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Influence of Al and Ti Elements on the Microstructure and Properties of Crnifecoal$_x$ti$_y$ Heas Fabricated By ECAS

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Abstract - CrNiFeCoAl$_x$Ti$_y$ alloy series which fabricated by ECAS, were investigated in view of microstructure and microhardness properties. The differences were determined by changing Al and Ti ratios. The alterations on microstructure and microhardness values were determined by apply homogenization heat treatment. According to the results sintering process was successfully performed in a short time. Diffusion activities as well as interfusion of powders were observed in the microstructures following the sintering process. The bright phase has high Fe and Cr content, while the gray phase holds high Al, Ni and Ti content. Diffusion processes ended by homogenization and obtained more homogeneous distribution. The high microhardness values which obtained by sintering were raised further.

Keywords: *HEA, ECAS, Microstructure, Entropy, Entalpy.*

1. Introduction

For thousands of years the development of practical alloy systems has been based mainly on one principal element as the matrix, as in iron-based, copper based and aluminum based alloys and nickel based superalloys limiting the number of applicable alloy systems. High-entropy alloys (HEAs) are a new class of materials which was first introduced by Yeh et al. and by Cantor et al. in the year 2004 and have attracted extensive research attention because of their unusual structural properties. [1,2] Most conventional alloys are based on one or two principal elements, with other elements in much smaller proportion. Distinctly HEAs were defined as having a minimum of five principal elements, each of them with an atomic concentration between 5 and 35 at.% [3-7].

This type of alloys is named “high-entropy alloys” since their liquid or random solid solution states have significantly higher mixing entropies than those in conventional alloys. Physical metallurgy knowledge and binary/ternary phase diagrams suggest that such multi-element alloys may develop different kinds of phases and intermetallic compounds, resulting in complex and brittle microstructures that are difficult to analyze, and probably have very limited practical value. Contrary to these expectations, the higher mixing entropy in these alloys facilities the formation of simple solid solution phases like face centered cubic (FCC), base centered cubic (BCC) or FCC+BCC. [5,6,8-15]

For conventional alloys that contain a single principal element, the mechanical behavior is determined by the principal element. The other alloying elements are used to develop some special properties. For HEAs, properties can be variety from any of the component elements. Strength and hardness of HEAs is dictated by the structure. With appropriate element constitutions, HEAs exhibits high wear resistance, corrosion resistance and mechanical properties [7,15-20]. The particular structures and properties offer many potential applications for high-entropy alloys, such as tools, molds and mechanical parts, etc. [14].

In the electric current-activated/assisted sintering (ECAS) technique, a cold-formed compact obtained with uniaxial compression or a loose powder is inserted into a container heated by the passing electrical current. Electric current is applied simultaneously with a mechanical pressure to consolidate or synthesize and to densify specific products into a desired configuration and density. The use of ECAS for consolidating samples not only provides a faster heating time and shorter process time but also ensures lower sintering temperatures [21-24].

In this paper CrNiFeCoAl$_x$Ti$_y$ high entropy alloy powder was prepared by mechanical activating and unlike the methods used in the literature; specimens were sintered by ECAS (Electric Current Assisted Sintering) technique. In addition, the effect of titanium/aluminum ratio on the microstructure and microhardness of the alloy was investigated.

2. Experimental

Elemental metallic powders of Cr, Ni, Fe, Al, Ti and Co having high-purity (>%99,5) and -325 mesh sized were used in alloys. Metallic powders were aggregated in order to compose 4 different compositions. The compositions of alloys are shown in Table 1. The alloys composed were subjected to mechanical activation and mixing during 4 hours in a container. Mixed powders were formed as compact under the 250 MPa hydraulic pressure. 1,8 cm diameter and 3 gr weight samples were placed in molds which each one disposable and fabricated for sintering. Sintering was applied for 300 seconds in ECAS unit. 50 MPa pressure was applied following samples were placed to unit in mold. It was reached to 2500 A current in 30 seconds and the applied current was held constant until the process is complete. The temperature of exterior surface of the mold was continuously measured by laser thermometer. In the end of sintering process, the mold was removed from unit when its temperature was decreased to 300°C and the specimens were removed from mold when the temperature was decreased to room temperature. After the SEM-EDS, optical microscope and micro hardness analysis of fabricated specimens were done, the specimens were processed homogenization during 20 hours at 1200°C and the same analyses were performed again.

Table 1: Chemical composition of samples.

