U.P.B. Sci. Bull., Series B, Vol. 80, Iss., 1, 2018 ISSN 1454-2331

MULTI-COMPONENT ALLOY SYNTHETIZED BY A POWDER METALLURGY ROUTE

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High entropy alloys are in the target of many researchers due to their tremendous potential. This paper aims to describe a CoCrFeNiMo high entropy alloy synthetized by mechanical alloying for 25h. The power obtained was characterized in terms of flowing rate, bulk and tap density, mean diameter. The microstructure of the powder mechanically alloyed for 25h revealed a homogenous structure and the EDS analyses identified all the component elements.

Keywords: high entropy alloys, geothermal steam, corrosion resistance, microstructure

1. Introduction

An alloy consists in a homogeneous mixture with metallic properties of two or more materials (chemical elements), of which at least one is metal and usually is in a larger quantity [1]. The physical and chemical properties of the alloys are generally different, sometimes significant, from those of the constituent substances. High entropic alloys (HEA), discovered by Jien-Wei YEH, represents alloys with a different design than traditional alloys. YEH has successfully obtained high entropy alloys in a vacuum arc remelting furnace [2, 6].

High Entropy Alloys (HEA) consisted in a major alloying elements where $n \geq 5$, with equimolar or near equimolar ratios, which easily lead to the formation of FCC or BCC single solid phase, nano-structures or even molded amorphous states.

Therefore, high entropy alloys are solid solutions with high strength, improved thermal stability, and higher hardening capacity compared with classical alloys, combined with superior strength under different environmental conditions [7].

High entropy alloys could be obtained in vacuum arc remelting plant, induction furnaces or by powder metallurgy methods. The powder metallurgy route allowed producing of a homogenous alloy with a controlled composition. The method was tested by [3-5] and the results were encouraging. Thus the

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method chosen to obtain the CoCrFeNiMo alloy was the mechanical alloying in RETSCH planetary ball mill presented in Fig. 1.

Being different from conventional alloys, high entropy alloys have complex compositions because of the equimolar concentration of each component. Yeh has mainly summarized four basic characteristics for high entropy alloys, which are: (1) thermodynamics: high entropy effect; (2) kinetics: slow diffusion; (3) structure: structural tensions; and (4) property: mixing effect [7, 8].

The high entropy effect, which tends to stabilize the high entropy phases, for example, the solid solution phase, was primarily proposed by Yeh [2]. The effects were counterintuitive because it was expected that the phases of the intermetallic compounds could form equi or nearly equi-atom alloy compositions found at the center of the phase diagrams (for example, a monoclinic compound of AlCeCo type at the center of Al-Ce-Co system). According to Gibbs phase equation, the number of phases (P) in a given alloy at constant pressure, in an equilibrium state is:

$$P = C + 1 - F \tag{1}$$

Where C represents the components number and F represents the maximum number of thermodynamic degrees of freedom in the system. The high entropy effect, it is basically utilized to explain the multi-element solid solution. According to maximum entropy (MEPP) obtaining method, high entropy tends to stabilize high entropy phases, for example solid solution rather than intermetallic phases. The intermetallic phases are usually phases that have low entropy. For intermetallic stoichiometric compounds, the entropy configuration is zero [10].

The sluggish diffusion effect is compared to that of conventional alloys, and metallic glasses formation. Recently, Yeh studied vacancies formation and composition of high entropy alloys, and compared diffusion coefficients for pure metal elements, stainless steels, and HEA, finding that the order of diffusion velocities varies as following: *high entropy alloys <stainless steel <pure metals* [12]. Lattice distortion effect it is usually compared to an alloy with dominant elements if the structure position is occupied mainly by the dominant component. For high entropy alloys, each element has the same ability to occupy its place in the composition, structure, if we ignore the chemical order. The size of various elements may differ, and sometimes this could lead to severe distortion of the structure. Yeh et al have studied the abnormal X-ray diffraction (XRD) depletion of CuNiAlCoCrFeSi alloy systems. A series of CuNiAlCoCrFeSi alloys with a systematic addition of pure primary elements to seven elements has been studied by X-ray investigations [2, 7]. The "cocktail" effect was commonly used as a term in the acoustic field, which was used to describe the ability to focus one's listening attention on a single speaker in a mixture of conversations and background noises, ignoring other conversations. For metal alloys, it indicates that the effect of

unexpected properties can be obtained after mixing many elements, which could not be obtained from any independent element. The "cocktail" effect of metal alloys was first mentioned by Ranganathan, which was later confirmed in mechanical and physical properties [1].

