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Production and Characterization of $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ Powders by Volume Combustion Synthesis

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Research Article

ABSTRACT

Nickel aluminide (NiAl) is an essential intermetallic material with a high melting point and excellent high temperature corrosion resistance. It is a solid solution of Ni and Al in 40-61 mol.% Ni range. In this study, $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders were formed by using nickel and aluminum elemental powders through volume combustion synthesis (VCS). MgO powder was utilized as the thermal diluent. According to adiabatic temperature calculations, MgO was added to the reactant mixture in 10-40 vol.% range for preventing the melting and sintering of the formed $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ particles. After VCS, the products were ground into powder form and leached in 3M HCl solution in order to remove the MgO particles. After VCS, the samples which were obtained with 10 - 30 vol.% MgO addition were quite hard and difficult to grind. This indicated the partial sintering of the formed particles. It was relatively easier to grind into powder form the samples which contained 40 vol.% MgO. Therefore, it was determined that the most suitable MgO ratio for the formation of $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders was 40 vol.%. Formed powders were mostly in 5-100 µm particle size range. The formation of single phase pure powders was confirmed by the XRD analyses. A shift of about 0.1 degrees to higher 2-theta values was determined in the XRD peaks of the $Ni_{0.55}Al_{0.45}$ powder as compared to the $Ni_{0.50}Al_{0.50}$ phase, after annealing the powders. The results were in agreement with the crystallographic data.

Keywords: NiAl powder, Thermal diluent, Volume combustion synthesis.

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Introduction

NiAl has useful traits such as high melting temperature, low density, good environmental resistance and high thermal conductivity. NiAl is a solid solution of Ni and Al in 40-61 mol.% Ni range [1]. Due to its beneficial properties, it has long been studied as a potential material in various areas requiring especially high temperatures, such as the aerospace industry [2,3]. NiAl provides excellent high temperature properties and specific strength that is close to those of superalloys and ceramics at high temperatures. This is mainly due to the strong bond between aluminum and nickel [4].

NiAl powders can be produced by different methods with certain compositions by using elemental powder mixtures of nickel and aluminum such as reactive sintering and combustion synthesis [1,5,6]. In the study of Portnoy et al. [1], NiAl powders were produced through mechanical alloying of Ni and Al powders. A vibratory mill was utilized and NiAl formation was seen to be completed after 220 min of milling. It was reported that the NiAl (B2) phase was obtained by a fast exothermic reaction in solid form, and no intermediate solid solutions formed. Samples were annealed at 720 °C homogenization. It was reported that better crystallinity was obtained, with reduction in the width of the XRD peaks and approaching of the lattice parameter to equilibrium value.

Povarova et al. [5] studied on production of NiAl powders by various methods. They conducted mechanical alloying, carbonyl decomposition and also by spraying of NiAl melts. For mechanical alloying, they employed an attritor. After annealing of the obtained powders, a decrease in the XRD peak width was observed. It was suggested that the reaction in reactive sintering starts in the solid phase and continues with diffusion, during which pore formation takes place as a result of Kirkendall effect. The NiAl particles which were obtained by melt spraying were in 100-400 micrometer size range. Microheterogeneity was detected in this type of powder, in which Al deficiency was observed near the grain boundaries.

Combustion synthesis is a technique that utilizes the exothermic enthalpy of the reactions. In volume combustion synthesis, the reaction between the reactants takes place in the whole volume of the reactant mixture instantaneously during heating [7,8]. Therefore, this method bears the advantages of being easy to apply, low cost and simple.

In the Ni-Al system, combustion synthesis results in partial melting of the product NiAl phase. Since the temperature of the products reaches the melting point of NiAl, as a result of the exothermicity of the reaction. In order to reduce the combustion temperature, thermal

diluents are utilized. Generally, some of the product powder is added to the initial reactant mixture in order to absorb some of the released heat and to decrease the combustion temperature [9,10]. In our previous study, effect of addition of preformed NiAl powder as the thermal diluent, on the formation of porous NiAl was investigated [10].

