

## HfNbTaTiZr HIGH ENTROPY ALLOY PROCESSED BY MECHANICAL ALLOYING

Ciprian Alexandru MANEA<sup>1</sup>, Ioana CSAKI<sup>2</sup>, Laura Elena GEAMBAZU<sup>3\*</sup>,  
Florin MICULESCU<sup>4</sup>, Mircea Ionuț PETRESCU<sup>5</sup>, Francesco FANICCHIA<sup>6</sup>,  
Mirela SOHACIU<sup>7</sup>, Lucian ROSU<sup>8</sup>

*This paper presents the investigation realized on the influence of the mechanical alloying parameters for HfNbTaTiZr high entropy alloy. According to literature, this alloy, processed in liquid state, presents good hardness values and good corrosion resistance. This paper approach on processing this high entropy alloy in solid state to achieve the optimum alloying degree for further processing.*

*The goal of this research is to develop a suitable material for the geothermal power plant in work components. Corrosion represents one of the important factors in geothermal field, mainly due to the geothermal steam composition (H<sub>2</sub>S and CO<sub>2</sub>), which affects the current stainless-steel components. The aim is to develop a high entropy alloy with increased corrosion resistance and good mechanical properties, suitable for this aggressive environment.*

**Keywords:** high entropy alloy, sizing, microstructure assessment, geothermal steam

### 1. Introduction

Developing a corrosive resistant material, represents a high priority in the geothermal field. Geothermal steam mainly consists of hydrogen sulphide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>), and so the geothermal environment is highly corrosive, affecting the in-work components of the geothermal installation.

---

<sup>1</sup> PhD Student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, ciprian.a.manea@gmail.com

<sup>2</sup> Assoc. Prof. Habil., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, ioana.apostolescu@upb.ro

<sup>3</sup> PhD Student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, laura.geambazu@gmail.com

<sup>4</sup> Prof. Habil., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania,

<sup>5</sup> Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania,

<sup>6</sup> PhD MSc., TWI, Cambridge, England

<sup>7</sup> Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania,

<sup>8</sup> Eng., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania,

High entropy alloys represent a novel type of alloy, with superior mechanical and functional properties. These alloy benefits of improved properties based on the cocktail effect, where each element brings its good into the final alloy. Based on over time results in this matter, the high entropy alloys might represent the new generation of coatings for the in-work components of the geothermal installation.

In this paper HfNbTaTiZr high entropy alloy processed by mechanical alloying will be studied, in order to obtain a suitable alloy that can be further used as a coating for the in-work components of the geothermal installation, thus improving the resistance to aggressive factors from the geothermal environment.

## 2. Materials and Methods

High entropy alloys are known due to their properties as oxidation resistance [1], high corrosion resistance [2] and fatigue endurance limit [3, 4], resulting in a desired material, suitable in the geothermal environment [5,6].

The composing elements of this high entropy alloy were selected taking in consideration their properties in order to obtain a suitable coating for the components. The coating is required to be corrosive, abrasive, high pressure and temperature resistant.



Fig.1. Hafnium powder

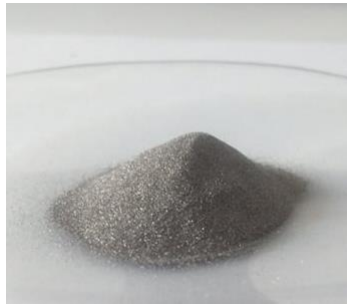


Fig.2. Niobium Powder



Fig.3. Tantalum Powder

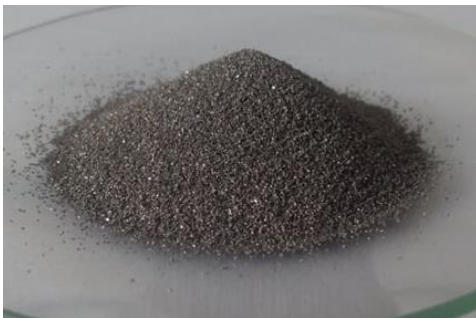


Fig.4. Titanium Powder



Fig.5. Zirconium Powder

Hafnium (fig. 1) is known for its high resistance to concentrated alkalis, but it can react with oxygen, nitrogen, carbon, boron, sulphur, and silicon at high temperatures. Because of its good absorption cross section for thermal neutrons, the material is extremely corrosion resistant, excellent mechanical properties and it is also used for reactor control rods.

Niobium (fig. 2) has superconductive properties and this property is often used in strong magnetic fields. It is used in super-alloys due to its corrosive resistant properties, in applications such as heat-resistant equipment, rocket subassemblies and engine components, being also a promising material for the electric power industry [7 - 9].

