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An Experimental Study on High Entropy Alloy Using Different Alloying Elements

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High entropy alloys are the combination of five and more than five elements in approximately similar atomic proportions. In this case, the structure obtained exhibit a different formation than conventional material types. In this study, the main alloy structure of Ni, Ti, Co, Mn, Fe was determined. This alloy design was made by selecting elements with different sizes and orbital valences from the main alloying elements such as Cr, Cu, Hf, Nb, V, and Zr. In this case, the atomic lattice diameters of the alloys obtained are incompatible, resulting in a type of hard and brittle material in general. The alloys obtained were reported using thermal and structural analyses.

Keywords: *High entropy alloys, arc melting, alloying elements, XRD*

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Introduction

Metals have a great role in the world in so many criteria. Especially smart materials could help in many ways to make life easier. Wherever there is a development in metallic materials that means one problem gets a solution. In early works to make alloys, the phenomena of alloying come out from combining two or three elements to achieve better and different properties in mechanical, physical, and chemical properties [1]. In conventional alloys, the procedure of making alloys was focused on one material which is named “base element”, this has a negative influence on that area’s working which means that makes a limit for research in that field of alloys [2]. In the last decays, the borders to study have been broken since when High entropy alloy (HEA) was produced and that leads to opportunities to study with these topics have been unlimited [3].

In 2004, a new alloy by Yeh et al. was defined and added to materials science when five or more elements combined for making an alloy, and these alloys termed High entropy alloys [4]. Additionally, each element which participate in making these new alloys have to be in equimolar or near equimolar ratios, the atomic percentage of any of them must be between 5 and 35 [5]. Besides this, non-equimolar alloys expand working with alloys and make dual or multiple phases [6]. Due to their special structures, microstructures, and adjustable properties, high-entropy alloys (HEAs) have attracted great attention [7]. HEAs should therefore exhibit a remarkable stable microstructure and diverse other unusual characteristics that derive from their complex compositions [8]. It describes HEAs in their random solution state, as an alloy containing entropy greater than 1,61R when R represents a gas constant [9].

In this work, HEAs with new compositions such as NiTiCoMnFe-X were fabricated and the thermal and structural variations were determined.

2 Experimental

High entropy alloys can show different properties thanks to their different structures. In this study, a high purity master structure with atomic ratios close to Ni, Ti, Co, Mn, Fe was chosen. By adding Cr, Cu, Hf, Nb, V, and Zr elements to this structure, changes were made to the master alloy. Master alloy and alloying elements are weighed using high purity elemental metals. The mixtures obtained after these weighing was compressed into pellets in a 20mm diameter moulded by a hydraulic press. Then, the pelleted compressed powders were placed in the arc melting furnace. The arc melting furnace is vacuumed first and then the chamber is filled with argon gas. This process was carried out twice to remove the undesired gases in the environment. Materials were melted using tungsten electrodes on the copper crucible. The melted materials were re-melted by reversing and thus, it was aimed to distribute the atoms homogeneously. The samples obtained after melting were prepared for DTA, SEM, and EDX, XRD analyses and the differences formed by the alloying elements on the master alloy were analysed.

3 Results and Discussion

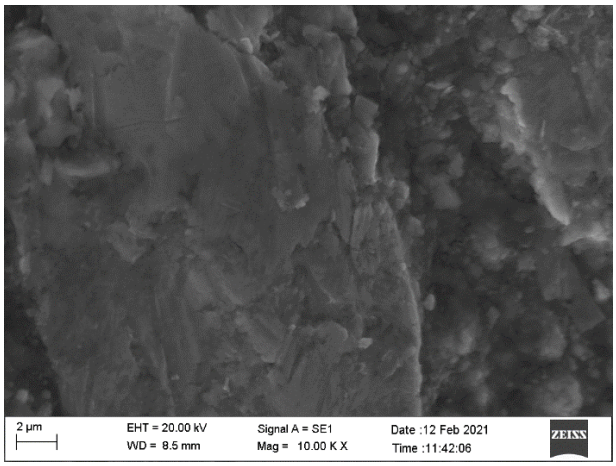
3.1. EDX and SEM analysis

EDX device was used to determine the chemical composition of the samples. The element ratios of the samples in the alloy are shown in Table 1.