In the present study, the thermal diluent MgO, which is used to prevent NiAl from melting during combustion synthesis is preferred because MgO does not react with the reactants or the products in the Ni-Al system. In addition, it does not melt during the reaction and can be selectively separated with the help of acid solution after the reaction. As to the knowledge of the authors, the utilization of MgO as a thermal diluent in the Ni-Al system has not been investigated in the literature, previously.

The aim of this study is to base the starting powder generation method for the production of $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders by volume combustion synthesis and to examine the structure of the produced powders. It was reported that the changes in the stoichiometry of the NiAl solid solution provides tailoring of some of the properties. For example, the thermal conductivity of $Ni_{0.55}Al_{0.45}$ is about 50 % less than that of $Ni_{0.50}Al_{0.50}$ [11]. Thus in this study, formation of powders in the solid solution region of NiAl has been demonstrated.

Materials and Methods

Sample Preparation

$Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders were produced via volume combustion synthesis (VCS) by using Ni, Al powders according to Reaction (1). Y denotes the amount of MgO, which was added to Ni and Al powder mixture.

$$Ni + Al + (Y)\ MgO_{(s)} = NiAl + (Y)\ MgO_{(s)} \tag{1}$$
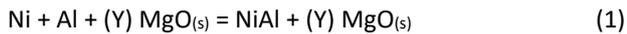
MgO powder (Merck, purity 99.5%, particle size <1 μm) was added to the Ni and Al starting powders as a thermal diluent in order to reduce the combustion temperature and to prevent the melting and sintering of the formed $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ particles. With the experiments, it was understood that MgO did not react with Ni and Al. Adiabatic temperature calculation was made by using the HSC Chemistry software and database, to determine the diluent MgO ratio to be used. In this study, according to adiabatic temperature calculations, MgO was added to the Ni-Al reactant mixture in 10-40 vol.% range. Ni and Al powders containing 10-40 vol.% MgO were weighed and mixed. The prepared powder mixture was taken into a steel mold with a diameter of 10 mm, a pressure of 50 MPa was applied.

The compressed sample was placed in a ceramic crucible and it was heated in an induction furnace (Indutherm, Model: MC20V, 3.5kW (Fig. 1)). Inside the ceramic crucible there was a graphite liner, which enabled the heating of the sample by induction current. Inside of the graphite liner was covered with hexagonal boron nitride coating (Ekamold) in order to prevent

contamination and sticking of the pellet to the crucible. The induction furnace is equipped with an optical pyrometer. 2 consecutive vacuum-argon filling cycles were applied prior to heating the samples. Thus, VCS reaction was conducted in an argon atmosphere.
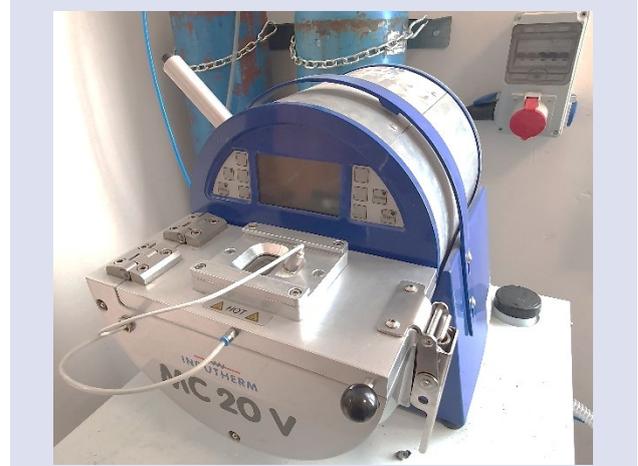
Figure 1. Induction furnace that was used in heating the samples for VCS under Ar atmosphere

It was determined that VCS reaction occurred with the hasty increase in temperature, which was measured by the optical pyrometer of the device.

