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Characterization of NiAl with cobalt produced by combustion synthesis

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ABSTRACT

In this study, as an alloying element the effect of cobalt addition by 2.5 wt.% and 5 wt.% on the NiAl intermetallic compound produced by pressure-assisted combustion synthesis method was investigated. As starting materials aluminum powder with 15 μm size, carbonyl-nickel 4–7 μm size and cobalt powders 10–44 μm size having 99%, 99.8% and 99.9% purity, respectively were used. The formation temperature of intermetallic compound for three different powders mixture determined by DSC analysis was approximately 654 °C. The production of NiAl was carried out in electrical resistance furnace in open air with a uniaxial pressure of 150 MPa at 1050 °C for 60 min. Optical and SEM studies showed that intermetallic compounds have low porosity and phase transformation has been completed. The distribution of alloying elements was confirmed by EDS analysis. The presence of NiAl and CoAl phases was determined by XRD analysis. The relative density of pure NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co materials was 99.65%, 99.48% and 99.30% and the microhardness of materials was about 368 $HV_{1.0}$, 398 $HV_{1.0}$ and 425 $HV_{1.0}$, respectively.

1. Introduction

The Ni–Al system is of particular interest. The strongly ordered B2 intermetallic NiAl has a number of unique physical and mechanical properties that make it attractive for use at high temperature and in aggressive environments due to its high-melting point (1640 °C), low density ($\rho = 5.89\ \mathrm{g/cm^3}$), excellent corrosion and oxidation resistance, combined with its ability to retain strength and stiffness at elevated temperatures [1,2]. However, poor room temperature strength is a significant obstacle to the alloy's structural use. Alloying behaviors of various elements in NiAl can be summarized the effects of transition metals on NiAl. The classified those elements as three types. Ti, Zr, Hf, Nb and Ta (type A) have low solubility in NiAl and exist in the form of ternary intermetallic compounds such as Heusler (Ni_2Al_x) phase and Laves ($NiAl_x$) phase. These ternary compounds can increase NiAl's creep strength dramatically. V, Cr, Mo and W (type B) can form pseudo-binary eutectic systems with NiAl and the eutectic structure improves NiAl's room temperature toughness. Fe, Co and Cu (type C) have high solubility in NiAl. These additions can be used to generate a second ductile phase to improve the NiAl alloy's room temperature ductility [3,4].

The characteristic features of the Ni–Al–Co system are complete solid solution series between B2-NiAl and B2-CoAl and between Ni and Co [5]. Co atoms replace the Ni lattice sites because exceptionally small formation energy is required for Co inserted into Ni sublattice its also easier to create vacancies in the Ni sublattice than in Al sublattice [6]. The martensitic phase transformation from the ferromagnetic state in Co–Ni–Al β alloy system has been found by the author's group [7–9]. The shape memory alloys are widely noticed because of their good hot/cold workability. β base Co–Ni–Al alloys have the B2 → $L1_0$ phase transformation, the Curie and the martensitic transition temperatures of the β phase increase and decrease with increasing the Co content, respectively [7,8]. Chen and Han [10] have added Co into NiAl and show that the compressive strength and compressive ductility of the stoichiometric NiAl have been greatly improved by adding proper amount of Co.

NiAl intermetallics have several potential applications including turbochargers, high-temperature dies and moulds, furnace fixtures, rollers in steel slab heating furnaces, hydroturbines, cutting tools, pistons and valves and various components within gas turbines [11]. There are many ways in order to produce intermetallic compounds such as self-propagating high-temperature synthesis, powder processing, casting and combustion synthesis [12]. One of the simple, fast and economic production process combustion synthesis (CS) process is based on the concept that an exothermic wave propagating in a self-sustained manner through a heterogeneous medium, is used to synthesize different advanced materials [13–17]. There are two modes by which CS can occur: self-propagating high-temperature synthesis (SHS) and volume combustion synthesis (VCS). In both cases, reactants may be pressed into a pellet, typically cylindrical in shape. The samples are then heated by an external source (e.g., tungsten coil, laser) either locally or uniformly to initiate an exothermic reaction [17,18]. On the other hand, the problem such as porosity has prohibited the

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wide spread use of combustion method [12,19]. The formation of porosity can be eliminated by careful control over the reaction and/or through the application of external pressure during CS [20].

