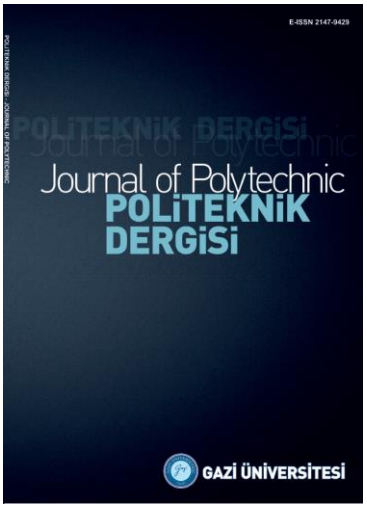

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The effect of process parameters on microstructure and porosity of layered NiAl(Co/Cr) alloy produced by SHS method

SHS yöntemiyle üretilen tabakalı NiAl(Co/Cr) alaşımının mikroyapı ve gözenek oranına işlem parametrelerinin etkisi

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SHS Yöntemiyle Üretilen Tabakalı Nial(Co/Cr) Alaşımının Mikroyapı ve Gözenek Oranına İşlem Parametrelerinin Etkisi

Araştırma Makalesi / Research Article

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ÖZ

Bu çalışmada SHS yöntemiyle üretilmiş olan tabakalı NiAl(Co/Cr)alaşımının mikroyapı ve gözenek oranına sıkıştırma basıncı, ön ısıtma ve alaşımlamanın etkisi incelendi. % 50 Ni-%50 Al tozlarına her tabakaya %3, %6 ve %10 Co ve Cr tozları ilave edilerek 300 dev/dk hızında 12 saat süreyle döner bir kap içerisinde karıştırıldı. Karıştırılan tozlar bir kalıp içerisinde soğuk presle 50,100 ve 200 MPa basınçla briketlendi. Elde edilen ham numuneler daha sonra argon atmosfer kontrolündeki bir odacığa alınarak ön ısıtmasız ve 250 ^{o}C ön ısıtmalı olarak ateşlenerek sentezlendi. Yanma reaksiyonu ile sentezlenen numunelerin mikroyapıları, elementel analizi ve faz analizi SEM-BSE, EDS ve XRD cihazlarıyla incelendi. EDS analizi sonucunda en yüksek değerde Ni elementinin olduğu, bunu takiben Al ve alaşıma göre Co ve Cr olduğu belirlendi. Faz bileşenlerini belirlemek için yapılan XRD analizinde ise en yüksek pik değerlerin NiAl olduğu, düşük değerdeki piklerin Ni_3Al ve $NiAl_3$ olduğu tespit edildi. Yapılan yoğunluk hesaplamaları sonucunda gözenek oranını etkileyen en önemli parametrenin sıkıştırma basıncının olduğu, bunun temel nedeninin basıncının artmasıyla tozların birbirine temasının artması sonuncunda yanma reaksiyonun kesilmeden ilerlemesi, ergimiş tozların yer değiştirme fırsatı olmadan katılaşmasından kaynaklandığı düşünülmektedir. En yüksek gözenek değerleri ön ısıtmasız 50 MPa basınca sahip numunelerde oluştuğu belirlendi.

Keywords: NiAl, NiAlCoCr, nikel alüminat, SHS, gözeneklik.

The Effect of Process Parameters on Microstructure and Porosity of Layered NiAl(Co/Cr) Alloy Produced by SHS Method

ABSTRACT

This paper deals with the investigation of microstructure and porosity of layered compounds of NiAl(Co/Cr) powders by SHS method. Layers of 50% Ni-50% Al powders were mixed with 3%, 6% and 10% of Co and Cr powders. These were mixed for 12 hours in a rotational container with a speed of 300 rpm. Mixed powders were cold compressed in a mould with pressures of 50, 100 and 200 MPa. The obtained samples were then synthesized in an argon controlled atmosphere with and without preheating to 250 ^{o}C. The microstructure of synthesized samples was analysed using SEM-BSE, EDS and XRD. The EDS results showed that the samples were containing Ni in majority along with Al, Co, and Cr. To determine the phase components, XRD spectra was analysed and the peaks of NiAl, Ni_3Al, and $NiAl_3$ were confirmed with NiAl having the highest peak intensity. The density calculations showed that the ratio of pores was affected the most from pressure. The main reason for this was attributed to the better contact of the powders under higher pressure which helped an uninterrupted reaction. The highest pore ratio values were obtained from samples produced under 50 MPa pressure.

Keywords: NiAl, NiAlCoCr, nickel aluminide, SHS, porosity.