Leaching and Characterization

The resulting product was crushed in a mortar and it was mixed in 3M HCl with a magnetic stirrer for about 2 hours to remove the MgO. In this process, a solid-liquid ratio of 1:100 was applied. Then, this mixture was separated by centrifugation (Eppendorf) at 5000 rpm for 5 minutes and the obtained powder was dried in an oven at 65 °C for 1 day. By applying the same processes, nickel aluminide powder with the stoichiometry of $Ni_{0.55}Al_{0.45}$ was also produced. Obtained powders were examined by a stereo microscope and scanning electron microscope (SEM, FEI at Süleyman Demirel University). XRD analyses were performed by using Cu-Kα radiation, at a scan rate of 2 degrees per minute, with 0.02 degrees steps (Rigaku, Multiflex at Hatay Mustafa Kemal University). Phase analyses were performed and the 2-theta values of the XRD peaks of the produced samples were acquired by the Quantitative Analysis Software.

Results and Discussion

Adiabatic Temperature

The adiabatic temperature is defined as the theoretical maximum temperature that the products can achieve, as a result of an exothermic reaction. The results of the adiabatic temperature calculations of the Ni-Al systems containing 0-60 vol.% MgO, made by the HSC Chemistry software and database according to Reaction (1) are presented in Fig.2. It can be seen that the adiabatic temperature keeps unchanged up to 25 vol.% MgO addition. 1638.9 °C is the melting temperature of NiAl.

When there is no diluent in the system, a certain fraction of NiAl in the products melts. When the diluent MgO is not sufficient, the high amount of liquid phase formed in the system causes the product pellet to lose its form. The ratio of the liquid phase is expected to decrease with increasing addition of the thermal diluent MgO to the initial mixture. Because, both the amount of Ni+Al that generates heat is reduced, and MgO takes some of the evolved heat.

The adiabatic temperature starts to decrease after 25% addition of MgO. Theoretically, the heat generated after this point is not sufficient to cause the formation of any molten phase, when the ignition temperature is 25 $^{\circ}$C. Therefore, there will be no liquid phase formation in the products. As a result of 40% MgO is addition to the Ni+Al mixture, the adiabatic temperature is calculated as 1460.8 $^{\circ}$C. Considering the preheating of the pellet and the fact that ignition takes place at about 500°C, the attained combustion temperature may be higher than the calculated adiabatic temperature. However, when the heat losses from the pellet to the substrate and the crucible is taken into account, it is possible to consider the calculated adiabatic temperatures as close to the attained combustion temperatures. Thus, in the present study, according to adiabatic temperature calculations, MgO was added to the reactant mixture in 10, 20, 30 and 40 vol.% range.
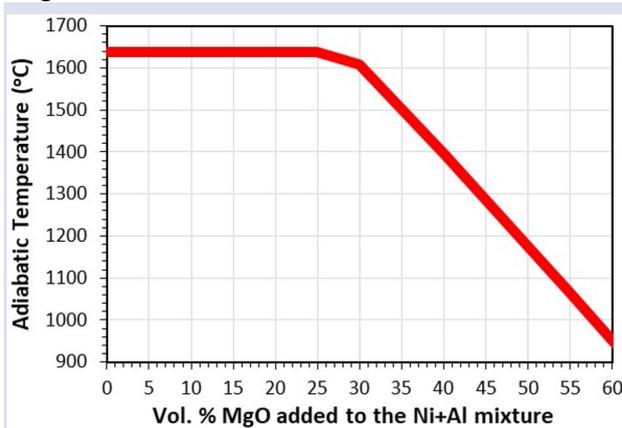
Figure 2. Change in the adiabatic temperature of Ni-Al system as a function of MgO thermal diluent addition.

Form of the Products After VCS

During heating in the induction furnace, the samples were found to ignite at about 660 $^{\circ}$C. An increase in the temperature was observed at that point. In some experiments during heating, the pellets that contained 10-30 vol.% MgO exhibited cracking and fragmentation. This was attributed to the fast temperature increase. In the sample which contained 10 vol.% MgO, formation of droplets of NiAl was observed on the surface of the product pellet (Fig. 3(a)). The form of the pellet was seen to be observed much better when 30 vol.% MgO was utilized (Fig. 3(b)).