The main aim of present study is to investigate the effect of cobalt on properties of NiAl intermetallics manufactured by pressure-assisted combustion synthesis.

2. Experimental details

2.1. Production of test materials

In order to manufacture intermetallic materials as starting materials gas-atomized aluminum powder with 15 μm size, carbonyl-nickel powder 4–7 μm size and cobalt powder 10–44 μm size having 99%, 99.8% and 99.9% purity, respectively were used. Ni and Al powders were mixed in stoichiometric ratio corresponding to the NiAl intermetallic phase, in a molar proportion of 1:1. The powders including 2.5 wt.% Co and 5 wt.% Co as alloying element were mixed in a ball mill for 10 min. in Ar + 3% H_2 gas medium with the addition of small amount of 0.1 ethanol. Prior to sintering, the mixture was cold pressed into a cylindrical compact in a metal die coated with a thin layer of boron nitride under a uniaxial pressure of 150 MPa. The diameter and height of the compact samples were 15 mm and 5 mm, respectively. The compacts were synthesized and simultaneously consolidated in open atmosphere. Then the samples were heated at a heating rate of 20 °C min^{-1} to sintering temperature, 1050 °C, and hold at this temperature for 60 min. Process was carried out without using vacuum and inert gas under a uniaxial pressure of 150 MPa. The samples were removed from the furnace having 900 °C in normal atmosphere then cooled to room temperature.

2.2. Characterization

Thermal analysis was performed by differential scanning calorimeter (DSC) to determine the reaction sequence and the ignition point in nitrogen atmosphere and at a heating rate of 20 °C min^{-1} on consisting of three different powders mixture. The relative and bulk densities of the synthesized samples were measured in terms of Archimedes' method. The samples were polished and etched using a solution of HNO_3 (33.3 vol.%), CH_3COOH (33.3 vol.%) and HCl (33.3 vol.%). The presence of NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co materials was determined using Rigaku X-

