Phase composition of macroporous Ni-Al alloys obtained by combustion synthesis

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Abstract. This paper discusses the phase composition of macroporous Ni-Al alloys obtained by self-propagating high-temperature synthesis. The alloys have been synthesized in a nonstationary combustion mode. The combustion wave consists of super adiabatic foci, and macroporous structure is realized under the action of capillary hydrodynamic effects. The influence of reaction mixture composition of aluminium in the range of 13.5-31.5 wt.% is also discussed. The specific requirements to obtain the single phase B2 NiAl and L¹² Ni₃Al as well as biphasic gas permeable alloys with the average size of structure elements in the range of 1.2-3.15 mm are described in the paper.

1. Introduction
The Ni-Al based intermetallic alloys are attractive functional materials because of their relatively low density, comparatively high melting temperature and excellent high temperature oxidation resistance [1]. Atoms of Ni and Al are bonded together by covalent/ionic bonds, therefore the alloys are characterized by mixed metal and ceramic properties [2]. There are the following phases in Ni-Al system: NiAl₃, Ni₂Al₃, NiAl, Ni₅Al₃ and Ni₃Al [3]. NiAl and Ni₅Al are currently of a considerable interest for a wide range of high-temperature industrial applications. NiAl, known also as β-NiAl, exists in a composition range of 42 - 55 at.% Al (25 - 36 wt. %), and it has a B2 body-centered cubic crystal structure, space group Pm3m (#221), lattice parameter a = 2.76 - 2.88 Å. Ni₅Al, also known as γ’ among Ni-Al alloys, exists in a range of composition from about 22 to 37 at.% Al (11.5 - 14.5 wt.%), and might be found in three different crystal structures: cubic L₁₂, tetragonal DO₂₂, and hexagonal DO₁₉. The cubic L₁₂ phase is stable up to its melting point (1395 °C), and it is the most stable phase among these three [4]. L₁₂ Ni₃Al has a face-centered cubic crystal structure, space group Pm3m (#221), and lattice parameter a = 3.55 - 3.68 Å.

NiAl is the most refractory phase among Ni-Al systems with the melting point 1639 °C, low-density ≈ 6 g/cm³ and superior oxidation resistance up to 1300 °C that is attributed to the formation of a dense and continuous α-Al₂O₃ scale on the alloy surface [5-10]. Unfortunately, B2 NiAl in a polycrystalline form is extremely brittle at a room temperature. Ni₅Al demonstrates good resistance to high-temperature oxidation and increases yield strength with the temperature. Increasingly, polycrystalline L₁₂ Ni₃Al shows room temperature tensile ductility of 11 - 13% in air [2,10,11]. Therefore, the optimal combination of strength characteristics and corrosion resistance corresponds to
two-phase structures of B2 NiAl plus L12 Ni3Al [12]. Due to the combination of advanced characteristics, Ni-Al intermetallics with 25 - 50 at.% (13.3 - 31.5 wt.%) of aluminium are promising for use as porous permeable products that are capable of operating under conditions of variable mechanical loads at high temperatures and oxidizing environment. Such conditions are basic for solid oxide fuel cells [13-17] or radiant burners of a cylindrical shape [18-19].

The most common and well-studied method for the production of porous permeable materials is the sintering of a powder sample. The sample can be formed either from powders of a target alloy or from a powder mixture of alloy components. The second approach is attractive since raw materials used are cheaper. However, the sintering of porous Ni-Al intermetallic parts from a porous preform made of Ni and Al powder is a complicated process due to the large enthalpy formation of NiAl and Ni3Al phases, 118.4 kJ/mol and 153.1 kJ/mol respectively [20]. In the process of the Ni+Al powder sample heating, a spontaneous exothermic reaction can be realized either (1) in a thermal explosion mode, when the whole powder media is sharply heated up to high temperatures, or (2) in a self-propagating mode, when the spatially constrained high temperature zone, a combustion wave, propagates through the powder mixture. These modes of material synthesis are studied within the scientific field known as Self-propagating High-temperature Synthesis (SHS) or Combustion Synthesis [21]. If the sintering process is performed without taking into account the SHS effects, the obtained materials can often be characterized by significant structural defects [17]. A method of reaction sintering is used in order to suppress the exothermic reactions [22]. In this process, the powder mixture is exposed to a specified moderate temperature with formation of fine layers of intermetallic phases between particles by means of a diffusion mechanism. The layer acts as a barrier and the uncontrolled exothermic reaction between the powders becomes impossible. However, for the directional synthesis of porous penetrable materials a soft thermal explosion sintering can be used [23]. In this process, the thermal explosion process is controlled by the intensity of heat losses between the synthesized material and special heat sink clamps. This method allows obtaining materials with a pore size in the range of 1 - 5 μm for composition range Ni + 7.0 - 31.5 wt.% Al.

