Microstructure characterization of HfNbTaTiZr High Entropy Alloy Processed in Solid State

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Abstract. This work investigates the alloying degree of HfNbTaTiZr high entropy alloy in equimolar percentages from raw, high purity powder, using solid state processing, for further uses in coating work components in harsh environments like marine, geothermal or oil and gas industry. The combination of elements was chosen according their properties, tailoring the composition for the final purpose. The alloying has been performed in a planetary ball mill with stainless steel vial and balls in a protective argon atmosphere to prevent oxidation, contamination or ignition and N-heptane as a process control agent to improve the material’s behavior during welding and re-welding in mechanical alloying process. Samples were taken at regular periods of time and analyzed to check the alloying degree evolution and to establish the optimum parameters for milling, best results being obtained at a speed of 300 rpm for 180 min (effective time) providing an alloying degree over 50% was achieved.

1. Introduction
In contrast to traditional alloy that are made up of a base metallic element and alloying elements, high entropy alloys, HEAs, consist in 5 or more elements in equiatomic or near equiatomic proportions, where each element brings its properties into the final alloy, phenomenon called “Cocktail Effect”, one of the 4 Core Effects of High Entropy Alloys. The others are “High Entropy Effect”, the “Sluggish Diffusion Effect”, and the “Severe Lattice Distortion Effect”. HEAs where firstly mentioned by Huang KH and Yeh JW in 1996 [1], but the interest for them didn’t develop until 2004 when considerable results have been published.

These alloys are solid solutions with improved thermal stability, high strength and higher hardening capacity compared to the traditional alloys, combined with superior strength under different environmental conditions [2], from where it turns out that HEAs might represents a new approach in the case of coatings for the in-work components from harsh environments like marine, geothermal or oil and gas, adding superior mechanical and functional properties.

High entropy alloys can be obtained by vacuum arc remelting, induction furnaces or by powder metallurgy. The powder metallurgy route allows the production of a homogenous alloy with a strict controlled composition. Mechanical alloying is a method that involves repeatedly cold welding and fracturing of powder particles in ball mills and by using it is possible to synthesize a variety of alloys, whether or not in equilibrium state, starting from powders mixtures. It is a 3 steps process, first being
the homogenization and milling, followed by pressing and ending with sintering. In general high entropy alloys are produced in order to be is used for turbine blades, aerospace components and a variety of advanced materials with preset properties.

This paper will presents the performed experiments with the aim of producing HfNbTaTiZr high entropy alloy processed by mechanical alloying in order to obtain a suitable powder alloy that can be further used for coating through different methods such as LMD or ESD to improve the resistance against corrosion, erosion, abrasion, high temperature and pressure.

2. Materials and Methods

High entropy alloys are known due to their properties as oxidation resistance [3], high corrosion resistance [4] and fatigue endurance limit [5, 6] resulting a desired material suitable for harsh environment [7, 8]. The elements that compose this high entropy alloy were selected considering their properties in order to obtain a proper coating that needs to be corrosive, abrasive, high pressure and temperature resistant, increasing the lifespan of the components.

High purity powders of Hf, Nb, Ta, Ti and Zr were milled using planetary ball mill Pulverisette 6 in a stainless steel vial with balls from the same material as the vial under argon atmosphere to prevent oxidation, contamination or ignition (figure 1). N heptane was used as a process control agent to improve the material’s behavior during welding and re-welding in mechanical alloying process.

After several trials, the powder was milled at 300 rpm with a ball to powder ratio of 10:1 [9] for 30 hours and samples were taken at certain intervals during the process to be analyzed to see the evolution of the alloying degree. The results were compared with the analysis of the homogenized sample. The purpose of the experiment was to obtain a fine-grained powder with a high degree of alloying.

For powder characterization of the obtained HfNbTaTiZr high entropy alloy, size distribution was measured by using a sieve analyzer, Fritsch Analysette 3 Spartan with 160 μm to 20 μm apertures sieves, followed by measurements of the flow rate using a calibrated Hall flow meter, apparent and tap density measured with a graduated cylinder, and the slope angle.

![Figure 1.](image1.jpg)  
(a) Fritch planetary mono mill used for the experiments; (b) Analysette 3 sieve analyzer used for assessing the size distribution of the HEA powder produced.

The apparent density of metallic powders is a fundamental property and defines the real volume occupied by a mass of free-flowing powder affecting directly their processing parameters, such as the design of the press and the magnitude of movements required to densify the metallic powder and
depends on the solid material density, surface area, particle size, distribution, shape, roughness and arrangement. Reducing particle size generally decreases apparent density.

