-l}, ΔH₂₉₈, are the enthalpy of aluminum fusion and the enthalpy of reaction at 298K. Finally reaction enthalpy at room temperature is expressed by:

$$-\Delta H_{298} = \int_{298}^{T_c} C_p(Al_xNi_{1-x}) dT + \Delta Q \quad (5)$$

where heat capacity C_p can be estimated from available thermodynamic data (e.g. Thermo-Calc, SGTE data).

This paper presents production attempts of porous structures for further infiltration with liquid alloy. Possible sources of the porosities are previously defined as [6,10]: (1) the eutectic melting; (2) initial porosity; (3) lower product density; (4) evolution of volatiles; (5) thermal migration of pores.

In contrast to typical synthesis new process parameters should provide open porosity preform with uniform microstructure able to resist infiltration pressure. Method was developed on the base of previous experiment results presented in [11].

2. Experimental procedure

Elemental nickel powder (99,8%, -325 mesh, AlfaAesar) and aluminum (99,5%, -325 mesh, AlfaAesar) in proper stoichiometric ratio were mixed to ensure homogeneous microstructure. Cylindrical samples were cold isostatically pressed under 500 MPa to 23 mm diameter and a height of 4 mm. Next the samples insulated with alumina fiber blanket were put into microwave heat chamber mounted in standard waveguide steel sleeve. Because microwaves are mostly reflected from the metal surface SiC susceptor touching samples ignited synthesis.

The microwave furnace contains a magnetron tube, transformer and controls. The system utilizes 0-900W power at 2,45 GHz. Continuous temperature measurement were made using one-color optical pyrometer (Raytek, model Marathon MM, temperature range: 540-3000°C). The measured spot on the surface was approximately 0,6 mm in diameter near the outer perimeter of the sample. Reactions were carried out in quartz tube under flowing argon. To check usefulness of prepared structures for reinforcing of composite materials performs were subjected to infiltration by direct squeeze casting method. Microstructure

observations were performed by using an optical and scanning electron microscopy JEOL JSM-5800LV with EDS analyzer.

3. Discussion of test results

Produced Al-Ni structures by combustion synthesis revealed in most cases poor arrangement of pores insufficient for composite reinforcing. When stoichiometric molar ratio of substrate leads to Al_3Ni compounds pores were embedded in relatively homogeneous microstructure of intermetallic compounds (Fig.2). With increase of Ni content to 3:2 stoichiometric ratio samples reacted vigorously, structures became more porous, frayed and irregular (Fig.3). Though almost no closed pores were observed and obtained structure was able to infiltrate with molten metal. In the case of combustion of Al+Ni compact reaction reached liquidus temperature, so pores were closed with relatively smooth walls and globular shape (Fig.4). Their arrangement in homogeneous intermetallic compounds was much better but still insufficient, further efforts are needed. On the other hand remelted products can be compressed during synthesis reducing porosities and producing final solid material.

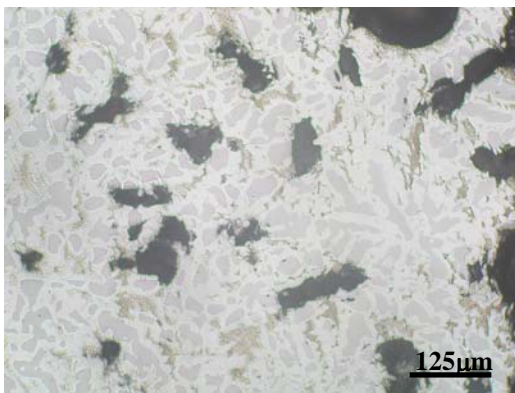


Fig. 2. Optical micrograph of porous structure made from 3Al+Ni compact (black spots - pores)

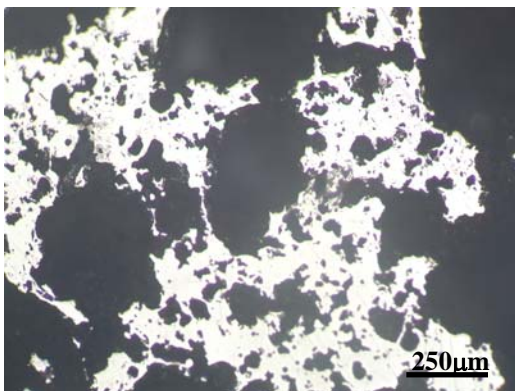


Fig. 3. The microstructure of porous Al_3Ni_2 sample (light area compound, dark – resin)

EDS analysis of sample microstructure (Fig.5) produced from 3Al+Ni compact showed chemical differentiation and presence of transient phases. Dark areas marked by E point are initial aluminum powder surrounded by Al_3Ni compound (Table 1). Probably due to fast process and low temperature, diffusion proceeded in short time and substrates reacted partly. Light areas (point B and A) represent Al_3Ni_2 compound which with time would pass to planned in this case final intentional product Al_3Ni .