Tantalum (fig. 3), presents a high affinity for the interstitial gases such as O<sub>2</sub>, N, C and H<sub>2</sub> and the resulting compounds are very stable at high temperature. High purity tantalum metal is ductile and its mechanical behavior is sensitive at high temperature and strain rate, but also can be strengthened and forms solid solutions with other refractory metals such as molybdenum, niobium and tungsten [10].

Titanium (fig. 4) is known for its good resistance to corrosion in a wide range of environments. The principle applications of the titanium use are chemical industry (where sea water and polluted estuarine water are used in steam condensers), desalination plants, marine engineering, oil production and metallurgical industries [11].

Zirconium (fig. 5) is exceptionally resistant to corrosion by many common acids and alkalis, by sea water, and by other agents [7]. The main applications of the material are for the chemical industry where corrosive agents are employed. With niobium, zirconium is superconductive at low temperatures.

For our experiments we have used raw, high purity powders of Hf, Nb, Ta, Ti and Zr and we placed the in a Fritsch planetary mono-mill (fig 6), with stainless steel vials and balls. The ball to powder ratio (BPR) used was 10:1. The milling performed was wet milling in N- Heptane. N heptane is also a good process control agent helping the material during welding and re-welding within the mechanical alloying process. The milling time varied from 125 min, 180 min and 225 min and 360 min. For 125-minute mechanical alloying we used 2 different rotational speed to determine the most appropriate for our application. The size distribution was measured with the sieve shaker presented in Fig. 6, having sieves with openings from 160 µm to 20 µm.

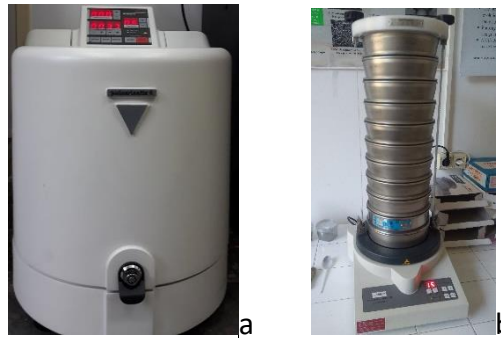


Fig. 6. a. Fritsch planetary mono mill used for the experiments and b. Analysette 3 sieve sizer used for assessing the size distribution of the HEA powder produced.

Sizing the powder was important in assessing the mechanical alloying process due to the fact that we can monitor the particle diameter reduction to a certain extent and to have the powder prepared for different processing. The idea of developing a bulk material of HfNbTaTiZr is for producing electrodes for electro-spark deposition process (ESD). The bulk HfNbTaTiZr high entropy alloy will be very expensive as cast or as sintered for using in a geothermal power plant. The idea of developing this material is for further producing coatings using different procedure as high velocity oxygen fuel spraying (HVOF) or laser cladding (LC). For these kind of coating we need powders with dimension between  $63 - 120\mu\text{m}$  (LC) or  $20 - 63\mu\text{m}$  (HVOF). The higher and the finer cut could be mixed together and consolidated to produce electrodes for ESD. Thus sieving was important in assessing the obtained powder.

### 3. Results and Discussions

One of the properties should be a good structure, suitable for this type of environment and according to literature HfNbTaTiZr high entropy alloy is characterized by BCC phases, which results in high hardness.

According to O.N. Senkov et. al., [12] BCC phases were obtained, when the high entropy alloy was prepared by vacuum arc remelting of the equimolar mixture, of the high purity elements. For a homogenous structure the alloy was remelted 3 times, keeping the alloy in a liquid state for 5 minutes, each melting. All the containing elements of this high entropy alloy have the BCC crystal lattices just below their melting temperature [13].

Mechanical alloying process is a completely solid-state processing technique, where limitations imposed by phase diagrams do not apply. This process also appears to be an economical process with vast potential and mechanically alloyed powders produce a variety of metastable phases.

One of the greatest advantages of MA is in the synthesis of novel alloys that are not possible by any other technique, such as alloying of normally immiscible elements [14].

To establish the optimum speed for these experiments we kept the time at 125 min and varied the speed. We used 200 rpm and 300 rpm for the vial. The powders initial dimension was around 63 $\mu$ m. the microstructure of the samples obtained are presented in Fig. 7.