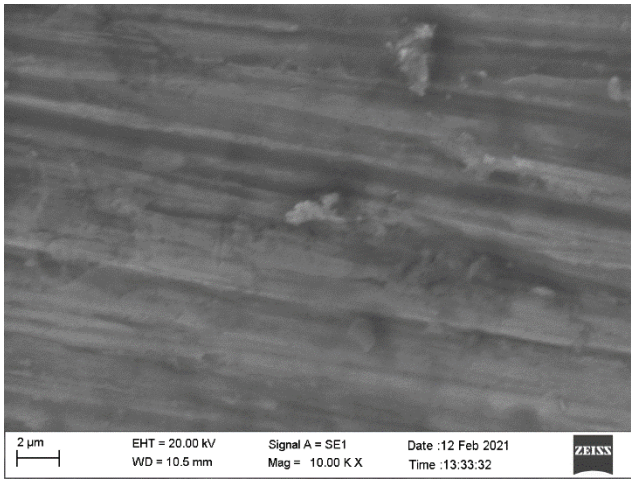
Table 1. Chemical composition of alloys at.%

Sample	Ni	Ti	Co	Mn	Fe	M-X
M-Cr	11.41	15.09	9.90	16.42	30.65	16.53
M-Cu	16.10	35.09	15.70	9.90	20.11	3.09
M-Hf	3.00	74.35	2.47	1.56	6.64	11.98
M-Nb	15.58	31.97	16.29	12.47	21.06	2.62
M-V	12.85	33.45	15.60	13.03	21.14	3.93
M-Zr	21.89	31.74	20.14	16.76	5.25	4.22

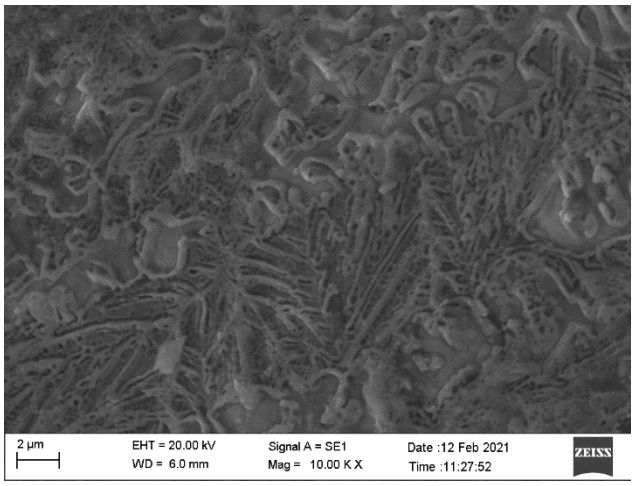
Alloying elements having different atomic numbers are mixed in small amounts as powder. During mixing, differences occur in the intended proportions and also during melting. High-scale pictures of the alloys were also taken on the SEM device. The topographic pictures of the materials are shown in Figure 1 and Figure 2.