1. INTRODUCTION

Intermetallic compounds are promising materials due to their high temperature oxidation resistance, excellent thermal stresses and low density [1]. Due to their resistance to elevated temperatures and aggressive environments, FeAl, Fe_3Al, NiAl and Ni_3Al are promising materials among intermetallic aluminides [2]. In the binary phase NiAl diagram, intermetallic compounds of $NiAl_3$, Ni_2Al_3, Ni_5Al_3, NiAl, and Ni_3Al are present. Of these intermetallic compounds, NiAl and Ni_3Al are the most stable structures of the system [3, 4].

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The production of intermetallic compounds can be performed by powder metallurgy methods, casting and conventional melting processes. On the other hand, the SHS (self propagating high-temperature synthesis) method is one of the powder metallurgy methods that is fast and does not require expensive equipment. There is no need for external heating since the synthesis is performed by self-propagation. This method allows the formation of desired shapes quite successfully [5].

Combustion synthesis, or reaction synthesis, is a method that helps obtaining a desired product in a short time. In other words an exothermic reaction occurs in the first instance of providing enough energy to the raw metal powders. Compared to conventional powder metallurgy methods, SHS method requires less time along with being a cheaper, cleaner and easier process. In the SHS process, the sample is ignited to create a burning wave. This combustion reaction produces exothermic heat, allowing the combustion wave to propagate through the sample [4, 6, 7]. However, the microstructure of materials produced by reaction synthesis contains a significant number of pores. Formation of gases due to impurities that have low boiling points and the expansion of NiAl-Ni_3Al phases at high temperatures leads to pore formation. In case of severe reactions, an explosion can also be observed in the briquette. If the product melts at the combustion temperature as in NiAl, the porosity induced by the solidification shrinkage may occur [4].

The main problem in intermetallic research is that the compounds such as NiAl are brittle, which introduces restriction in shaping. [8].Therefore, finding a solution to those limitations is an important part of this research field. However, in this study rather than focusing on finding a solution to aforementioned problem, the porosity ratio was investigated since this parameter affects mechanical and thermal properties of the formed material [8, 9].

The manufacturability of NiAl alloy was investigated by adding 3%, 6% and 10% layers of Cr which is stated to increase toughness and ductility and Co which is stated to increase the hardness and porosity of the samples according to the changing parameters [8, 9, 10, 11, 12]. Also, SEM-BSE and optical microscopy were used to determine the microstructure. Elemental analysis and phase analysis were performed by EDS and XRD

Table 1. Physical properties of metal powders used in the experiments

Materials	Purity (%)	Powder Size (mesh)	Melting Temperature (^oC)	Specific weight (gr/cm^3)
Aluminium	99.99	325	660	2.700
Nickel	99.99	325	1453	8.908
Cobalt	99.99	325	1495	8.920
Chromium	99.99	325	1875	7.190

Table 2. Atomic and mass ratios with theoretical densities of mixtures of metal powders

Powder Metal Mixture	Atomic Ratio	Mass Ratio	Theoretical Densities
NİAl	50% Ni, 50% Al	76.74% Ni, 23.26% Al	5.804
NiAlCo(3%)	48.5% Ni, 48.5% Al, 3% Co	73.26% Ni, %22.21 Al, 4.53% Co	5.848
NiAlCr(3%)	48.5% Ni, 48.5% Al, 3% Cr	73.91% Ni, 22.40% Al, 3.69% Cr	5.846
NiAlCrCo(1.5% -1.5%)	48.5% Ni, 48.5% Al, 1.5% Co, 1.5% Cr	73.58% Ni, 22.30% Al, 2.27% Co, 1.84% Cr	5.872
NiAlCo(6%)	47% Ni, 47% Al, 6% Co	69.90% Ni, 21.18% Al, 8.92% Co	5.990
NiAlCr(6%)	47% Ni, 47% Al, 6% Cr	71.12% Ni, 21.55% Al, 7.33% Cr	5.890
NiAlCrCo(3%-3%)	47% Ni, 47% Al, 3% Co, 3% Cr	70.53% Ni, 21.38% Al, 4.49% Co, 3.63% Cr	5.940
NiAlCo(10%)	45% Ni, 45% Al, 10% Co	65.56% Ni, 19.88% Al, 14.56% Co	6.110
NiAlCr(10%)	45% Ni, 45% Al, 10% Cr	67.45% Ni, 20.45% Al, 12.10% Cr	5.940
NiAlCrCo(5%-5%)	45% Ni, 45% Al, 5% Co, 5% Cr	66.49% Ni, 20.15% Al, 7.38% Co, 5.96% Cr	6.030

2. MATERIALS AND METHODS

Metal powders of Ni, Al, Co and Cr used in this study were purchased from a commercial supplier. Each stage of the experiment was carried out in the Argon atmosphere. The first sample was prepared using atomic ratios of 50% Ni and 50% Al. 3%, 6% and 10% of Co and Cr were added to prepared Ni-Al mixture. Table 1 provides information on these metal powders.