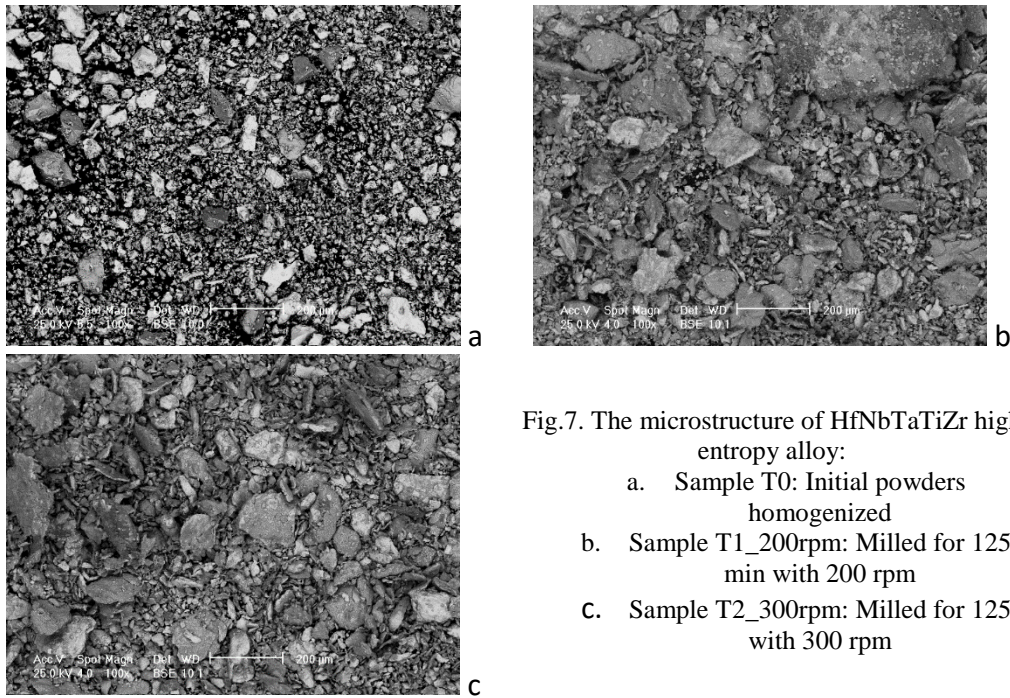


Fig.7. The microstructure of HfNbTaTiZr high entropy alloy:

- a. Sample T0: Initial powders homogenized
- b. Sample T1\_200rpm: Milled for 125 min with 200 rpm
- c. Sample T2\_300rpm: Milled for 125 min with 300 rpm

The powders were sieved to see if a reduction in the diameter occurred to establish the proper rotational speed for the vial. The results are presented in the Fig. 8.

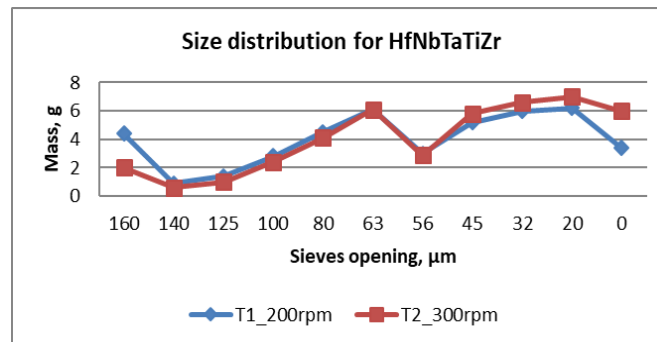


Fig. 8. The size distribution of HfNbTaTiZr high entropy alloy for different rotational speed.



The 300rpm speed used provided us a lower powder dimension so we decided to use further this rotational speed for the vial. The milling time was increased due to the homogeneity problems encountered at 125 min. The microstructure revealed that the sample were not homogenous, and the alloying degree was very poor. The samples were named as T2 - sample milled for 125 min with 300 rpm, T3 - sample milled for 180 min with 300 rpm, T4 - sample milled for 225 min with 300 rpm and T5 - sample milled for 360 min with 300rpm. The microstructures of the produced samples are shown in Fig. 9.