M-Cr

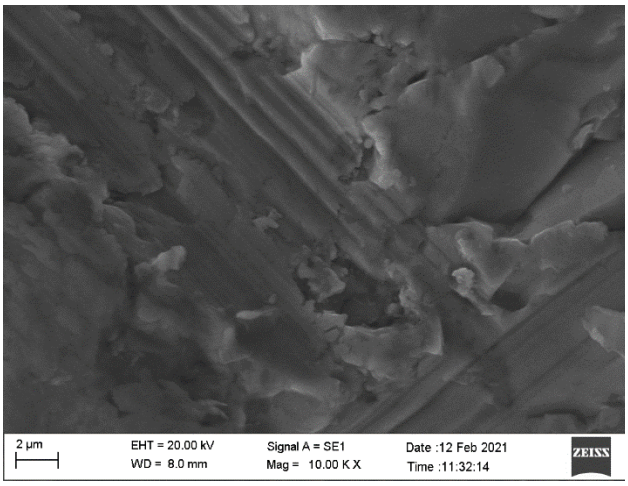


M-Cu

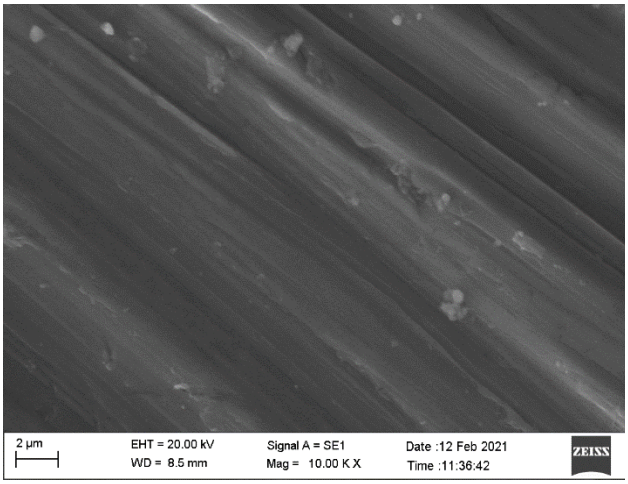


M-Hf

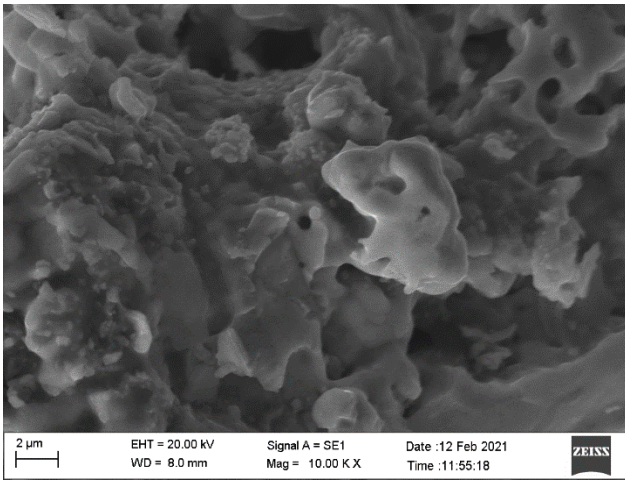
Fig.1. SEM images of M-Cr, M-Cu and M-Hf alloys



M-Nb



M-V



M-Zr

Fig.2. SEM images of M-Nb, M-V and M-Zr alloys

The melted samples revealed a very brittle structure and different images were obtained. A very different structure form of Hf and Zr alloys was observed in Figure 1 and Figure 2 compared to other images. The high atomic weight of the Hf element and the high Ti element in the alloy is thought to cause a porous and fibrous structure. Due to the structure, the thickness of the fibers is about 0.2µm and the high solidification temperatures and the high-density differences in the structure may cause the formation of fibers. The atomic mass weight of the element Hf is about 3 times the other elements in the alloy, it is also thought that this situation provides different chemical composition values for M-Hf alloy. Nb and Zr elements, on the other hand, have a mass difference almost 2 times. These differences are seen in the images on the building as porous forms that disrupt the integrity. For the other alloys, it was determined that the whole structure was not damaged.

3.2. Thermal analysis

Thermal analysis is used to determine the phase changes or degradation of the structure of the material against temperature and heat energy input. Thanks to this situation, solid-state phase transitions of the material can be observed. Therefore, DTA analyses of the samples were made and the phase changes within the structure were analysed. DTA analysis of the samples is given in Figure 3.