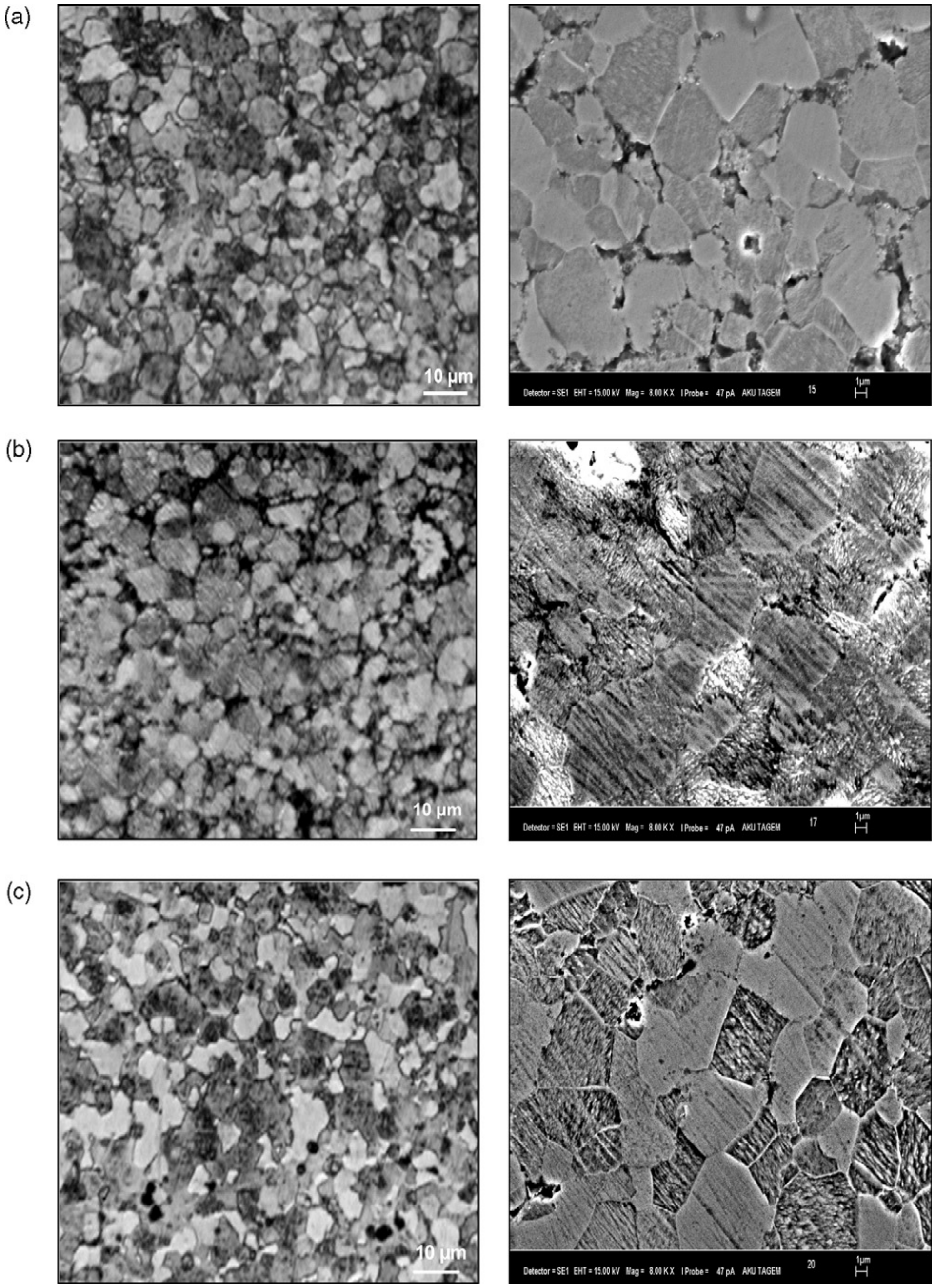

Fig. 1. Optical (left side) and SEM (right side) views of (a) NiAl, (b) NiAl + 2.5 wt.% Co, and (c) NiAl + 5 wt.% Co.

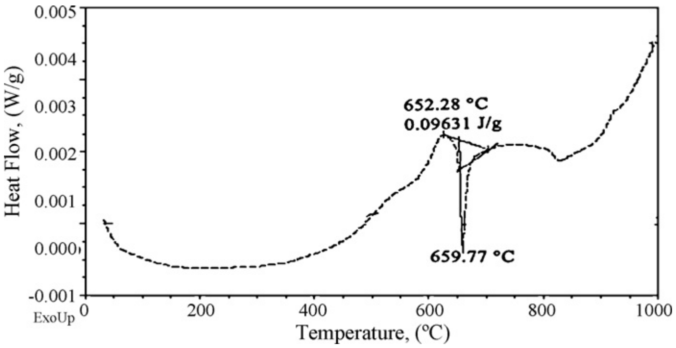

Fig. 2. DSC analysis of NiAl intermetallic containing 5 wt.% Co.

ray diffractometer with CuKα radiation with a wavelength of 1.5418 Å over a 2θ range from 10° to 90°. Microstructural analyses were performed by SEM and optical microscopy. Microhardness of sintered samples was determined using Vickers indentation technique with a load of 10 N on polished transversal cross-sectional area of test materials. The morphology and distribution of alloying elements within test materials were determined by light microscope and SEM–EDS.