After VCS, the samples which were obtained with 10-30 vol.% MgO addition were quite hard and difficult to grind. This indicated the partial sintering of the formed particles. It was relatively easier to grind into powder form the samples which contained 40 vol.% MgO.

| (a) | (b) |
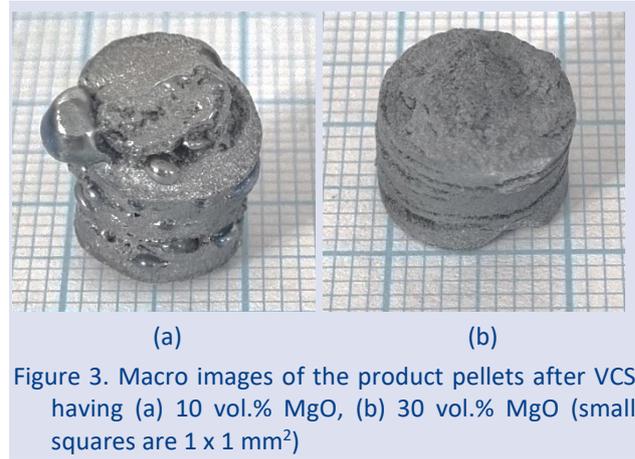
Figure 3. Macro images of the product pellets after VCS having (a) 10 vol.% MgO, (b) 30 vol.% MgO (small squares are 1 x 1 mm^2)

Therefore, it was determined that the most suitable MgO ratio for the formation of Ni$_{0.50}$Al$_{0.50}$ and Ni$_{0.55}$Al$_{0.45}$ powders was 40 vol.%. This result shows that MgO acted as an effective thermal diluent and melting and sintering of the formed NiAl particles could be prevented.

XRD Analyses After VCS

The production of Ni$_{0.50}$Al$_{50}$ and Ni$_{0.55}$Al$_{0.45}$ powders was carried out by the same methods. Ni$_{0.55}$Al$_{0.45}$ composition is in the NiAl solid solution region according to the Ni-Al phase diagram [12]. The XRD patterns of Ni$_{50}$Al$_{50}$ and Ni$_{55}$Al$_{45}$ powders obtained from VCS reaction of 40 vol.% MgO added reactants, after acid dissolution, centrifugation separation and drying are presented in Fig. 4. The indices of the pertaining planes are indicated on the XRD peaks.

The XRD peaks of Ni$_{55}$Al$_{45}$ is expected to be at about 0.1 degrees to higher 2-theta values as compared to those of Ni$_{50}$Al$_{50}$ according to the provided international center for diffraction data (ICDD) card values given in Table 1. The obtained results are in favor of this expectation. The 2-theta values of the XRD peaks of the produced samples were acquired by the Quantitative Analysis Software. According to the XRD analysis, it was understood that single phase, pure Ni$_{50}$Al$_{50}$ and Ni$_{55}$Al$_{45}$ powders were obtained by the applied method. All of the peaks in the XRD patterns in Fig. 4 pertain to the expected phases. From XRD analysis, it was inferred that Reaction (1) was completed and no by-products were formed. In addition, there were no MgO peaks in the XRD patterns. This shows that the MgO used as the thermal diluent was completely removed from the products.
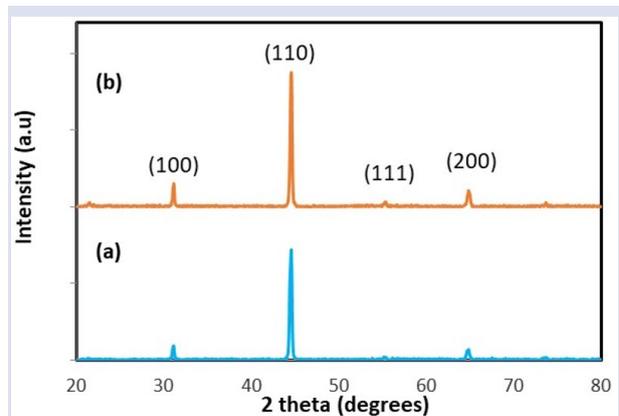
Figure 4. XRD patterns of VCS produced a) Ni$_{0.50}$Al$_{0.50}$ and b) Ni$_{0.55}$Al$_{0.45}$ powders.