Metal powder combinations were mixed for 12 hours at 300 rpm in a mixer [13]. Calculations of the atomic and mass ratios and theoretical density of mixtures of Ni, Al, Co and Cr metal powders are given in Table 2.

The powder mixtures obtained at the end of this process are compressed into a cylindrical mold using cold press at 50 MPa, 100 MPa and 200 MPa. Mixture densities were calculated and taken into account in order to obtain the same volume of layers. The porosity of the porous samples calculated with equation [14]:

$$f = 1 - \frac{m}{d.v} \qquad (1)$$

In the latter equation RPW% stands for percentage ratio of weight and ARP is described as atomic ratio percentage. Figure 1 (b) shows the schematic view of raw samples made from 3%, 6% and 10% alloy admixtures in NiAl alloy layers along with the process diagram to achieve it.

An ignition unit was designed to be used for ignition and pre-heating of the pressed samples in the argon atmosphere. This ignition unit consists of preheating chamber, ignition center and reservoir, along with temperature control knob and argon gas inlet-outlet sections. The SHS based production method is depicted in Figure 1 (b) [15]. Samples were classified into two groups. The first group was treated with preheating to 250^{o} C. The other group was not preheated.

The compacted samples were fired in the synthesis chamber with external heat under an argon atmosphere. The theoretical density of the mixtures and the density of the raw samples were obtained. Then, these values were compared to the density of the samples after the synthesis. The porosity to volume ratios of the synthesized samples were determined by weight and size measurements as the samples had regular geometries.

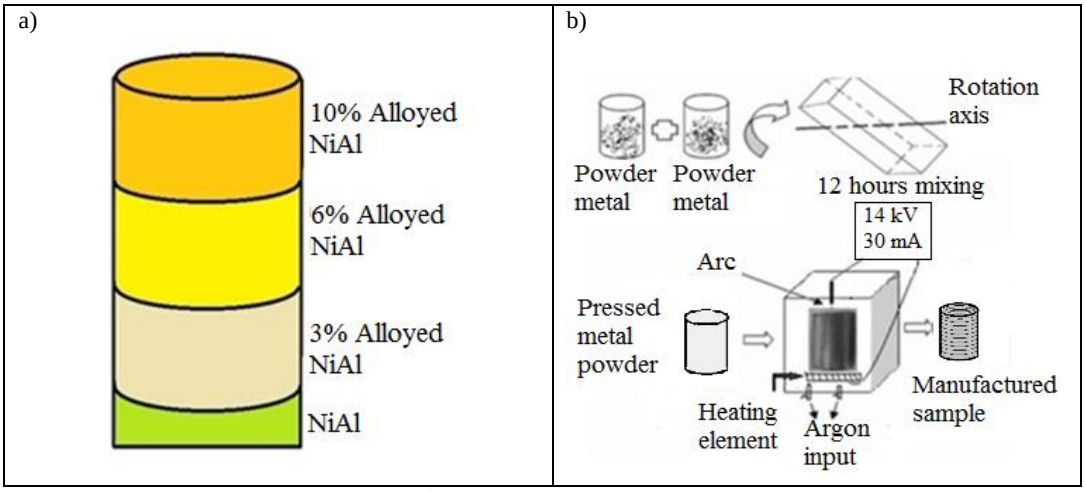

Figure 1. a) Schematic view of raw samples, b) Sample production process diagram

where f stands for pore percentage, m is sample weight, d is theoretical density of the sample and v is porous sample volume. The theoretical density of the porous samples calculated by equation [14] :

$$d_t = \frac{d_1 + d_2 + \cdots + d_n}{v_1 + v_2 + \cdots + v_n} \qquad (2)$$

where d is density v is volume. The ratio of porous samples (weight percentage ratio) calculated by equation [14]:

$$RPW_1\% = = \frac{d_1 * ARP_1}{d_1 * ARP_1 + d_2 * ARP_2 + \cdots + d_n * ARP_n} * 100 \qquad (3)$$

Samples were cut on the cutting disc for metallographic analysis after synthesis. The cut samples were polished using 240, 400, 600, 800, 1000 and 1200 mesh abrasives. After this process, the samples were polished with polishing broadcloth using a 1 µm diamond paste solution for final polishing. 33% HF, 33% HNO3, 33% water solution was used for 15 seconds to perform microstructure analysis of the polished samples [13]. For the microstructure analysis of samples after etching, a Leica optical microscope and a Jeol JSM-5410LV brand SEM-BSE device were used. The elemental analysis of the samples was performed by a Jeol JSM-5410LV EDS device and the phase components were detected with a Rigaku brand XRD device.