The materials properties are in close relationship with their microstructure. There is no exception for high entropy alloys. Microstructure can be modified by manufacturing methods, plastic deformation (e.g.: rolling, forging), and heat treatment. Casting and powder metallurgy can be used to produce nearly finished products. The detailed tridimensional characterization of high entropy alloys microstructure is important for the material properties interpretation, such as tenacity and fracture mechanisms [12].

Thermo-mechanical controlled processing can be used to promote the formation of preferred granular texture and / or grain boundary character distribution. Nanometric columns may be produced of high entropy alloys using focusing ion beams (FIB), and single phase columns with desired properties can be manufacture and they can be genes for materials. Then new materials can be designed based on the properties of the genes. Large plastic deformation can be used to refine structures of sub micro- or nanoscale form using the equal angular-channel press method. The high entropy alloys porous components, with controllable micro and nano scale pore size can be processed using casting methods or chemical methods. High porous entropy alloys could be used as robust filters for purifying hot water and air or smoke at high temperatures and hostile environments. Detailed deformation and fracture mechanisms have not been clearly identified. Disclosed structures, before and after fracturing, need to be investigated. Understanding the interaction between dislocations and solutions can provide insights into the alloying elements effects. In addition, for the fatigue study, limited data was reported and at room temperature only, but high temperature fatigue behavior needs to be explored. Reducing these defects is particularly important for improving fatigue resistance of high entropy alloys.

2. Materials and method

High purity metal powders of Co, Cr, Mo, Fe and Ni were mechanically alloyed in a RETSCH planetary ball mill. The process control agent (PCA) used was N-heptane. N-heptane acts as a process control agent to avoid welding of the particles during grinding and to prevent oxidation of the alloy.

The experiments were carried out in argon atmosphere. To prevent sample contamination due to the high grinding time, steel vials and balls were used. The milling time chosen for this alloy was 25 hours. Samples were taken before and after the experiments. The grinding speed used was 300 rpm. The ball to powder ratio was 8:1.

Sizing for the each component powder and for the HEA obtained was realized using a RETSCH AS 200 sizing device using sieves with apertures of 25, 32, 40, 63, 71, 100, 125 microns.

The powders were investigated in terms of microstructure using QUANTA INSPECT scanning electron microscope equipped with a field emission electron gun, and with energy dispersive radiation analysis to determine the elemental distribution at different points across the sample.

The flowing rate of the power was determined using a calibrated Hall flow meter and a Carney funnel was used to measure the bulk and tap density and Carr angle of fall.

3. Results and discussions

The mean diameter of the powder particles for HEA processed by mechanical alloying 25h was calculated after powder sizing. For comparison the sizing was realized for component powders and for final HEA.