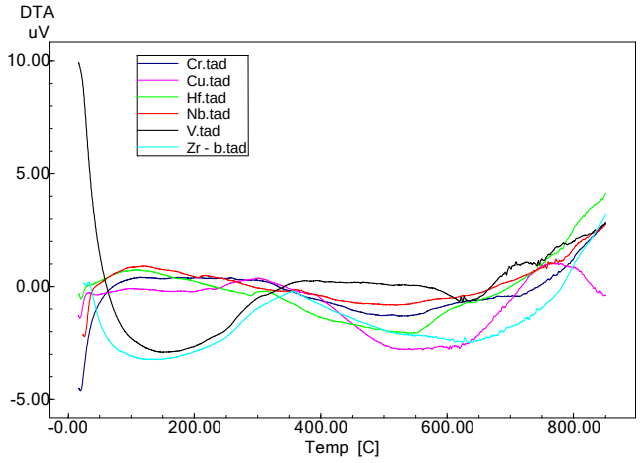


Fig.3. Multiple Graphs for all elements with DTA analysis with heating rate 20 °C/min

DTA experiments were carried out at a 20 ° C / min heating rate. Endothermic (down) and exothermic (upward) reactions took place within the structure. DTA analyzes were performed up to 800 ° C and different reactions were recorded on the structure. The M-V alloy showed a solid-state phase transition peak around 620 ° C. Similar transitions were also encountered in M-Cr alloy around 680 ° C. Alloys M-Cu, M-Hf and M-Zr appear as a deep and wide transition around 400 ° C. This deep and wide peak range may also be the slow realization of the required transition energy as a function of time, as a result of the multiple phase transitions or the limited movements of the incompatibly stacked intermetallic structures. The jagged plotline curves encountered around 800 ° C indicate the onset of local oxidation on the material. The data in Table 2 are presented by calculating the properties of high entropy alloys

according to the chemical components of the alloys in Table 1.

Table 2. Different property values of alloys

Sample	ΔSconf	*ΔSmix	*ΔHmix	VEC	Ω	δ
M-Cr	-1.50R	12.47	-29.51	15.24	1.43	5.2
M-Cu	-1.65R	13.70	-38.57	16.34	1.2511	4.73
M-Nb	-1.89R	15.70	-19.91	8.17	1.94	6.61
M-V	-1.88R	15.64	-20.93	8.60	1.93	6.62
M-Zr	-2.02R	16.80	-35.43	12.33	1.64	5.57

*ΔSmix (J.(K mol.)-1) , ΔHmix (kJ.mol-1)

According to this table, ΔHmix table prepared according to Miedema's model was used in Takeuchi and Inoue studies[10]. However, since the ΔHmix value of the Hf element could not be found according to the elements in the other alloy, the necessary calculations could not be made.

ΔSconf (configurational entropy) value is higher than 1.5R in calculated values. The fact that these values are above 1.5R value indicates that the alloys calculated have high entropy. Ω (competition between enthalpy and entropy) and δ (the atomic size difference), according to Yang and Zhang [11], when [$\Omega \geq 1.1$ and $\delta \leq 6.6\%$ is a stable solid-solution. At the same time, the high mixture entropy makes the solution phase more stable as it reduces the Gibbs energy value[12]. In this case, M-Cr, M-Cu, and M-Zr alloys have shown that they have a stable structure by providing the condition. Although the structure is stable, the atomic weights and sizes of the Zr, Nb, and Hf elements cause the atomic lattice structure to distort. This situation prevents the dislocation movements within the structure and ensures that the material has a brittle structure.

VEC (Valance electron concentration) value gives information about the lattice status of the structure. In this case, the requirement BCC ≤ 6.87 <BCC + FCC <8 <FCC is stated [13, 14]. In this case, it can be said that the structure is FCC Laves and σ since all alloys are larger than 8 VEC values.

3.3. XRD analysis

Thanks to XRD analysis, the lattice systems in the crystal structure provide information about the material. High entropy alloys are generally expected to exhibit an amorphous structure during solid-solutions. Therefore, not many peaks are expected in the crystal structure. There are corresponding patterns on the existing peaks.