3. Experimental results

3.1. Microstructure

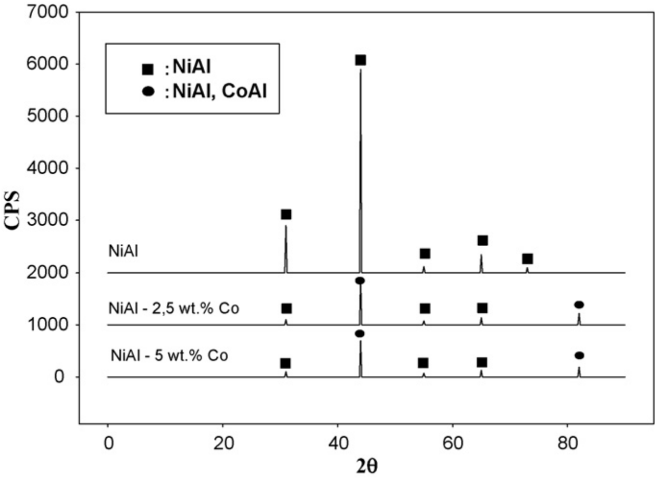

Fig. 3. XRD patterns of NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co.

Fig. 1a–c shows the microstructure of NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co intermetallics compounds produced by pressure-assisted combustion synthesis method which confirmed by optical (LM) and scanning electron microscopy (SEM) examinations. After 1 h at 1050 °C the reaction is completed and the samples having a uniform NiAl structure with small amount of porosity were produced. As it can be seen in Fig. 1 the microstructure of NiAl manufactured by pressure-assisted combustion synthesis has dense and equiaxed grain morphology. It was observed that addition of Co into NiAl makes more prominent formation of eutectic like structure.