The self-propagating mode of SHS can be successfully used to obtain materials with a pore size of significantly larger than a size of powdered reagents used. The nonstationary combustion modes might provide the conditions for melting and coalescence of a reacting media within the combustion wave zone what can lead to the synthesis of coarse-pored materials with a size of structural elements of 1 mm and more [24]. It has been known that combustion synthesized materials can comprise unreacted reagents or transition phases because of incomplete reactions. The objective of this study is to investigate the phase composition of macroporous Ni + 13.3-31.5 wt. % Al intermetallics obtained by a nonstationary mode of SHS.

2. Experimental methods

Combustion synthesis was carried out on laboratory samples obtained by vibroforming of the reaction mixture Ni + 13.3 - 31.5 wt.% Al + 0.0 - 2.0 wt.% Ca(OH)2 in a cylindrical mould (diameter 20-40 mm, height 40-80 mm). The nickel powder grade UT-1 (average size 10 μm, Norilskii Nickel, Russia) and aluminium powder grade ASD-4 (average size 10 μm, RusAl, Russia) were used as initial reagents. Ca(OH)2 was used in order to provide a nonstationary combustion mode of SHS. Reaction samples were placed in a reaction chamber connected to a vacuum pump and argon supply. The combustion synthesis was initiated by a spark plug ignition from the upper end of the powder sample.

The structural characterization of the prepared alloys was made by X-ray diffraction measurements on DRON-II powder diffractometer with Co Kα radiation, PDF4+ database and Powder Cell 2.4 full-profile analysis software. The porosity structure of the materials was studied with an Axiocert 200M-Mat optical microscope (Carl Zeiss, Germany) and Image Scope software (SMA, Russia) using a stereometric metallographic analysis described in [23]. The morphology of the materials (BSE and Secondary Electron Imaging) was studied with a Philips SEM 515 scanning electron microscope and an instrument QUANTA 200 3D. The latter was also used for EDS analysis. A conventional technique for metallographic sample preparation was used, and the specimens were treated with etching solution:
L1₂Ni₃Al alloys in 25 g of CrO₃ in 50 ml H₂O + 150 ml HCl, B2 NiAl alloys in 45%CH₃COOH+35%HNO₃+10%HCl+10%H₃PO₄ [10]. The material characterization mentioned above was performed on the equipment of National Research Tomsk State University (Tomsk regional center for collective use of scientific equipment).

3. Experimental results and discussion

It has been found that without using the Ca(OH)₂ additives the maximal temperature in the combustion wave zone is less than liquidus one and the synthesized materials are characterized by microporous or defect porous structures. Ca(OH)₂ additives have to be used in order to obtain macroporous materials. Ca(OH)₂ is decomposed to CaO and H₂O at 400-500 °C [25] in the preheating zone of the combustion wave, which presumably provides two effects. Firstly, the chemical composition of additives acts as a flux for the oxide layers destruction on the reagents surface and activates the capillary interaction of the melts (eutectic melting in Al₂O₃-CaO binary system takes place at 1415 °C). Secondly, the generated gas must loosen a layer of the reaction mixture with stirred-fluidized bed formation. As a result of the Ca(OH)₂ action, the flat combustion wave falls into foci. Superadiabatic conditions are realized in the foci on the inside of which the temperature briefly exceeds the liquidus for the Ni-Al system i.e. 1911 K. The powdered media in close vicinity to the high-temperature foci is melted and the drops from up to 10⁷ powder particles have been formed under the action of capillary hydrodynamic effects [26]. It has been found that it is possible to adjust the size of the reaction foci i.e. the size of the structure elements by the synthesis conditions control: relative density and/or preheating of the reaction sample (figure 1).