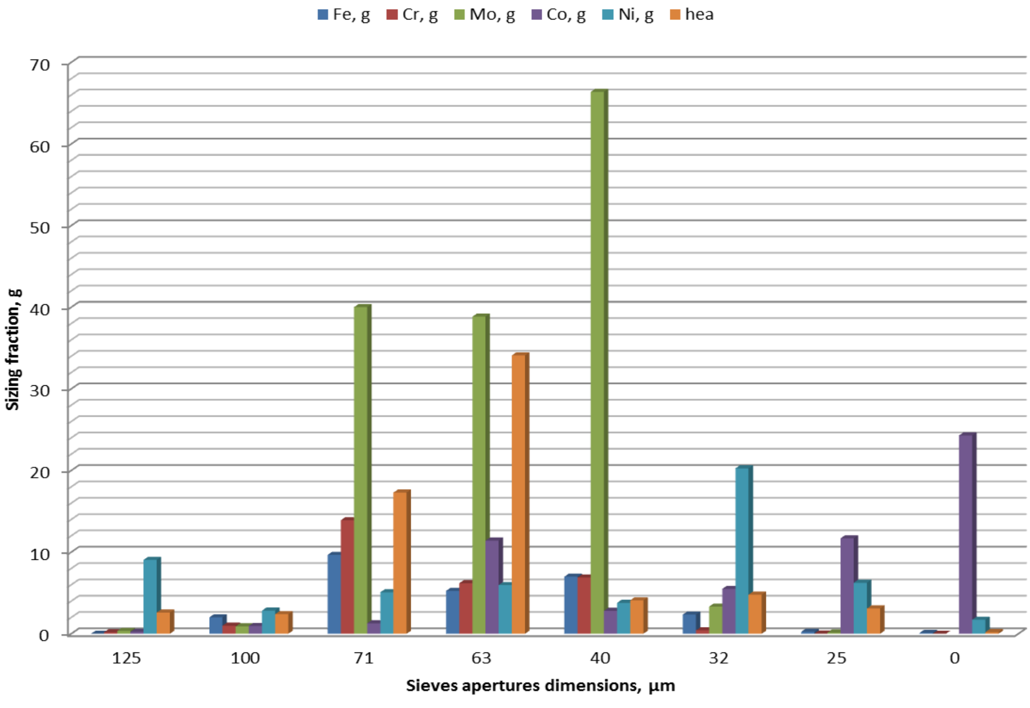


Fig. 3. Sizing for component powder

The mean diameter calculated for the CoCrFeNiMo produced by mechanical alloying for 25h was realized using the formula:

$$D_{(mean)} = {}^{100}\Big/_{\sum_{i=1}^{5} {}^{x_i}/_{d_{mean\ i}}} = 91.64\mu m \qquad (2)$$

where x_i is the sizing fraction of the HEA in grams and $d_{mean\ i}$ is the mean diameter of 2 adjacent sieves apertures.

The apparent density of metallic powders or the weight of a unit volume of powder, expressed in g / cm3, is one of the fundamental properties of a powder. The feature that defines the real volume occupied by a mass of free-flowing powder directly affects their processing parameters, such as the design of the press and the magnitude of movements required to densify the metallic powder.

The apparent density of the metallic powder depends on the solid material density, particle size, particle size distribution, particle shape, surface area, particle roughness and particle arrangement [17]. Reducing particle size generally decreases apparent density. The larger the particle, the specific surface area of the powder is also larger. This phenomenon increases friction between particles and then decreases apparent density.

Low friction forces between the powder particles are present due to the spherical shape of the particles (atomized), such as complex powders. The effect of decreasing particles size is important until their dimensions reach below 20 microns. Density in free and compressed state was achieved using the Carney funnel. The results obtained are shown in Fig. 5.

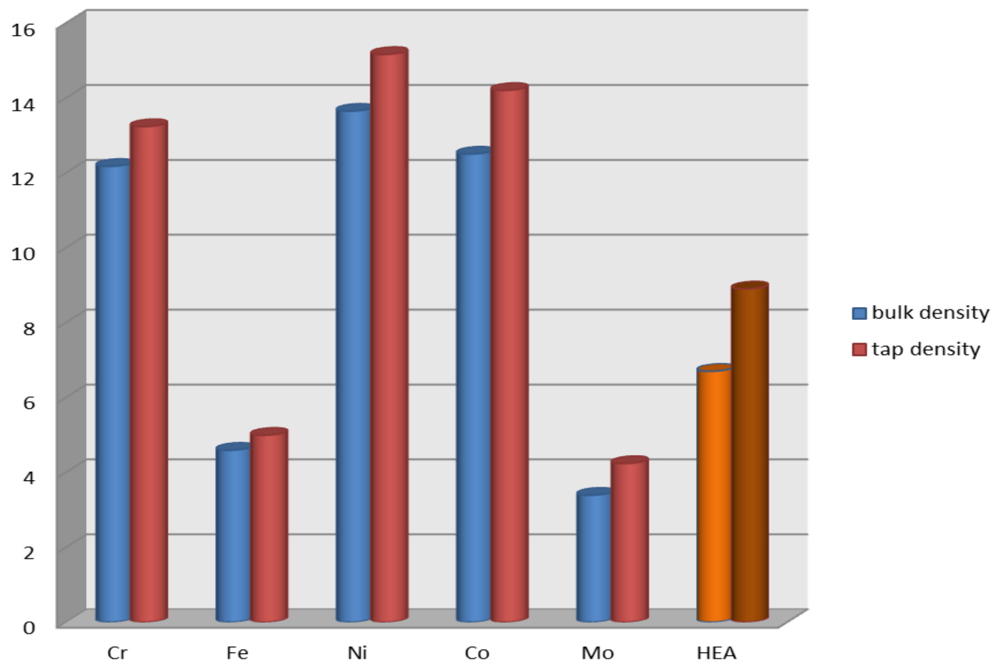


Fig. 5. The bulk and tap density for component powders and high entropy alloy.