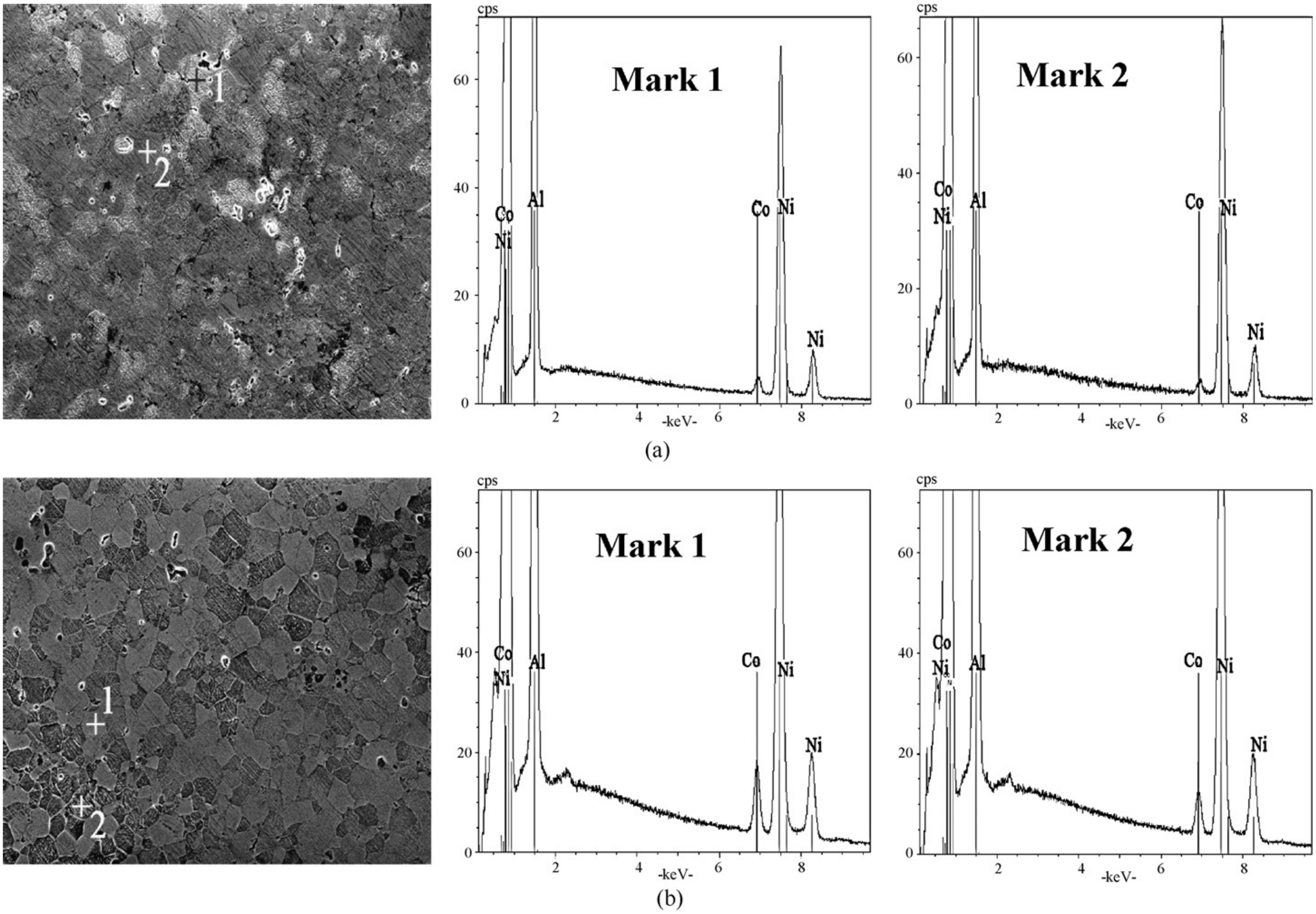

Fig. 4. EDS analysis of (a) NiAl + 2.5 wt.% Co and (b) NiAl + 5 wt.% Co.

Table 1
DSC results of test materials.

Sample	Exothermic temperature (°C)	Enthalpy of fusion (J/g)	Endothermic temperature (°C)
NiAl	654.26	0.06115	661.92
NiAl + 2.5 wt.% Co	653.73	0.05888	661.91
NiAl + 5 wt.% Co	652.28	0.09631	659.77