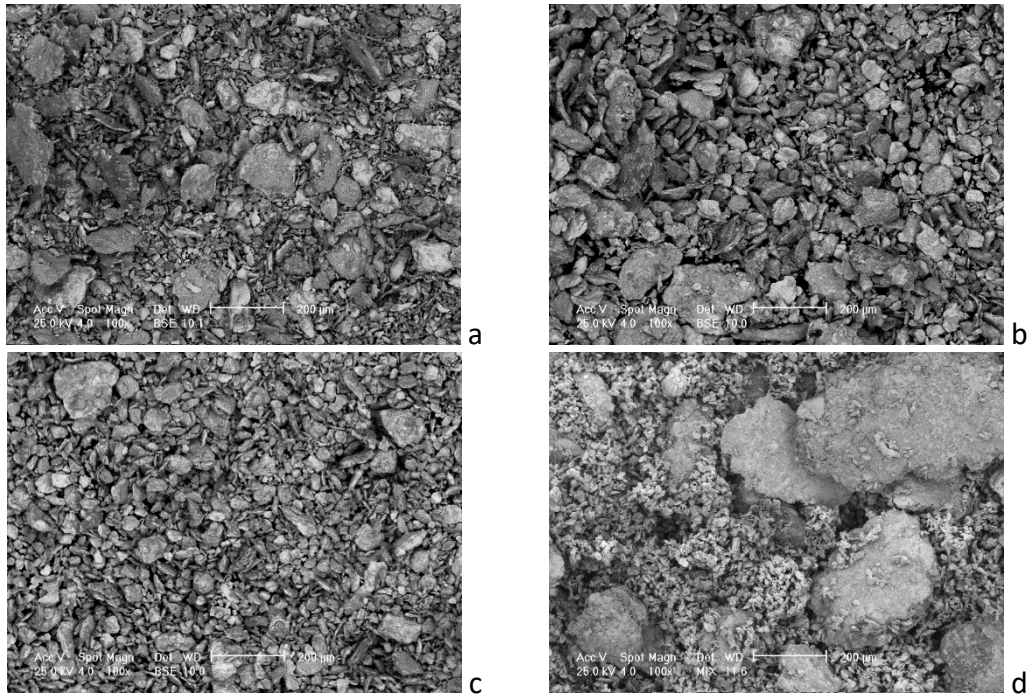


Fig. 9. Microstructure of the samples: a. T2, b. T3, c. T4, d. T5 revealing a composition from inhomogeneous to homogenous in case of T5 sample

The EDS analyses results for the sample T5 are presented in Fig. 10 to confirm the composition investigate.

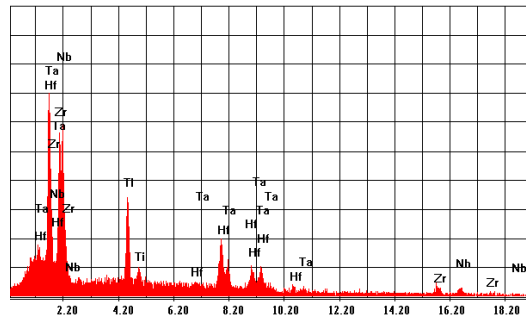


Fig.10. EDS analyses results revealing all the elements for HfNbTaTiZr high entropy alloy

From the microstructure analyses we can observe that between the sample T2 and T3 there is a small difference regarding the homogeneity degree and the powder particles dimensions. The Samples T3 and T4 are just slightly difference showing that the increase of time from 180 min to 225 min resulted in very small changes. Thus, we decided to increase the time at 360 min and the alloying degree was clearly improved and the final high entropy alloy obtained is much more homogenous. There is some agglomeration of the particles in T5 samples, probably due to the Ti powder properties but in further processing this powder will behave much better than the other samples.

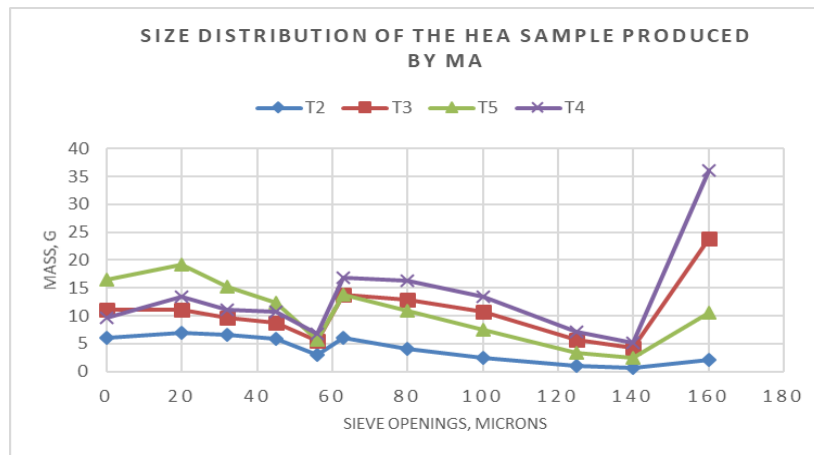


Fig.11. Size distribution for the processed HEA samples T2 to T5, finer cut being the highest in case of sample T5.