Table 1. Two-theta and interplanar spacing (d) values of the produced $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders after VCS, as acquired by the Quantitative Analyses Software. (Crystallographic database values are also presented).

hkl	$Ni_{0.50}Al_{0.50}$ #20-0019		$Ni_{0.50}Al_{0.50}$ After VCS		$Ni_{0.55}Al_{0.45}$ #44-1185		$Ni_{0.55}Al_{0.45}$ After VCS	
	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)
100	30.92	2.89	31.05	2.8779	31.08	2.876	31.10	2.8734
110	44.37	2.04	44.50	2.0343	44.51	2.034	44.55	2.0322
111	55.04	1.667	55.10	1.6654	55.26	1.661	55.30	1.6599
200	64.48	1.444	64.80	1.4376	64.77	1.438	64.85	1.3626

The expanded 44-45 degrees region of the XRD patterns of the $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders are presented in Fig. 5. The peaks pertaining to the (110) planes of the obtained powders can be seen. The $Ni_{0.50}Al_{0.50}$ powder exhibited a double peak at 44.35° and one is at 44.55° 2-theta values. This can be attributed to in insufficient diffusion, which may have resulted from quick heating and cooling that took place during VCS. In addition, it is probable that some Al may have been lost, due to probable oxidation during synthesis. Thus, the stoichiometry of the $Ni_{0.50}Al_{0.50}$ powder seems to have slightly shifted to Ni rich values. Nevertheless, the difference in the lattice parameters of the NiAl powders having 2 different compositions can be seen in the XRD analyses. The (110) peak of the $Ni_{0.55}Al_{0.45}$ is at 44.55°.
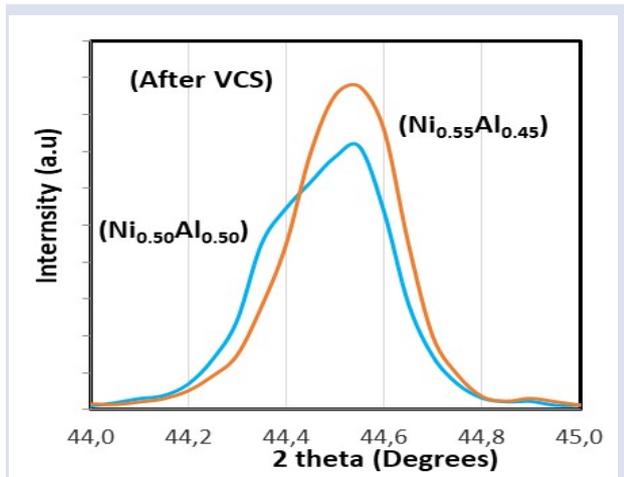
Figure 5. Expanded 44-45 degrees portion of the XRD patterns of VCS produced samples exhibiting the peak pertaining to the (110) plane. $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders.