%	Cr	Ni	Co	Fe	Al	Ti
S1(CrNiFeCoAl)	20	20	20	20	20	0
S2($CrNiFeCoAl_{0,75}Ti_{0,25}$)	20	20	20	20	15	5
S3($CrNiFeCoAl_{0,5}Ti_{0,5}$)	20	20	20	20	10	10
S4($CrNiFeCoAl_{0,25}Ti_{0,75}$)	20	20	20	20	5	15

3. Discussion

3.1. Microstructure

SEM microstructure images of the sintered samples are presented in Figure 1. Sintering process is obtained by the resistance against to the current applied to the sample. A rapid temperature rising is provided by the resistance of the sample and mold to electric current. During the sintering process, temperature was determined with the help of laser thermometer. The temperature was about 650°C in 120 seconds outside of the mold. At the end of the sintering process, the temperature was increased to about 950°C. In the sample, the interaction occurred between the powders under these temperatures. It is observed in the samples that there is more than one phases, powders cannot protect its pure state and the powders are begun to mixing. It is determined in the EDS analysis that Ni, Al and Co ratios are high in the light gray phase. When the light color of the phase changes to the darker tone, Ni ratio decreases. However, the amount of Co and Al has increased as rich elements. In the light gray phases, it is determined that ratio of the Cr and Fe is rich and Co is also detected as a thirdly elements. Elemental distribution is approximately like this in almost all samples. Also, minor changes were observed depending on the increasing ratio of titanium and decreasing ratio of aluminum. With the increasing amount of Ti, darker phases are appeared in the samples. These are Ti elements that were unable to complete the diffusion. In the edges, the diffusion of the Co and Ni elements on the Ti powders were observed. Also, it is determined that Ti was being to get rich by these elements. If it is discussed as a whole, after sintering process Co is determined approximately in same proportion in both group phases. Al, Ni and Ti are getting enriched in a phase and Fe, Cr are getting enriched in other phase.

SEM microstructures of $CrNiFeCoAl_xTi_y$ alloys after annealing at 1200°C for 20 hours are shown in Figure 2. If microstructure images are examined, it can be seen that the number of phases are decreased compared to the sintered samples. The presence of porosity, which is general characteristic property of the sintered samples, is observed in all samples. Thus, a high proportion of the black oxide groups are presented in the sample that is coded as S1. Al oxide was formed in the black color phase because of the absence of Ti in these alloys. In the other samples, black oxide phases were decreased with the increasing ratio of the Ti. After homogenization, more homogenous formations are determined in the samples which were begun in the sintering process. At higher magnification, two phase (dark gray and light gray) formation was seen in the samples. In the EDS analysis performed, higher ratio of the Fe and Cr were found in the light gray phases Al, Ni and Ti were found in the dark gray phases at a higher rate. Fe and Cr constitute the 40-49% of the dark gray phases. Al, Ni and Ti constitute the 42-57% of the light gray phases. Co exists about 14-20% in both phases. With increasing ratio of the Ti, ratio of the Al, Ni and Ti is increased from 42% to 57% in dark colors.