Limited information available in the literature for the raw powder materials lead to following the same classic metallurgy powder characterization. Due to powder reactivity, special precautions were taken into consideration and the powder handling was performed with increased attention in a glovebox under argon atmosphere with a concentration of oxygen under 3%.

3. Results and Discussions

According to O.N. Senkov et. al. [10] BCC phases were obtained when the high entropy alloy was prepared by vacuum arc remelting of the equimolar mixture of the high purity elements resulting an alloy with a high hardness and a good structure. All the containing elements of this high entropy alloy have the BCC crystal lattices just below their melting temperature [11], but mechanical alloying process is a completely solid-state processing technique, where limitations imposed by phase diagrams do not apply. One of the greatest advantages of mechanical alloying is the synthesis of novel alloys that are not possible by any other technique because of the immiscibility of the elements [12].

Preliminary tests consist of the comparison between homogenized and alloyed powder at different speeds to establish the optimum parameters (figure 2).

![Figure 2](image)

**Figure 2.** Microstructure of HfNbTaTiZr high entropy alloy: (a) Sample milled for 125 min at 200 rpm; (b) Sample milled for 125 min at 300 rpm.

![Figure 3](image)

**Figure 3.** Particle size distribution for the high entropy alloy milled for 75 min and 450 min.

The average powder dimensions used for these experiments were specified by each producers and it was approximatively 63 \( \mu \text{m} \). Particle size distribution comparison between the preliminary and the final sample is presented in figure 3 [9].

A significant reduction of particles size is observed so it turns out that experiment was a success, the main concern was the ductility and the large granulation of titanium.
Figure 4. Comparison of apparent and tap density and the flow rate between the elements and the alloyed powder.

It can be observed from the chart (figure 4) that the characteristics of the alloyed powder are improved compared to raw elemental powders.

Figure 5. Comparison of the slope angle and flow rate between the elements and the alloyed powder.

The slope angle and flowing rate were measured in order to check if the powder fulfills the condition to be used in coating processes, thus meaning to have a flowing rate in the range of “good flowing” and a slope angle lower the 35° giving a better indication about the powder flowing rate (figure 5).

In figure 6 the SEM image for the homogenized powder is presented. The EDS analyses indicate all the elements present in the mixture. The mixture is unhomogeneous and the different shapes of the particles could be visible in the microstructure.

Figure 6. SEM image and EDS analyzes results for HfNbTaTiZr high entropy alloy homogenized.
The samples were taken at regular time intervals to investigate how the powder morphology was changed during mechanical alloying and to evaluate an alloying degree. We took into consideration the fact that the powder will be further used for spraying a coating so our goal was to obtain a uniform distribution and an alloying degree that could help us for further use of this powder. The alloying will be complete after further processing (pressing and sintering or spraying for a coating). The microstructure evolution is presented in figure 7.

![SEM images for the High entropy alloy samples taken at: (a) 150 min, (b) 225 min, (c) 300 min, (d) 375 min, (e) 450 min, (f) EDS analyzes result for the last sample (most homogeneous).](image)

**Figure 7.** SEM images for the High entropy alloy samples taken at: (a) 150 min, (b) 225 min, (c) 300 min, (d) 375 min, (e) 450 min, (f) EDS analyzes result for the last sample (most homogeneous).

SEM analyses indicate the obtaining of a more homogenous alloy. The particles sizes decreased and the shape is cuboidal for the particles in figure 7(e). The high entropy alloy particles are welding and breaking during mechanical alloying process. Also the agglomeration process is produced especially when the process control agent is consumed. We can observe that the dimensions of the particles in figure 7(e) are slightly larger than the one in figure 7(d), due to the agglomeration process during analyzing the particles. The EDS of the last samples (the most alloyed one) presented in figure 7(f) reveals all the elements inside the high entropy alloy and lake of oxygen or iron meaning that the samples were not contaminated. We evaluated an alloying degree of 50% which will ensure a good processing for the powder. The alloying degree will be increased to over 99% after further processing of the powders, as in spraying with HVOF to achieve a high corrosion resistant coating.
4. Conclusions
HfNbTaTiZr high entropy alloy was produced by solid-state processing technique and the assessment of the alloying degree performed due to microstructure analyses and size distribution analyzing revealed that the optimum rotational speed was obtained at 300 rpm for the vial with the increasing of the milling time up to 30 hours.

The alloying degree after mechanical alloying is hard to be predicted but from previous experience in producing powders that will be further used for coating process, an alloying degree over 50% is desired. The alloy is designed for further use as coating for components that are exposed to highly aggressive environments.

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Acknowledgements
The work has been funded by the Operational Programme Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705.