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IOP Conf. Series: Materials Science and Engineering **572** (2019) 012024 doi:10.1088/1757-899X/572/1/012024

New refractory high entropy alloys

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Abstract. The paper presents researches on the microstructure and mechanical properties of a new types of refractory high entropy alloys, which can be used for thermal engine components as well as for military incendiary bullet. The main characteristics required for such applications are high compression resistance, microstructural stability during thermal stress, hardness and corrosion resistance. To obtain such specific characteristics, the raw materials must be melted in inert protective atmosphere, and then heat treated for the homogenization of the microstructure and chemical composition. In the paper, there have been studied three types of high entropy alloys, HfMoNiTaW, 2HfMoNi2Ta and MoNiTaW obtained in the vacuum arc remelting (VAR) equipment. The heat treatment, performed at 800 ºC with a holding time of 4 hours, allows obtaining a good homogenization of the chemical composition while generating a decrease in the microhardness, from a maximum value of 637 $HV_{0.2}$ to a minimum value of 527$HV_{0.2}$.

1. Introduction

Refractory alloys are designed to operate under heavy-duty conditions, including high temperature values, particularly chemical aggressiveness of the working environment, dynamic stresses, over long periods of time. In recent years, there has been developed a number of high entropy alloys containing refractory elements such as W, Ta, Hf, Mo, V or Nb in their chemical composition. It is rather difficult to obtain homogeneous alloys containing simultaneously a number of refractory chemical elements due to their high melting temperatures. Nanostructured metallic matrices were obtained by mechanical alloying using VNbMoTaW powders, for which high hardness values (over 11 GPa) [1] were reported.

The equimolar HfNbTaTiZr alloy was corrosion tested in 3.5 wt% NaCl solution, yielding a higher corrosion resistance compared to 316L stainless steel. This behaviour was attributed to the formation of a uniform and homogeneously distributed passivation layer. An important role in increasing the breaking strength and the immunity to the chemical solution was attributed to the Ta element in the alloy composition [2]. The mechanical characteristics of refractory high entropy alloys largely depend

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on the equilibrium conditions established by the production and processing methods, the number of phases in the alloy, as well as on the temperature and the test method [3]. In general, the yield stress value decreases with a higher temperature rise in the case of single phase (disordered or ordered) alloys compared to those featuring two phases or more.

The heat treatments can produce a number of microstructural changes in the refractory high entropy alloys. Thus, it was found that the refractory alloy $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ has only one phase after annealing at 900 ^{o}C for two weeks. However, there was observed a tendency to form fine precipitations on the grain boundaries in the samples treated at 800 ^{o}C, while in those treated at 700 ^{o}C there were observed precipitates with petaloid morphology, with the BCC structure on both the grain boundaries and intergranular.

The annealing at 500 ^{o}C highlighted the formation in the microstructure of multiple phases, with complex morphologies [4, 5]. The Zr-Nb-Ti-V-Hf type alloys obtained in levitation furnaces and heat treated for homogenization at 1500 ^{o}C for 6 hours revealed a one phase microstructure, without any secondary phases [6].

Another method of producing NbTaTiV refractory alloys was by powder metallurgy and sintering at 1700^{o}C. It has been found that these alloys feature high hardness values simultaneously with good plasticity [7]. The VNbMoTaW type alloys produced by powder metallurgy (5GPa pressure at temperatures between 800 and 1500 ^{o}C under argon atmosphere) have very high hardness values. The finer the powder (nano grains), the higher the hardness values, up to doubling [8].

The equiatomic HEAs have special mechanical properties, such as wear and fatigue resistance, which have been attributed mainly to the ability to form complex solid solutions, in which the formation of fragile intermetallic compounds is partially or totally supressed as a result of the high mixing entropy and enthalpy [9]. According to the latest assessments [10-15], the criteria for forming simple solid solutions in high entropy alloys must meet the following conditions:

- The configuration entropy (ΔS_{conf}) for high entropy alloys must be above 11 J/mol K
- The mixing enthalpy (ΔH_{mix}) of the alloy must be between -11.6 kJ/mol and 3.2 kJ/mol.
- The difference between the atomic radii (δ), stating that the phases containing predominantly solid solutions are formed for values below 6.6% (at values below 4% only solid solutions are formed).
- The derivative parameter Ω, which includes ΔS_{conf} and ΔH_{mix} and which is taken into account only with δ. If $\Omega > 1.1$ and $\delta < 3.6\%$, only solid solutions are formed. If $1.1 < \Omega < 10$ and $3.6\% < \delta < 6.6\%$, solid solutions and intermetallic compounds are formed, and if $\Omega > 10$, only solid solutions are formed.
- The electronegativity difference $\Delta\theta$ (according to Allen) of the various components of the alloy must be between 3 and 6% to form only solid solutions.
- The critical correlation ratio, k_1^{cr}, must be calculated to obtain only solid solutions. It depends on homogenization temperature, configuration entropy, mixing enthalpy (for solid solution, ΔH_{mix} and for intermetallic compounds, ΔH_{IM}) and the ratio of compound formation entropy to that of solids formation (k_2 considered 0.6).