The flow rate is the time it takes for a sample of powder with a standard weight (50g) to flow under normal conditions through Hall flow meter in the container. A determination of the powder flow rate is important in the manufacturing process which depends on the quick, uniform and consistent filling of the container. The term free flow refers to physical properties: particle shape and size, type of material, environmental factors, a.s.o. [13].

The characteristics of powder surfaces, such as surface oxide films affect the flow characteristics. The presence of the oxide film on the surface of the powder particles modifies the friction between the particles by increasing the flow rate. Powders with a lower content of surface oxide flow slower than powders with higher levels of oxide. In general, reduced flow rates are found in powders that exhibit one or more of the following characteristics: low weight, low apparent density, high friction coefficient for fine particles, and high moisture content.

Ideal composite powders for plasma deposition applications are those that allow the powder to flow easily into the mold cavity. The flow rate of metal powders is determined by standard methods developed by the American Society for Testing of Materials (ASTM) and the Metal Federation for Powder Industries (MPIF). Flow resistance depends primarily on the area where a particle prevents the free flow of other particles either by direct or indirect contact. This is mainly determined by the coefficient of friction between the particles. Particles may prevent movement; separate from temporary adherence. In this way, the formed groups can occupy a considerable volume. The cluster formation phenomena depend on the circulation and the type of powder, varying significantly with the size and structure of the flow particles. If the particles were spherical, they would generally fall easily into a cavity. This can rarely be achieved with commercial powders, as the difference between size and shape is inevitable [11].

Powder flow is influenced by the type of material. The major influence is the theoretical density. Other features such as adhesion and cohesion of surface properties or electrostatic interactions are also factors that influence the flow rate.

Exposed powder to air with a relatively high humidity absorbs moisture on the particle surfaces, which causes the flow rate to decrease. Very low temperatures can produce moisture condensation.

A metallic powder having a lower specific weight (Al or Ti) generally has a lower flow rate compared to high specific weight powders such as Ni or Cr. At the same time, the apparent density of a given material is higher as the flow rate is higher.

The ratio between apparent density and specific weight can be used to correlate the properties of different metallic powders [18].