3. RESULTS AND DISCUSSION

In this study, different samples were obtained by changing the compression pressure, preheating temperature and reinforcement ratios, which were selected as variables in the process parameters. The porosity of these samples is given in Table 3. The graphs of these values are shown in Figure 2.

As the compression ratio increases, the contact of the powder particles to each other increases and the porosity decreases (14). In addition, the increase in contact is thought to prevent the formation of pores by allowing the raw powders to burn without falling into the cavities during synthesis.

On the other hand, preheating at 250 °C before the synthesis increased the porosity. It is thought that the expansion due to the heat energy given in the raw state increases the porosity due to the fact that the samples do not have time to shrink, together with the rapid rate of the synthesis reaction. Co and Cr additions with different ratios have been determined to increase the porosity in different ratios. However, the Cr addition alone decreased the porosity while the Co addition increased the porosity. This supports the data in the literature [12, 16, 17]. The SEM-BSE images, the optical microscope images and the XRD of the NiAlCo alloy are shown in Figure 3, of the NiAlCr alloy are shown in Figure 4 and of the NiAlCrCo alloy in Figure 5 and the EDS measurements shown in Table 4.

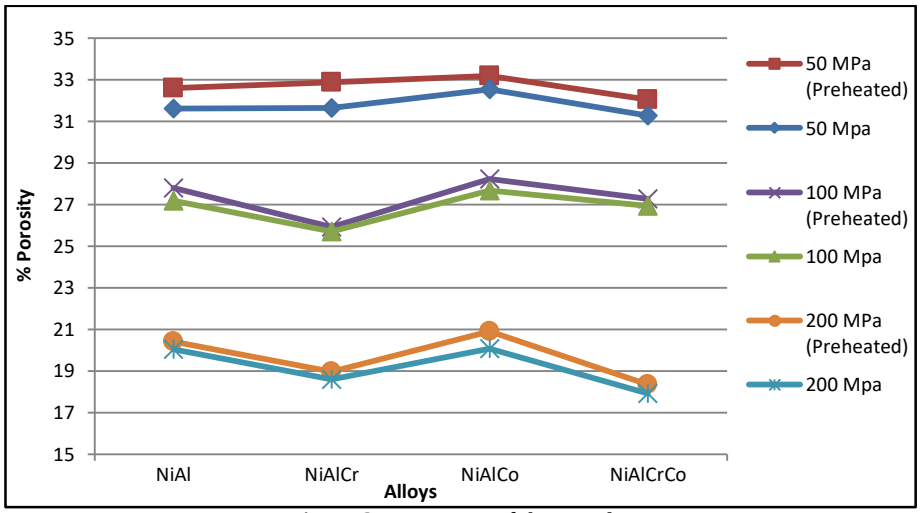

Figure 2. Pore ratios of the samples

Table 3. Pore ratios of samples

	Pressure (MPa)	Pore Ratio	
		Without Preheating (23 °C)	Pre-heated (250 °C)
NiAlCr	50	31.64	32.87
	100	25.69	25.92
	200	18.60	18.97
NiAlCo	50	32.53	33.19
	100	27.69	28.23
	200	20.06	20.90
NiAlCrCo	50	31.29	32.04
	100	26.95	27.28
	200	17.90	18.35
NiAl	50	31.63	32.60
	100	27.17	27.81
	200	20.03	20.40