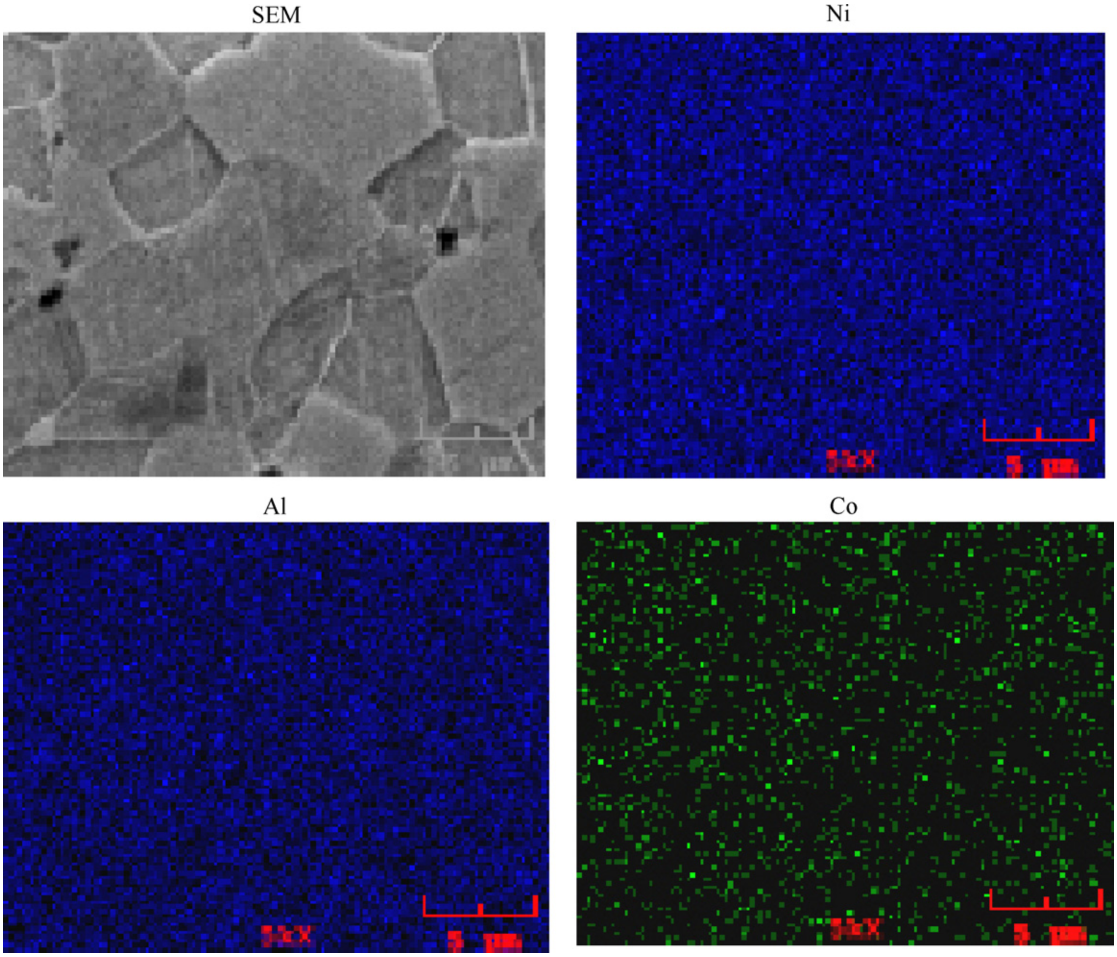

Fig. 5. Map analyses of NiAl + 5 wt.% Co.

3.2. Material characterization

The formation temperature of intermetallic compounds which consisting of NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co powders mixtures was determined by DSC analysis, and exothermic reaction temperature, endothermic temperature and heat capacity of powder mixtures during the combustion synthesis were given in Table 1. As it can be seen in Table 1 there is no remarkable effect of Co on formation temperature of NiAl intermetallic compound (Fig. 2).

The formation mechanism of intermetallic nickel aluminides was given in previous study [13]. The XRD patterns of test materials indicate that the NiAl and CoAl are dominant phases in the samples (Fig. 3a–c).

The distribution of alloying elements on the surface of test samples was determined by energy dispersive spectroscopy (EDS) analysis as shown in Fig. 4a and b. Fig. 5 shows map analyses of Ni, Al and Co elements.

The hardness of NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co samples measured using Vickers indentation technique with a load of 10 N was approximately 367.5 ± 17 $HV_{1.0}$, 398.4 ± 21 $HV_{1.0}$, 424.7 ± 6 $HV_{1.0}$, respectively. The densities of the samples calculated according to Archimedes' principle were approximately 5.63 g/cm^3, 5.68 g/cm^3, and 5.72 g/cm^3, respectively which are in good agreement with theoretical density (approximately 5.65 g/cm^3, 5.71 g/cm^3, and 5.76 g/cm^3). The relative density of pure NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co materials measured in terms of Archimedes' principle was 99.65%, 99.48% and 99.30%, respectively. It can be concluded that the addition of Co into NiAl intermetallics increases hardness reasonable but no remarkable effect on the density of them (Table 2).

4. Discussion

Both optical and SEM cross-sectional examinations revealed that pure NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co intermetallics compounds manufactured by pressure-assisted combustion synthesis without using vacuum or inert gas have a dense microstructure with very low amount of porosity (Fig. 1a–c). There are two distinct regions in test materials containing 2.5 wt.% Co

Table 2
The variation of hardness and density of NiAl intermetallic as a function of Co content.

Sample	Calculated density (g/cm^3)	Theoretical density (g/cm^3)	Relative density (%)	Hardness (HV$_{1.0}$)
NiAl	5.63	5.65	99.65	367.5 ± 17
NiAl + 2.5 wt.% Co	5.68	5.71	99.48	398.4 ± 21
NiAl + 5 wt.% Co	5.72	5.76	99.30	424.7 ± 6