Chemical analyze along line L1 confirmed composition of distributed phases. Transition between them followed with abrupt element concentration, though on the Al side some extent saturation with Ni was observed. It should be emphasized that no anticipated Al(Ni)- Al_3Ni eutectic was detected. Usually in prolonged combustion processes eutectic is the first phase occurred before synthesis ignition [12,13]. This may prove that melted aluminum engulfed solid Ni particle but there was no time to completely react.

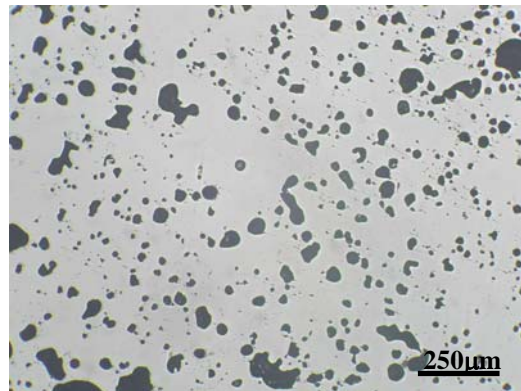


Fig. 4. The microstructure of porous AlNi product (dark pores)

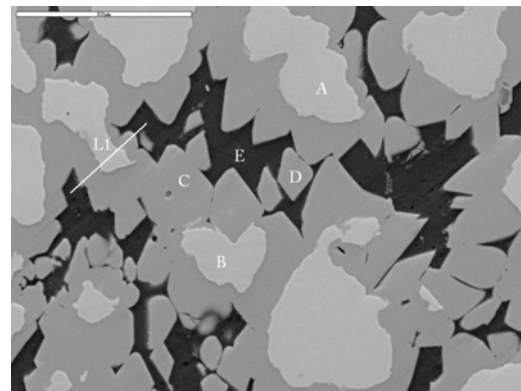


Fig. 5. SEM micrograph showing microstructure of Al_3Ni sample with analyzed composition points presented in Table 1

Table 1. Results of EDS analysis in points presented in Fig. 5

Element	A	B	C	D	E	F
	% at.	% at.	% at.	% at.	% at.	% at.
Al	58,50	58,69	72,48	72,84	99,33	99,27
Ni	41,50	41,31	27,52	27,16	0,67	0,73

Temperature measurement by means of pyrometer allows for determination of synthesis steps and phase transitions. In relatively low exothermic 3Al+Ni reaction maximum temperature was lower than 1500K. Exceeding peritectic and eutectic temperature during cooling led to these phase transitions what was confirmed by stops on the temperature curve (Fig. 6a). With increase of Ni content combustion temperature increases and for Al+Ni sample reached liquidus temperature (plateau distance, Fig.6b).

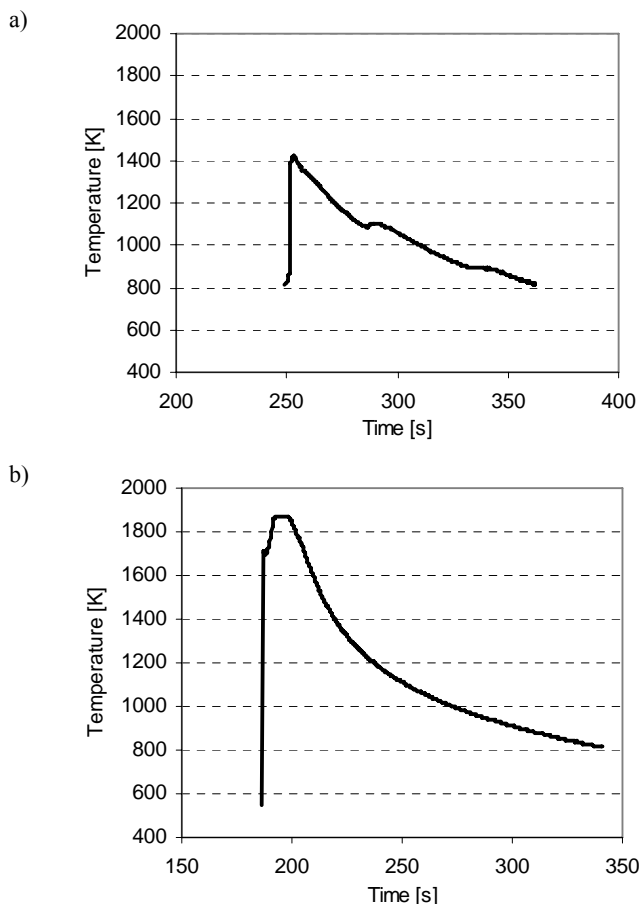


Fig. 6. Temperature profiles for Al₃Ti (a) and AlNi (b) synthesis

4. Conclusions

Based on the microstructural and temperature analyses of Al-Ni compounds fabricated by the combustion synthesis, the following conclusion can be drawn:

1. Microwave activated combustion synthesis was successfully utilized to manufacture intermetallic perform but porous structure is irregular and at some stoichiometric ratio closed pores cannot be infiltrated.
2. The powder mixtures 3Al+Ni reacts at relatively low temperature to Al-Al₃Ni-Al₃Ni₂ multi-phase product.

3. With increase of Ni content reaction proceeded more vigorously at higher temperature. It leads to melting of intermetallic compounds, coagulation and closing of pores.

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