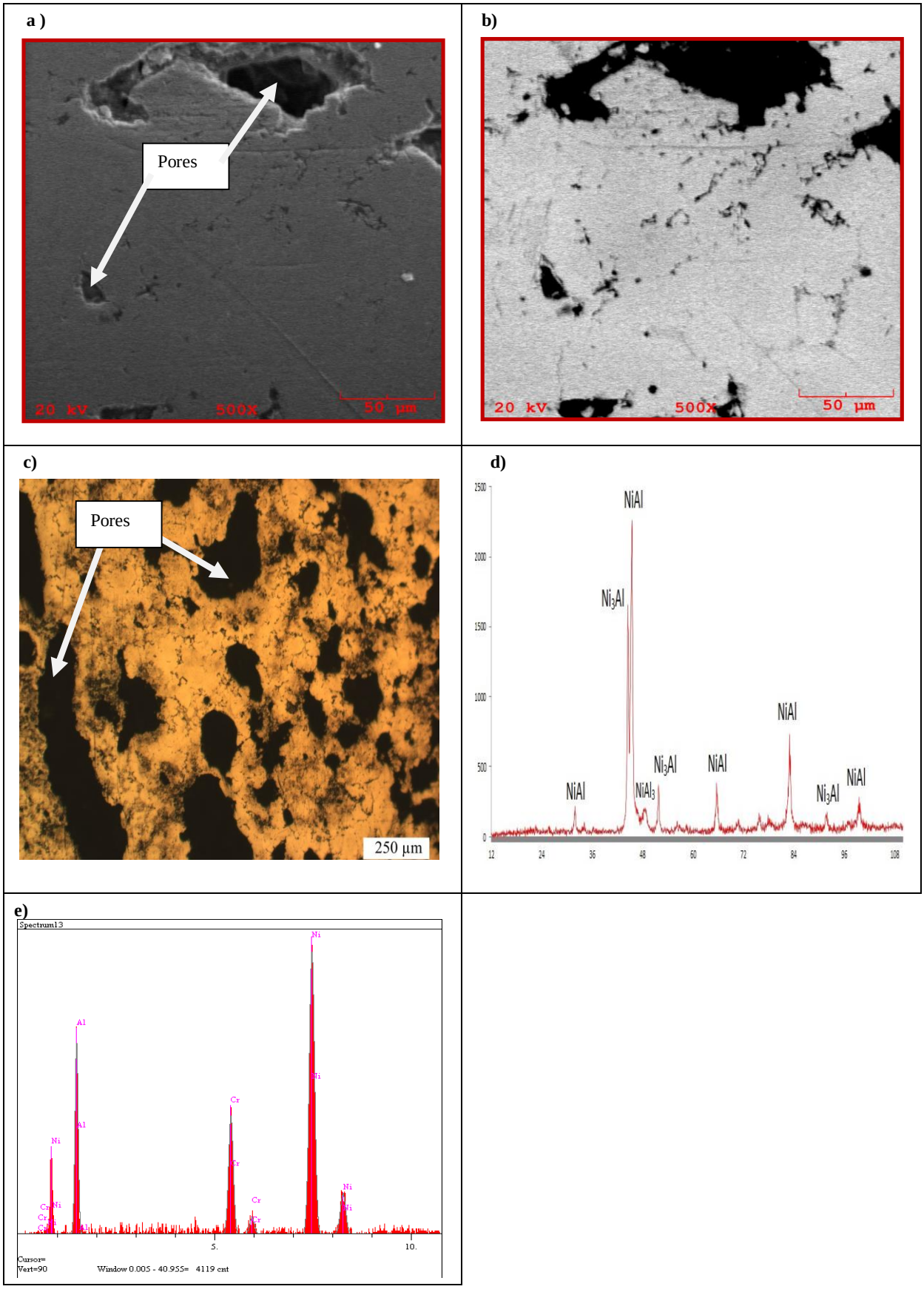

Figure 3. a) SEM, b) BSE and c) Optical microscope images, d) XRD and e) EDS measurements of NiAlCr alloy