XRD Analyses After Annealing

XRD patterns of VCS produced a) $Ni_{50}Al_{50}$ and b) $Ni_{55}Al_{45}$ powders after annealing at 1200 °C for 2 h are presented in Fig. 6. It was observed that the width of the XRD peaks decreased after annealing of the produced powders. Similar findings were also reported by Portnoy (2002)[1] after annealing the NiAl powders which were produced by mechanical alloying. The decrease in the width of the XRD peaks may be attributed to the increase in the crystallite size [13].
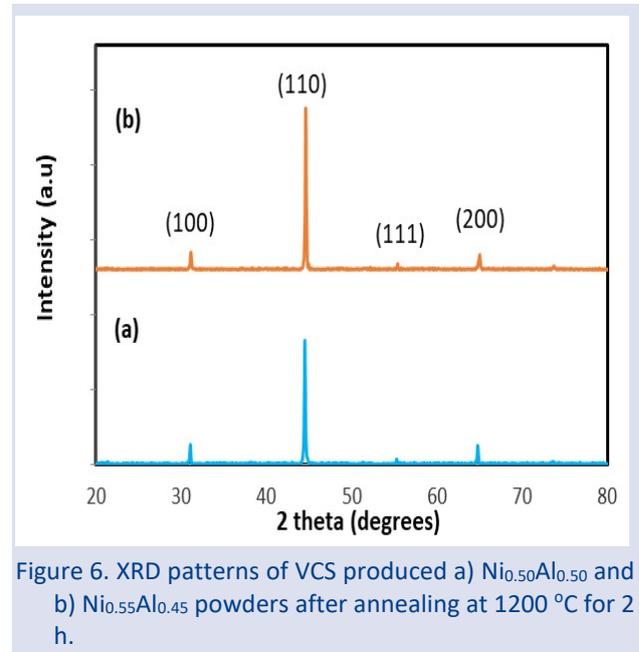
Figure 6. XRD patterns of VCS produced a) $Ni_{0.50}Al_{0.50}$ and b) $Ni_{0.55}Al_{0.45}$ powders after annealing at 1200 °C for 2 h.

In addition, the XRD peaks of $Ni_{55}Al_{45}$ was seen to which to slightly higher 2-theta values as compared to the non-annealed condition (Table 2).

Table 2 Two-theta and interplanar spacing (d) values of the produced $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders after annealing at 1200 °C for 2h. (Crystallographic database values are also presented).

hkl	$Ni_{0.50}Al_{0.50}$ #20-0019		$Ni_{0.50}Al_{0.50}$ After VCS and annealing at 1200 oC		$Ni_{0.55}Al_{0.45}$ #44-1185		$Ni_{0.55}Al_{0.45}$ After VCS and annealing at 1200 oC	
	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)	2 theta (deg.)	d (A°)
100	30.92	2.89	31.10	2.8734	31.08	2.876	31.15	2.8689
110	44.37	2.04	44.50	2.0343	44.51	2.034	44.60	2.030
111	55.04	1.667	55.30	1.6599	55.26	1.661	55.35	1.6585
200	64.48	1.444	64.75	1.4386	64.77	1.438	65.00	1.4336

The expanded 44-45 degrees region of the XRD patterns of the $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders after annealing are presented in Fig. 7. The double peak which was present in the XRD pattern of $Ni_{0.50}Al_{0.50}$ powder before annealing was seen to convert into a single peak at 44.50 degrees. This is believed to take place due to diffusion during annealing at 1200 °C. The (110) peak of the $Ni_{0.55}Al_{0.45}$ is at 44.60°. The 2-theta values of the $Ni_{0.55}Al_{0.45}$ sample is at about 0.1 degrees higher 2-theta values, as compared to $Ni_{0.50}Al_{0.50}$ sample. This result is in accordance with the ICDD data. The width of the peaks can be seen to decrease by annealing, as compared to the peaks of the non-annealed samples given in Fig.5. These results are in agreement with the literature. In the study of Portnoy (2002), similar results were obtained.

Figure 8. Macro image of the produced $Ni_{0.50}Al_{0.50}$ powder (small squares: 1 x 1 mm^2)

Figure 7. Expanded 44-45 degrees portion of the XRD patterns of VCS produced samples after annealing at 1200 °C for 2 h, exhibiting the peak pertaining to the (110) plane. $Ni_{0.50}Al_{0.50}$ and $Ni_{0.55}Al_{0.45}$ powders.
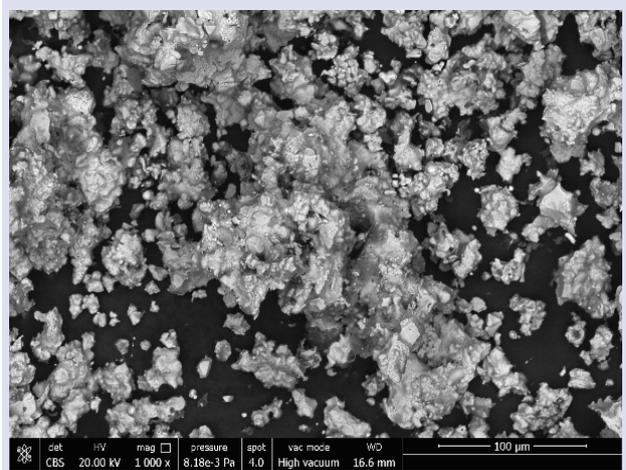
Figure 9. SEM image of the produced NiAl powder (1000X)