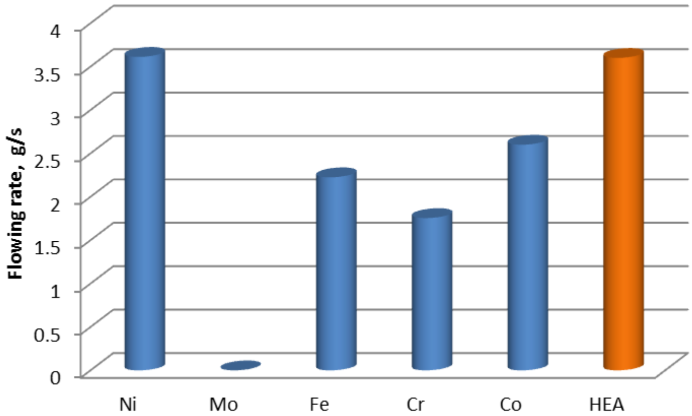
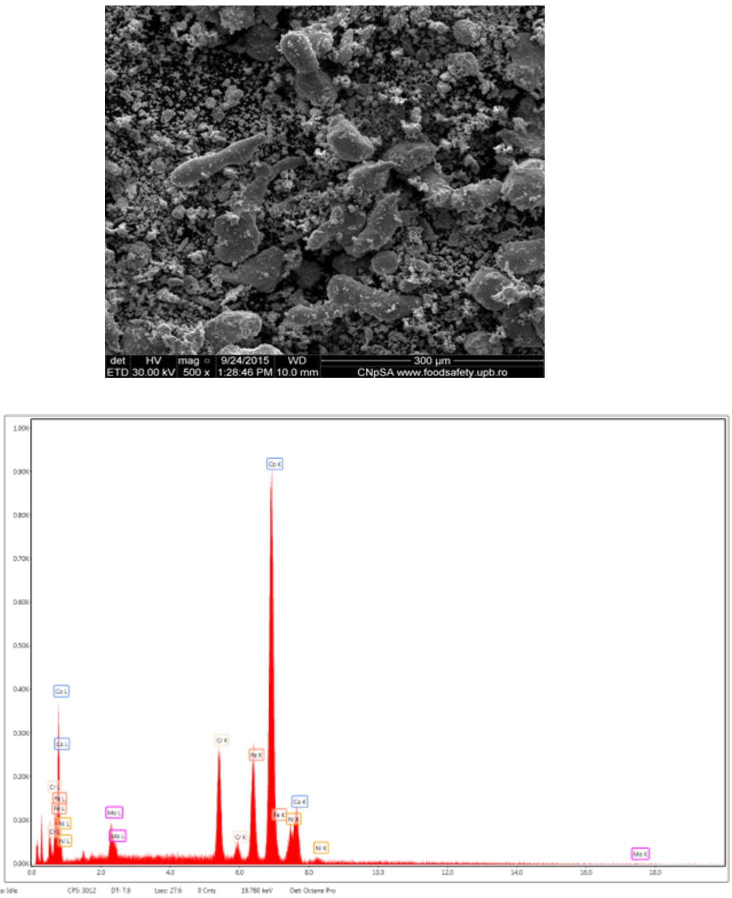
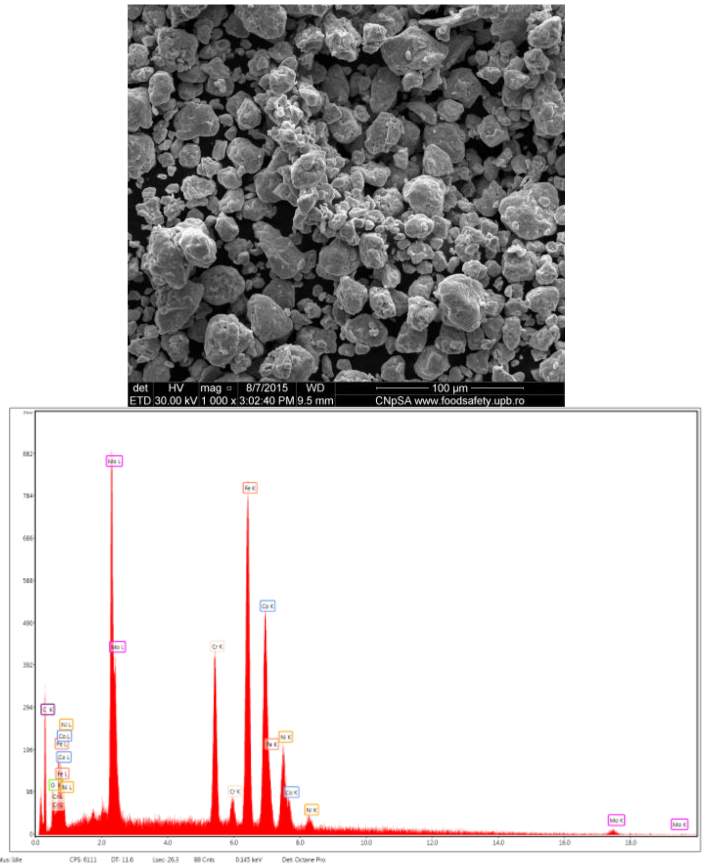


Fig. 6. The flow rate of the component powders and the final alloy obtained

Fig. 7 shows the SEM images and EDS analyze result identifying all the component elements for the homogenized alloy and for the 25 h mechanically alloyed HEA.



a – 0h



b – 25h

Fig. 7. SEM images and EDS analyze results for homogenized (a) and (b)25h mechanically alloyed HEA

The microstructure reveals a homogenous structure and the mean particle diameter value is confirmed, the particles being below 100 microns. Although the alloying degree could not be assessed by the microstructure we can see that the powder is changed in comparison with the homogenized powder.

We can also say that the elements Co, Cr, Fe, Ni and Mo are identified by EDS analyze [19, 20, 21, 22].

4. Conclusions

The paper presented a synthesis of a high entropy alloy by mechanical alloying.

The assessment of the powder obtained after 25h is necessary for taking the decision of going further to reach and advanced alloying degree or using the powder obtained after 25h for coating parts needing high resistance to corrosion.

The powder obtained was alloyed, mean diameter was 91.64microns. The microstructure of the powder obtained was homogeneous and the EDS analyze identified all the component elements in the high entropy alloy.

The flowing rate for the powder was calculated using a Hall flowmeter and the value is almost the same with Ni powder, 3.5g/s. The flow rate of the obtained HEA allows us to use this alloy for further experiments in coating different parts.

The bulk density and tap density were calculated and the results were encouraging for using the CoCrFeNiMo powder as coating layer for high corrosion resistance parts.

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