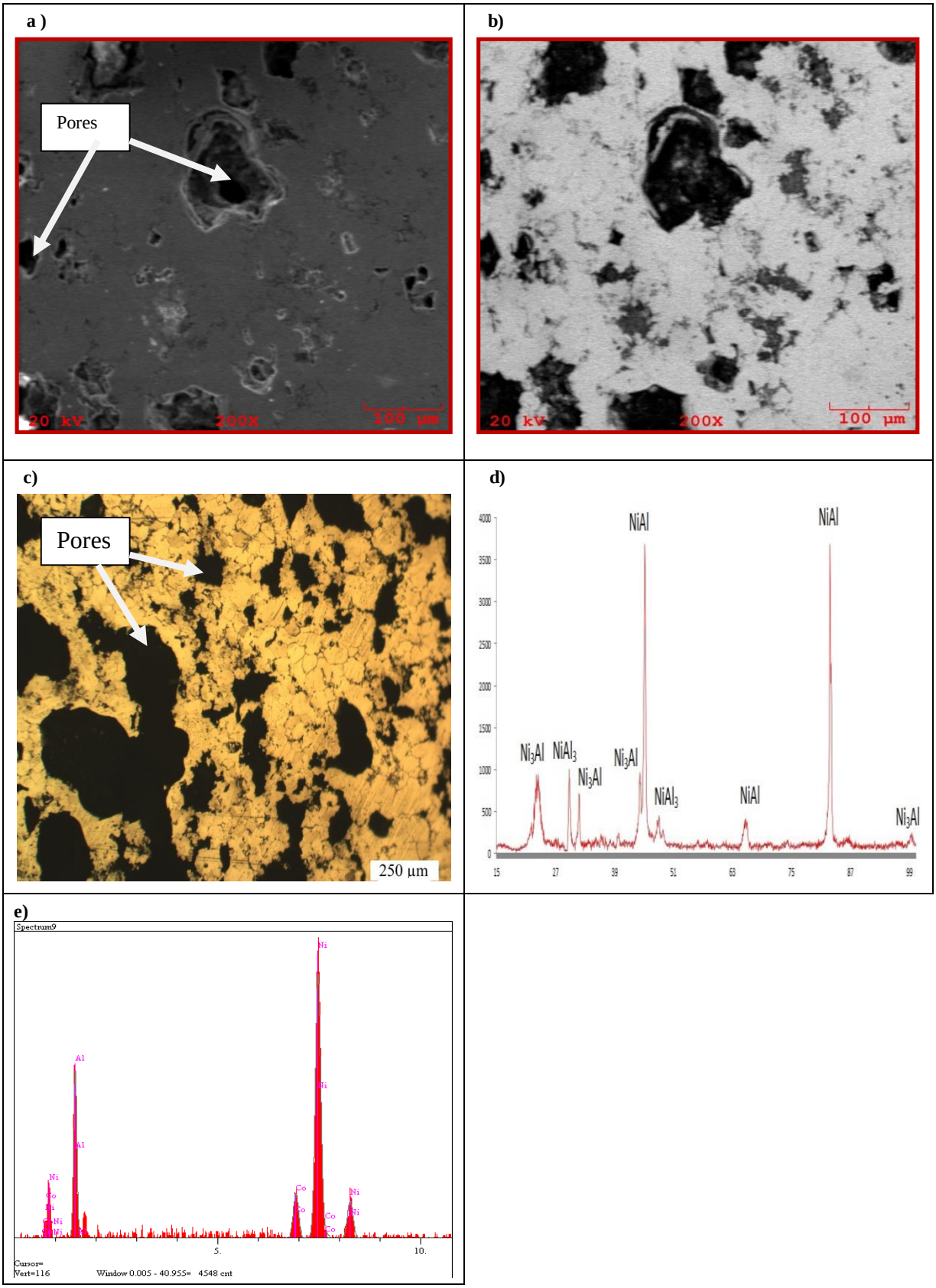

Figure 4. a) SEM, b) BSE and c) Optical microscope images, d) XRD and e) EDS measurements of NiAlCo alloy