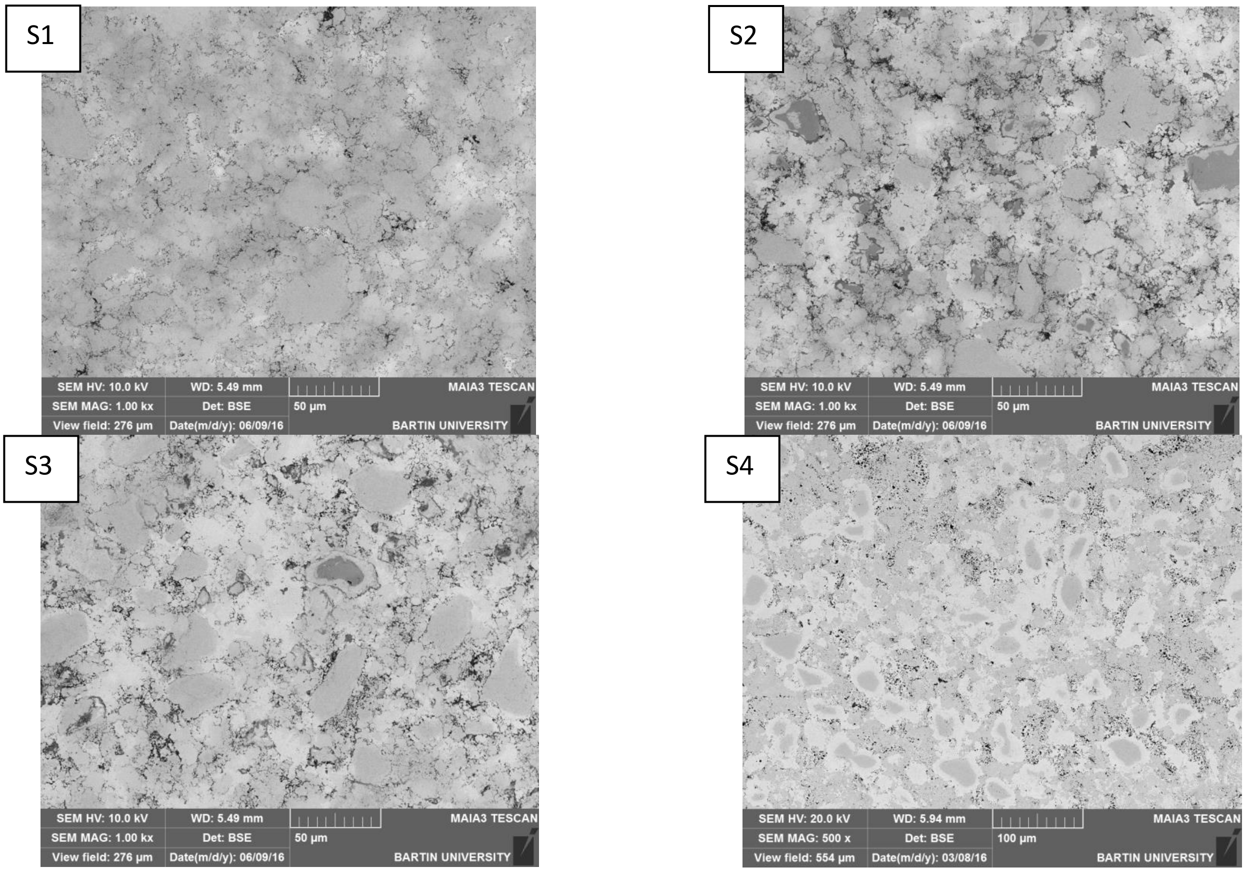

Fig. 1: Microstructure images of the sintered samples.