Figure 1. Macroporous structures of combustion synthesized Ni-Al alloys. An average size of Ni-Al element is 1200 μm (part a), 1700 μm (part b), 3150 μm (part c).

The XRD patterns have shown cubic B2 NiAl and L1₂ Ni₃Al phases as major structures of the investigated alloys. The minor amounts of the tetragonal distortions of B2 structure, L₁₀ NiAl have also been revealed for alloys with 31 - 38 at.% (17 - 22 wt.%) Al (figure 2). It has been known if NiAl alloy are rapidly cooled, the high-temperature B2 phase called austenite undergoes a thermoelastic transformation to a low-temperature phase called martensite. This transformation is observed in Ni-rich compositions Ni₃Al₁₋ₓ with x = 0.62 - 0.69 and occurs with relatively small and highly correlated atomic displacements [27]. The martensite is shown to have a L₁₀ body-centered tetragonal structure, space group P4/mmm (#123) with lattice parameters a = 2.56 Å, c = 3.2 Å [28], according to other data a = 3.7883 - 3.8083 Å, c = 3.1926 - 3.2459 Å [29]. It is also known that a thin-plate long-period martensite is sometimes interpreted as a crystallographically distinct 7R structure or 14M with lattice parameters a = 4.2053 - 4.2085 Å, b = 2.6688 - 2.6787 Å can be observed in the Ni-Al system [29]. It is difficult to unambiguously identify the 7R martensite on X-ray diffractogram because only one line (117) has a unique position; all other lines coincide with the reflexes of phases B2 NiAl and L₁₀ NiAl.
Figure 2. X-ray diffractograms observed for Ni-Al alloys with 17 - 22 wt.% Al: alloy obtained by combustion synthesis (part a), after the 1 hour 1000 °C annealing (part b).

Figure 3. Synthesized Ni-Al alloys with 17 - 22 wt.% Al after SHS (part a) and after annealing (part b).

Figure 4. X-ray diffractograms: 31.5 wt.% Al (part a), 25 wt.% Al (part b), 20 wt.% Al annealed (part c), 17.5 wt.% Al annealed (part d), 13.5 wt.% Al (part e).
It is also worth pointing out that local atomic arrangement around the anti-site Al atom of Al-rich L1₂ Ni₃Al is close to the L1₀ NiAl structure [30]. For instance, Ivanovski et al. have studied the structure of polycrystalline Ni₃Al doped with Hf [31,32] and some diffraction peaks located at the same angles as for L1₀ NiAl were interpreted as L₆₀ tetragonal distortion of L1₂ Ni₃Al phase (Strukturbericht symbol L₆₀ refers to prototype Cu₄Ti₃, space group P4/mmm). Interestingly enough, according to Binary alloy phase diagrams of ASM International [3] there are no stable or metastable structures with composition Cu₄Ti₃.

The martensitic phase contains multiple twins arranged in domains and plates [28] therefore laminar surface relief of L1₀ NiAl phase can be clearly observed using an optical microscope [33,34]. The figure 3a shows the relief of synthesized alloys with 17-22 wt.% Al composition where the martensitic structure type is clearly observed. The strains associated with the martensitic reaction might contribute to the spalling of Al₂O₃ protective scale, which is detrimental for corrosion resistance of the alloy [35]. However, the NiAl alloy is unstable in the L1₀ structure and the tetragonal distortion toward the B2 structure will occur [36]. It has been found that after annealing (1000 °C per one-hour) the XRD patterns showed only cubic B2 NiAl and L1₂ Ni₃Al phases. The minor amounts of the L1₀ NiAl are annealed during heat treatment (figure 4). Electron microscopy has also revealed only B2 NiAl and L1₂ Ni₃Al phases in annealed materials and no martensitic relief (figure 3b).

4. Concluding remarks
Using the system of Ni + 13.3 - 31.5 wt.% Al + 2.0 wt.% Ca(OH)₂, the phase composition of self-propagating high-temperature synthesis products with a large-pore structure was studied. It has been established that the synthesized alloys may contain an unstable phase of martensite L1₀ NiAl. One hour annealing at 1000 °C makes it possible to bring the composition to equilibrium: B2 NiAl for 25 -31.5 wt.% Al alloys, L1₂ Ni₃Al for 3.3 wt.% Al alloys and B2-L1₂ composite for 14 - 24 wt.% Al alloys.

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