Microscopic Examination of the Produced Powders

Macro image of the produced $Ni_{0.50}Al_{0.50}$ powder, which was obtained by a stereo microscope, is presented in Fig. 8. The NiAl powder can be seen as the black particles on the graded paper (small squares are 1 x 1 mm^2). The product pellet could be finely ground. Particles having sizes below 100 µm were obtained. No difference in the size and morphology of the produced NiAl powders having different compositions was observed by the microscopic examinations.

SEM images of the prepared powders are presented in Figure 4. In SEM examinations, it was observed that the produced NiAl particles had irregular shape. They generally consisted of 5-10 µm sized parts (Figure 4 (a)) and partially incompletely fragmented porous chunks of about 100 µm (Figure 9). Formed powders were in 5-100 µm particle size range.

It can be proposed that the particles size of the formed powder can be modified by altering the duration of grinding operation.

The chunks are seen to have a porous character (Fig. 10). This may be due to the removed MgO particles from the structure. In addition, during the reaction between Ni and Al, micro porosity was suggested to form due to Kirkendall effect, and also due to the density difference between the reactants and the products.
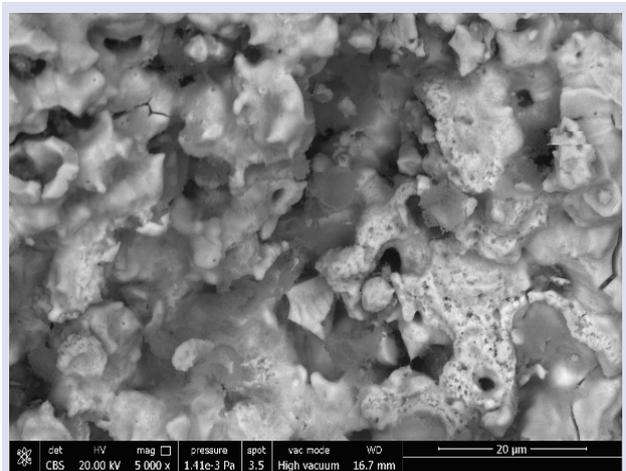
Figure 10. SEM images of the produced NiAl powder showing the structure of a large particle (5000 X)

Conclusion

Formation of $Ni_{0.50}Al_{0.50}$ and $Ni_{0.45}Al_{0.55}$ powders was achieved by volume combustion synthesis through heating the Ni, Al and 40 vol.% MgO powder mixtures in an induction furnace. When the samples were produced by adding 10-20 vol. % MgO, they exhibited partial melting. The samples which contained 10-30 vol. % MgO were hard and difficult to grind. As the MgO ratio by volume increased (40% MgO), it was easier to grind the produced samples. For this reason, the 40% vol. MgO was chosen as the most suitable ratio for the production of NiAl powders. The particle sizes of the produced powders were in the range of 5-100 μm. Formation of single-phase pure powders of $Ni_{0.50}Al_{0.50}$ and $Ni_{0.45}Al_{0.55}$ were verified by XRD analyses. After annealing the powders, the XRD peaks of the $Ni_{0.55}Al_{0.45}$ powder were at about 0.1 degrees higher 2-theta values as compared to the $Ni_{0.50}Al_{0.50}$ phase. The results were in agreement with the crystallographic data.

Acknowledgements

Conflict of Interest

Authors declare no conflict of interest.

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