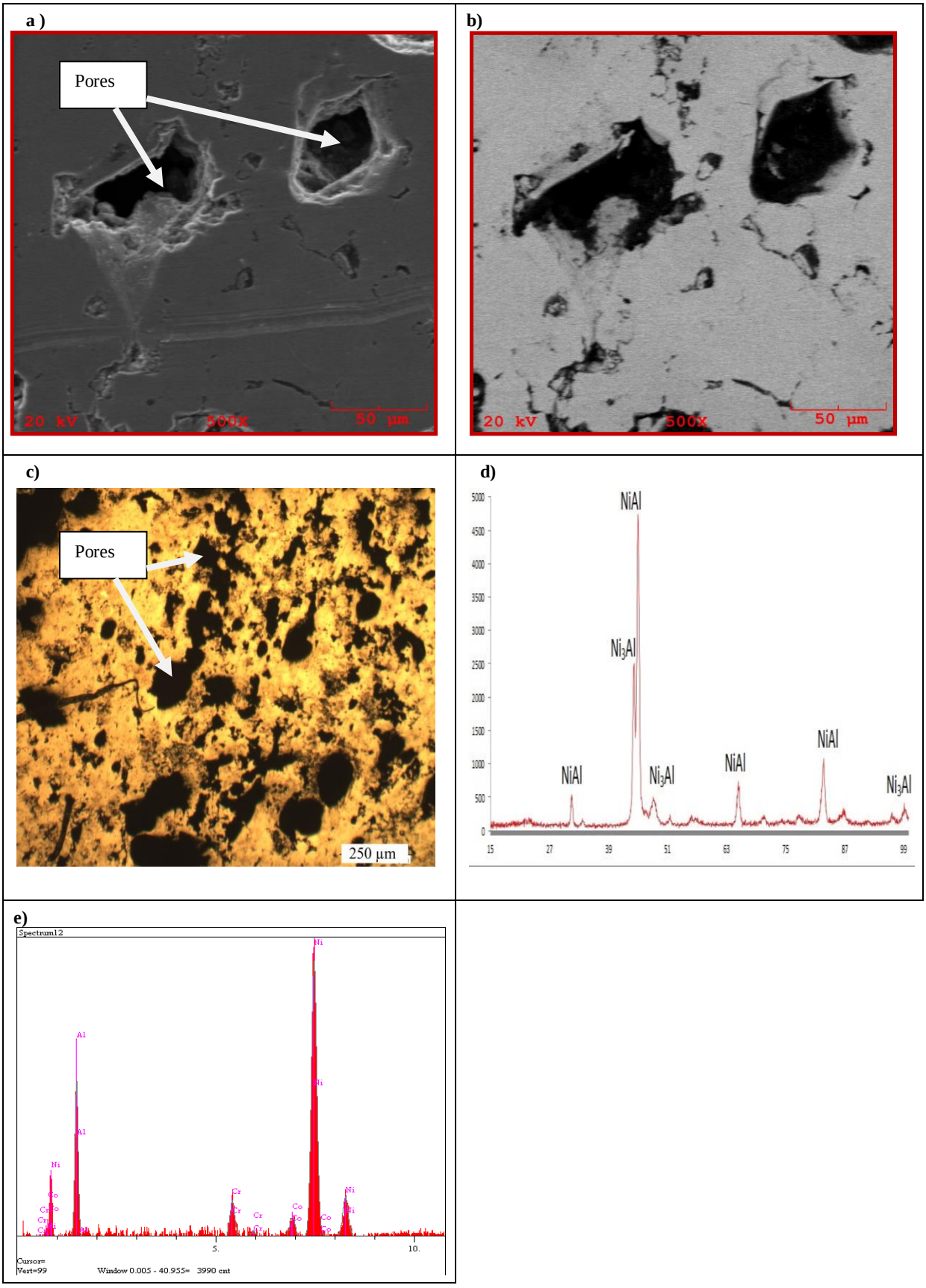

Figure 5. a) SEM, b) BSE and c) Optical microscope images, d) XRD and e) EDS measurements of NiAlCrCo alloy

Table 4 . EDS analysis of NiAlCr, NiAlCo and NiAlCoCr alloys

Element	Intensity						Concentration wt.%		
	NiAlCr		NiAlCo		NiAlCoCr		NiAlCr	NiAlCo	NiAlCoCr
	(c/s)	2-sig	(c/s)	2-sig	(c/s)	2-sig			
Al	18.72	1.580	21.1	1.677	17.00	1.505	16.891	15.141	13.771
Cr	16.98	1.505	-	-	5.69	0.871	10.686	-	4.011
Co	-	-	8.88	1.088	3.32	0.694	-	9.942	4.571
Ni	46.26	2.483	55.49	2.720	50.90	2.605	72.423	74.917	77.648

Raw porosity, pre-heating temperature, gas formation during the reaction, thermal migration, volume reduction of the reactants and the difference in diffusion between the elements are effective in the formation of pores. Part of the gas is trapped due to increasing external pressure while part of the gas is leaving the sample. In addition, shrinkage occurs when the alloy is formed. During shrinkage, the gas may leak and be trapped in the sample. The samples consist of closed pores and small chambers after this process. When the shrinkage is not fully closed, the chambers open to each other or to the canals by narrow passages. Thus, small open pores are formed. The shapes of the pores can be in different forms. As can be seen from SEM images of porous NiAl with 30% and 14% Al content sintered at 1000 °C from a previous study[17], pore size of NiAl alloys is generally greater than Ni_3Al pore size. And it has been reported in the studies that Al content has a great effect on the pore structure of aluminide intermetallic. They also stated that the total pore ratio of NiAl (50%) was greater than Ni_3Al's(30%) as a result of the measurements made by Archimedes method in water.

Figure 2, Figure 3 and Figure 4 shows SEM and optical microscope images taken in this study. The formation of large and small pores can be determined from those images. This is attributed to the escape of the gases that trapped between powders during the combustion reaction. Also, low compacting values can lead to formation of such structures [3]. In the EDS elemental analysis taken from the 10% Co addition sample, 74.917% Ni, 15.141% Al and 9.942% Co were determined and from the 10% Cr addition sample, 72.4% Ni, 16.9% Al and 10.7% Cr were detected. In the EDS elemental analysis taken from 5% Co and 5% Cr added samples, 77.6% Ni, 13.8% Al, 4.5% Co and 4% Cr were determined. According to these EDS data, it can be said that metal powders are homogenously distributed within the structure. In the XRD analysis of the same samples, the highest NiAl and Ni_3Al phases and a low ratio of $NiAl_3$ phase determined in NiAl-Cr alloy, the highest NiAl and a low ratio of Ni_3Al and $NiAl_3$ phases determined in NiAl-Co alloy, and the highest NiAl andlow ratio of Ni_3Al in NiAl-CoCr alloy.