which are dark and bright areas in optical microstructures. EDS quantitative analysis studies showed that the Co content of bright area is 3.32 wt.% Co whereas the Co content on dark one is 2.24 wt.% Co (Fig. 4a). It can be concluded that the Co content of bright area is high in comparison to dark one. The Co amount of NiAl + 5 wt.% Co having the form of eutectic like lamellar structure and the Co amount of smooth lamellar-free structure was determined as 4.68 wt.% Co and 6.65 wt.% Co by EDS (Fig. 4b). Also, map analyses show that the distribution of Co in NiAl + 5 wt.% Co is uniform (Fig. 5). DSC studies showed that there is no remarkable effect of Co on exothermic reaction temperature of NiAl (T_{exo}: 654 °C) (Fig. 2). It was observed that the addition of Co to NiAl intermetallic compound resulted in formation of CoAl intermetallic which confirmed by XRD analysis (Fig. 3). The previous study done by Tian et al. [5] indicated that Co locating sublattice of Ni forms (Ni, Co)Al phase. Nickel and cobalt have similar atomic diameter (0.125 nm) and atomic mass (58.69 and 58.93) but Ni with face centered cubic and Co with hexagonal close packed crystal structure. The stacking of atoms in these two crystal structures are similar therefore, it is possible to claim that each element solve in each other that is, make solid solution. As a matter of fact that a dense NiAl, NiAl + 2.5 wt.% Co and NiAl + 5 wt.% Co intermetallic were obtained which have approximately relative density of 99.65%, 99.48%, 99.30% confirmed by density measurements (Table 2), and the hardness of the samples was approximately 367 ± 17 HV$_{1.0}$, 398.4 ± 21 HV$_{1.0}$, 424.7 ± 6 HV$_{1.0}$, respectively (Fig. 6). Hardness of CoAl (50 at.% Al) compound is 400 kg/mm^2 while hardness of NiAl (50 at.% Al) compound is 300 kg/mm^2 [21]. It is possible to claim that, with the increase of Co content the hardness of test materials increases. Additionally, strength of CoAl is noticeably superior to that of NiAl [22].

In order to prevent porosity being the most obvious disadvantage of combustion synthesis method, by means of pressure quite dense qualified as near to ideal relative density (99.9%) specimens were manufactured. Matsuura et al. [23] revealed that the relative density of NiAl increases with increase in pressure but over 100 MPa the effect of increment decreases. As for at high pressure applications e.g. 300 MPa, the specimens having the density close to ideal density have been obtained. In the present study, similar results were obtained by applying a pressure of 150 MPa. In NiAl-based specimens with high aluminum the reason for obtaining high relative density is caused entering of aluminum which forming liquid phase into porosities. Although, with addition of Co having high-melting temperature into NiAl, a decrease has been observed in relative density, the densities of all specimens manufactured are satisfactory. However, with increasing of addition of Co the hardness of specimen consisting of NiAl + 5 wt.% Co was improved approximately 15%.

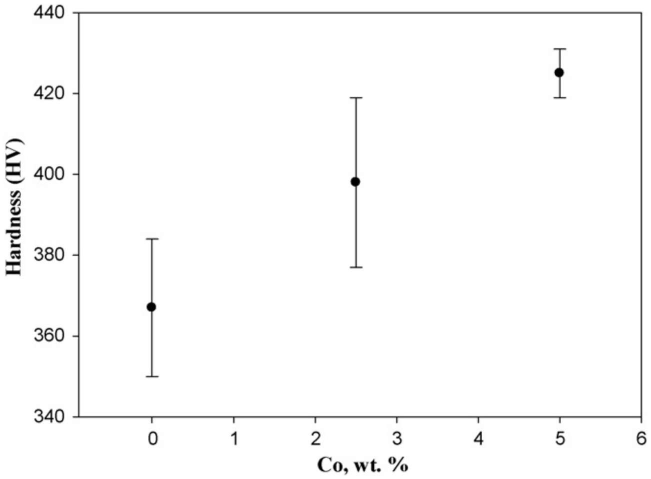

Fig. 6. The variation of hardness of test materials as a function of Co content.

5. Conclusions

The following results can be derived from present study:

(a) Intermetallic compounds produced by combustion synthesis have low porosity and phase transformation has been completed.
(b) The presence of NiAl and CoAl phases was confirmed by XRD analysis.
(c) The relative density is 99.6% for pure NiAl, 99.48% for NiAl + 2.5 wt.% Co and 99.3% for NiAl + 5 wt.% Co.
(d) The microhardness of materials measured by Vickers indenter was increased from 368 HV$_{1.0}$ to HV$_{1.0}$ 398 and 425 HV$_{1.0}$ due to solid solution hardening.

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