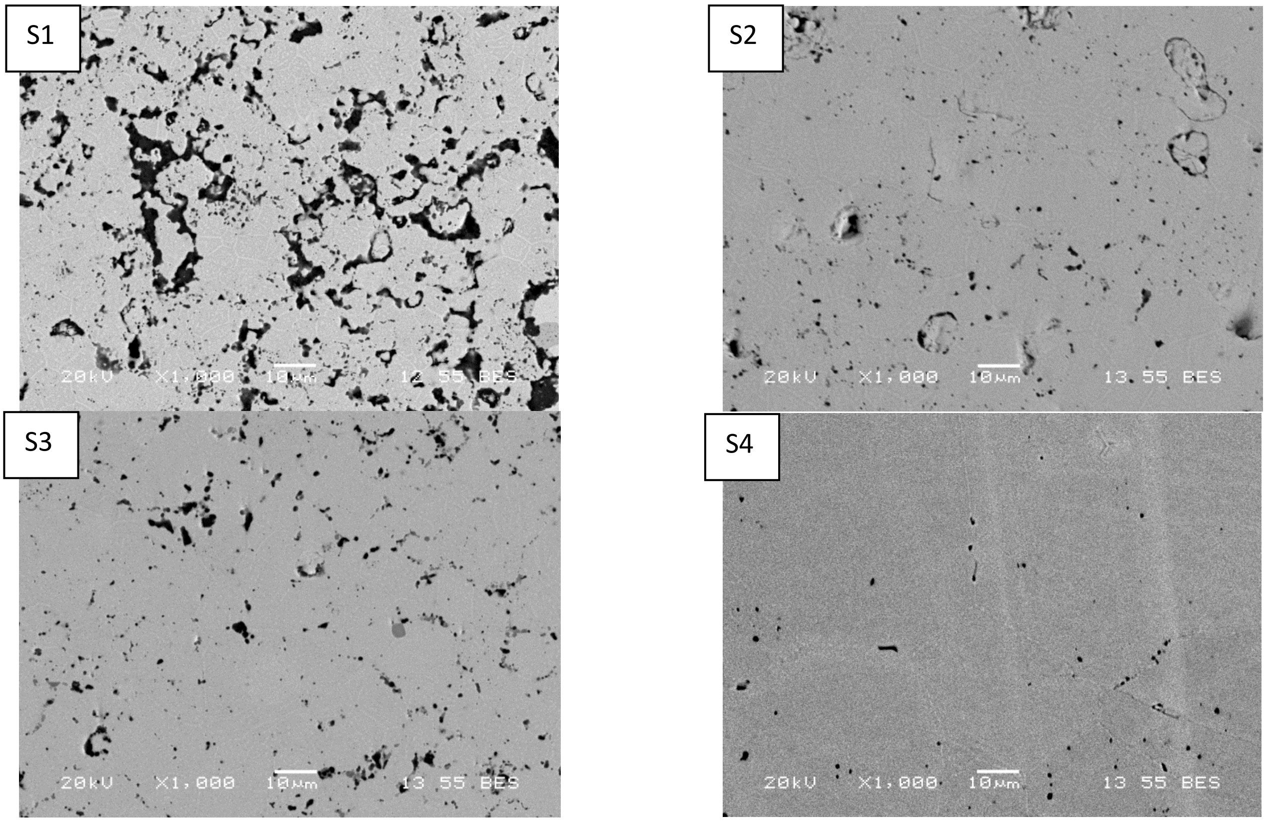

Fig. 2: Microstructure of $CrNiFeCoAl_xTi_y$ alloys as-homogenized conditions.

Condensation of Fe-Cr in a phase and Al-Ni-Ti in other phase, which were started during the sintering process, were resulted with the homogenization process. This is attributed to the mixing enthalpies of the constituent binary alloys. At high temperature, the large entropic contribution to the Gibbs free energy permits the formation of a simple solid solution. With the decrease of the temperature the entropic contribution to the Gibbs free energy reduces significantly, and the solid solutions are not energetically stable. The large negative mixing enthalpy of Al, Ti and Ni facilities the formation of the Al-Ni-Ti rich phase during sintering [15]. For $CrNiFeCoAl_xTi_y$ alloy, the mixing enthalpies between Al and Ni, Ti, Co, Fe and Cr are -22, -30, -19, -11, -10 kJ/mol, respectively [25]. So, Al attracks Ni and Ti to dark gray phase. And the Fe–Cr rich phase subsequently precipitate around the Al–Ni–Ti rich phase due to high concentrations of Fe and Cr. The Co is almost homogeneously distributed in both phases.

3.2. Microhardness

Microhardness values of the samples after sintering and homogenization are shown in the Table 2. And as it is shown in the Table 2 generally high average microhardess values were obtained for the samples even for the sample which has the lowest hardness value. There is a significant distribution is observed after sintering in the hardness value which is reduced after homogenization. This is a result of non-homogenizes sample structure obtained from sintering. After sintering, the obtained hardness especially for the dark colored phases was found significantly higher the average hardness value. HEA can show higher hardness depending on its components. In this study the higher hardness value is attributed to presence of Al and Ti. Due to the higher atomic size of the Al and Ti in a lattice, they contribute to solid solution hardening. As a result of the increase in the Ti rate and decrease in the Al rate leads small increase in the hardness after homogenization. This is most likely due to the atom size differences between Al (1,43 Å) and Ti (1,45 Å). Since the higher the atom size of an element in a lattice leads the higher the lattice expansion.

Table 2: Microhardness of sintered and homogenized samples (Hv).

	Sintered	**Homogenized**		**Sintered**	**Homogenized**
S1	**402 ±90**	**399 ±11**	**S2**	**514 ±186**	**637 ±40**
S3	**484 ±220**	**650 ±31**	**S4**	**505 ±145**	**669 ±17**

4. Conclusions

In summary $CrNiFeCoAl_xTi_y$ high-entropy alloys were successfully fabricated by ECAS method in 4 different concentrations. The sintering of powders were occurred on very short time as 5 minutes. The fabricated specimens were investigated in view of SEM, EDS analysis and microhardness values. It is observed that dual phase structure which formed following sintering process end up with homogenization process. In EDS analysis it was determined that Fe-Cr was rich in dark-gray phase and Al-Ti-Ni was rich in light gray phase that was relevant to mixing enthalpies of atom pairs. However it was determined that the Co is approximate values in both phases. High hardness values which obtained in microhardness tests were attributed to distortion in lattice because of Al and Ti large atomic radius. Large deviation in microhardness values which was occurred with sintering was decreased by homogenization. As Al percentage increases with respect to Ti, higher atomic radius of Ti contributes to the increase in hardness.

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