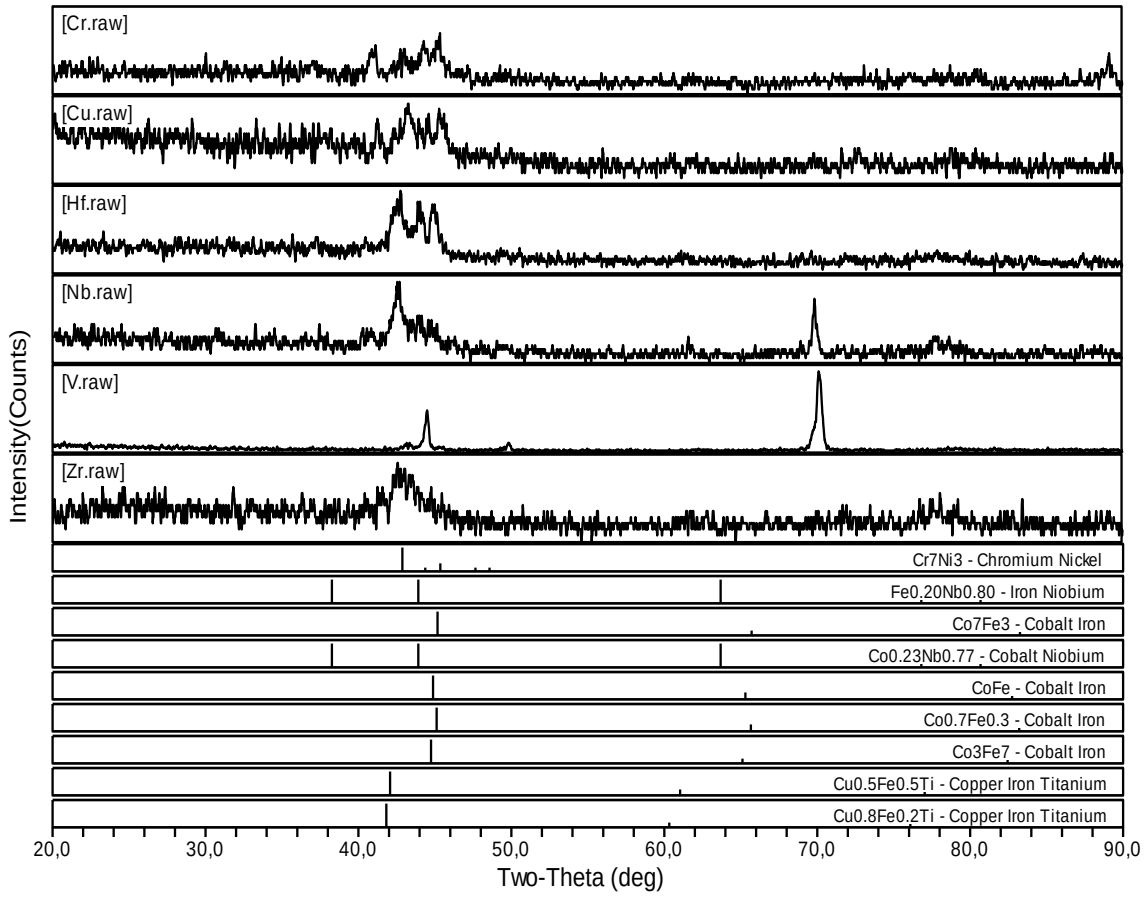


Fig.4. Multiple Graphs for all elements with XRD analysis at room temperature

The existing structures within the structure generally indicate the presence of Laves and σ phases. These phases indicate that the material is in a brittle state. Generally, multiple phases around 42 ° indicate the complex and amorphous structures.

4 Conclusions

High entropy alloys are a type of material made with a new generation alloy design and its capabilities have not yet been determined. In this study, the main alloy of Ni, Ti, Co, Mn, Fe was determined and elements in different groups such as Cr, Cu, Hf, Nb, V, and Zr were added to this alloy. Among the main alloying elements, elements such as Hf, Zr, and Nb, which have very high atomic weight, distort the structure, limiting the lattice structures and dislocation movements, resulting in very brittle alloys. Likewise, Cu elements with smaller atomic weights, V and Cr, similar in diameter but with different orbitals, again exhibit properties close to the structure of the main material and have formed a relatively stable internal structure.

1. References

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