4. CONCLUSIONS

In this study, the manufacturability and the porosity ratio of NiAl alloy was investigated by adding 3%, 6% and 10% of both Cr and Co layers. Layered NiAl (Co / Cr) intermetallic compound was successfully produced with SHS method by using different combinations of process parameters such as pressure and preheating. SEM, EDS and XRD analysis were performed and the porosity ratios were examined. The following characteristics of samples were observed;

1. As expected, the porosity in each of three separate samples decreased with increasing pressure.
2. The porosity of the preheated samples partially increased.
3. Adding Co relatively increased the porosity while adding Cr decreased it. In the case where these two elements were added together, the pore ratio increased near the average.
4. The addition of Co had a reducing effect on the secondary phase formation alongside NiAl.
5. The addition of Cr provokes the formation of Ni_3Al phase along with NiAl phase.
6. According to density calculations, it can be seen that the compression pressure is the most effective parameter that changes the porosity. The main reason for this is thought to be the increase in contact points of powders with increasing pressure resulting in an uninterrupted combustion reaction. Therefore, the molten powders solidify without the possibility of displacement.

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REFERENCES

[1] Li, Y.,Liu, Y., Geng, H., Nie, D., "Synthesis and cladding of Ni_3Al intermetallic on steel substrate by laser controlled reactive synthesis", ***Journal of Materials Processing Technology***, 171: 405–410, (2006).

[2] Wang Y.,. Chen W, "Microstructures, properties and high-temperature carburization resistances of HVOF thermal sprayed NiAl intermetallic-based alloy coatings", ***Surface and Coatings Technology***, 183: 18–28, (2004).

[3] Brammer M.T., "Improving the phase stability and oxidation resistance of β-NiAl", ***MSc Thesis***, Iowa State University, Ames, Iowa, (2011).

[4] K. Morsi, "Review: reaction synthesis processing of Ni–Al intermetallic materials", ***Materials Science and Engineering***, A299: 1–15 (2001).

[5] Dey G. K., "Physical metallurgy of nickel aluminides", ***Sadhana***, 28, (Parts 1 & 2): 247–262, (2003).

[6] La, P.,Bai, M., Xue, Q., Liu, W., "A study of Ni_3Al coating on carbon steel surface via the SHS casting route", ***Surface and Coatings Technology***, 113: 44–5, (1999).

[7] Kılıç, M., "The investigation of microstructures and fabrication of functionally graded intermetallic materials by self-propagating high-temperature synthesis", ***Batman University Journal of Life Sciences***, 5: 87-98 (2015).

[8] Ulu R.," Effect of Alloying elements on the microstructure and mechanical properties of NIAl alloys", ***M.Sc. Thesis***, Karabuk University Graduate School of Natural and Applied Sciences, Karabuk (2013).

[9] Yong C., Peixian Z., Jingchuan Z., Yong L.," First-principles study of NiAl alloyed with Co", ***Computational Materials Science***, 111: 34–40 (2016).

[10] Kiyotakai M., Khan T. İ., Ohmi T., Kudoh M, "Reactive casting of B2 Ni-Al-Co ternary intermetallic alloys", ***Materials Transactions***,.42(2): 263-268 (2001) .

[11] Cotton J.D., "The influence of chromium on structure and mechanical properties of B2 Nickel aluminide alloys", ***PhD Thesis*** ,University of Florida,1(991).

[12] Chen L, Han Y., "The microstructure and compressive properties in NiAl(Co) alloys by HPXD technique", ***Materials Science and Engineering*** A329–331 725–728, (2002).

[13] Kılıç, M., "Investigation of production of NiTi and Ni_3Al functionally graded material by reaction synthesis method", ***PhD Thesis***, Fırat University Graduate School of Natural and Applied Sciences Department of Metal Education, (2014).

[14] Tosun G., Özler L., Kaya M., Orhan N., "Investigation of porosity of NiTi alloys produced by shs method", ***5th International Powder Metallurgy Conference***, Ankara, 1353-1367, (2008).

[15] Kaya, M., "Investigation of metallurgical and mechanical characteristics of NiTi shape memory alloys produced by powder metallurgy", ***PhD Thesis***, Firat University Graduate School of Natural and Applied Sciences, (2008).

[16] Kovalev A.I., Barskayab R.A., Wainstein D.L., "Effect of alloying on electronic structure, strength and ductility characteristics of nickel aluminide", ***Surface Science***, 532 35–40, (2003).

[17] Dong H.X., Jiang Y., He Y.H., Zou J., Xu N.P., Huang B.Y., Liu C.T., Liaw P.K., "Oxidation behavior of porous NiAl prepared through reactive synthesis", ***Materials Chemistry and Physics***, 122: 417–423, (2010).

[18] Dong, H.X.,Jiang, Y., He, Y.H., Song, M., Zou, J., Xu, N.P., Huang, B.Y., Liu, C.T., Liaw, P.K., "Formation of porous Ni–Al intermetallics through pressureless reaction synthesis", ***Journal of Alloys and Compounds***, 484: 907–913, (2009).