The results of the size distribution is presented in Fig. 11. The size distribution reveals a larger fine cut for the sample T5. The best alloying degree was obtained after milling 360 min with 300 rpm rotational speed for the vial.

#### 4. Conclusions

HfNbTaTiZr high entropy alloys samples were produced in solid state. The assessment of the alloying degree performed due to microstructure analyses and size distribution analysing revealed that the optimum rotational speed was obtained at 300 rpm for the vial. Stainless steel vials and balls were used, and EDS analyses results confirmed no contamination of the samples. After increasing the milling time and assessing the microstructure for the produced sample resulted that the best mechanical alloying time is 360 min for HfNbTaTiZr high entropy alloy. The alloy is designed for further use as coating for geothermal components inside a geothermal power plant, which are exposed to highly aggressive geothermal steam.

### Acknowledgements

This work is part of the H2020 EU project Geo-Coat: Development of novel and cost-effective corrosion resistant coatings for high temperature geothermal applications. Call H2020-LCE-2017-RES-RIA-TwoStage (Project no. 764086).

### REFERENCES

- [1] *M.H. Chuang, M.H. Tsai, W.R. Wang, S.J. Lin, J.W. Yeh*, Microstructure and wear behavior of  $\text{Al}_x\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_y$  high-entropy alloys, *Acta Mater.*, **vol. 59** (16), 2011, pp. 6308-6317
- [2] *Y.L. Chou, Y.C. Wang, J.W. Yeh, H.C. Shih*, Pitting corrosion of the high-entropy alloy  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.1}$  in chloride-containing sulphate solutions,” *Corrosion Science*, **vol. 52**, no. 10, 2010, pp. 3481–3491
- [3] *M.A. Hemphill, T. Yuan, G.Y. Wang, J.W. Yeh, C.W. Tsai, A. Chuang, P.K. Liaw*, Fatigue behavior of Al 0.5 CoCrCuFeNi high entropy alloys, *Acta Mater.*, **vol. 60**, 2012, pp.5723-5734
- [4] *M. Feuerbacher, M. Heidelmann, C. Thomas*, Plastic deformation properties of Zr–Nb–Ti–Ta–Hf high-entropy alloys, *Philosophical Magazine*, 2015, pp. 1221-1232
- [5] *S. Serghiuta, I. Csaki, S.N. Karlsdottir, L.E. Geambazu, C.A. Manea*, Multi - component alloy synthesized by a powder metallurgy route, UNIVERSITY POLITEHNICA OF BUCHAREST SCIENTIFIC BULLETIN SERIES B-CHEMISTRY AND MATERIALS SCIENCE, **vol. 80**, Issue: 1, 2018, pp. 163-172
- [6] *I. Csaki, K.R. Ragnasdottir, A. Buzaianu, K. Leosson, V. Motoiu, S. Guðlaugsson, M.V. Lungu, H.O. Haraldsdottir, S.N. Karlsdottir*, Nickel based coatings used for erosion-corrosion protection in a geothermal environment, *Surface and Coatings Technology*, **vol. 350**, Sept. 2018, pp. 531-541
- [7] *D.R. Lide*, *CRC Handbook of Chemistry and Physics*, Internet Version 2005, <<http://www.hbcpnetbase.com>>, CRC Press, Boca Raton, FL, 2005.
- [8] *R.E. Lenga, K.L. Volonpal*, The Sigma Aldrich Library of Regulatory and Safety Data., **vol. 3**, Sigma Chemical Co. and Aldrich Chemical Co., Inc. 1993.
- [9] *R.J. Lewis*, *Hazardous Chemicals Desk Reference*, 4th ed., John Wiley & Sons, New York, Dec. 1997.
- [10] *S.M. Cardonne, P. Kumar, C.A. Michaluk, H.D. Schwartz*, Tantalum and its Alloys, *Int. J. of Refractory Metals & Hard Materials*, **vol. 13**, 1995, pp. 187- 194
- [11] *W.T. Roberts*, *Titanium*, Endeavour, **vol. 7**, Issue 4, 1983, pp. 189-193
- [12] *O.N. Senekov, J.M. Scott, S.V. Senkova, D.B. Miracle, C.F. Woodward*, Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy, *Journal of Alloys and Compounds*, **vol. 509**, 2011, pp. 6043-6048
- [13] *T.B. Massalski, H.Okamoto, P.R. Subramanian, L. Kacprzak*, *Binary Alloy Phase Diagrams*, 2<sup>nd</sup> ed., ASM International Materials Park, Materials, OH, SUA, 1990.
- [14] *C. Suryanarayana*, Mechanical alloying and milling, **vol. 46**, Issues 1–2, January 2001, pp. 1-184