Depending on how the metallic matrixes are made, there can be obtained [11]:

- Only solid solutions (for low mixing enthalpy and low atomic size differences); the formation of a single-phase solid solution corresponds to the range values of -15 kJ/mol < ΔH_{mix} < 5 kJ/ml and $0 < \delta < 5$.
- Different phases, with the increase in ΔH_{mix} (mixing enthalpy) and δ (atomic size).
- Metallic glass as a metastable structure (with increase in δ (> 8) and decrease in the negative ΔH_{mix} value (< -15 KJ).

The paper presents microstructural aspects regarding several types of high entropy alloys, i.e. HfMoNiTaW, 2HfMoNi2Ta and MoNiTaW.

The experimental alloys were obtained in the vacuum arc remelting (VAR) equipment and then heat treated at 1100 ^{o}C and held for 24 h at the maximum temperature range followed by slow cooling with the furnace, i.e. at 800 ^{o}C, holding 4 and cooling with the furnace. The heating speed of about 0.25^{o}C/hour was obtained using the electronic control of the furnace Nabertherm LT 15/12/P320 used for heat treatments, fitted with a temperature regulator. In order to compare the results, there was conducted a metallographic analysis of the high density HEA alloy samples before the heat treatment and after the application of the homogenization heat treatment.

During the heat treatment performed at 1100 ºC, there occurred strong oxidation effects while the heat treatment, performed at 800 ºC with a holding time of 4 hours, allows obtaining a good homogenization of the chemical composition while generating a decrease in the microhardness, from a maximum value of 637 $HV_{0.2}$ to a minimum value of 527$HV_{0.2}$.

2. Materials and methods

2.1. Materials

The high entropy alloys have been designed to be used to produce the tips of high velocity piercing penetrators. The weight of the tip (bullet) should be appropriate for the amount of powder that is inserted into the cartridge so as to obtain rapid combustion and achieve the correct launch speed. The main features that metallic materials used in special applications need to feature for the best impact behaviour is as follows [10]:

- **Highest hardness** providing resistance to rapid penetration into the surface of the targets, with permanent shape changes, when being subject to a static or dynamic force.
- **High density** (to increase the penetration power and the impact precision)
- **Impact resistance** (high compression resistance) to preserve the geometry of the tip during target penetration.
- **Toughness** (tenacity, high impact strength) providing the ability to absorb the breaking energy and to limit the tendency of fragmentation and crack propagation.)

Figure 1. Buttons of heavy alloys obtained by melting in the VAR equipment.

Starting from these considerations, the following chemical elements with high densities were selected for the production of heavy high entropy alloys: Hf (ρ_{Hf} = 13.31 g/cm^3); Mo (ρ_{Mo} = 10.28 g/cm^3); Ni (ρ_{Ni} = 8.91 g/cm^3); Ta (ρ_{Ta} = 16.68 g/cm^3); W (ρ_W = 19.26 g/cm^3).

Table 1. The chemical composition of heavy high entropy alloys.

Chemical element, wt%	**2HfMoNi2Ta**	**HfMoNiTaW**	**MoNiTaW**
Hf	40.8	14.07	-
Mo	11	13.73	12.94
Ni	6.76	23.08	17.67
Ta	41.48	25.89	51.72
W	-	23.08	17.67

The experimental alloys were obtained by melting in the VAR MRF ABJ 900 equipment, in an inert argon atmosphere. The buttons obtained (figure 1) were rotated and re-melted at least 5 times on each side to improve homogeneity and allow the dissolution of the refractory materials.

The chemical composition of the alloys obtained, as average value measured in 3 different points by EDS analyse, is given in Table 1.

The values of the evaluation parameters calculated for assessment of the microstructures of experimental high entropy alloys, using the combination of the chemical elements Hf, Mo, Ni, Ta, W are summarized in Table 2.

Table 2. Calculated values of the assessment parameters for experimental high entropy alloys.

Parameter, units	**2HfMoNi2Ta**	**HfMoNiTaW**	**MoNiTaW**
ΔS_{conf}, J/molK	11.05	13.38	11.52
ΔH_{mix}, kJ/mol	-17.22	-16	-12.75
δ, %	8.09	7.73	4.91
VEC, %	6.33	7	7.75
$\Delta\chi$ (Allen), %	12.91	14.8	16.82
Ω	1.19	1.94	2.62
ΔH_{IM}, kJ/mol	-34.44	-32.64	-30.81
$k1^{cr}$	1.38	1.48	1.58
$\Delta H_{IM}/\Delta H_{mix}$	2.00	1.91	2.41
T^*_m, K	1868.43	2322.52	2903.15
ρ, g/cm^3	13.53	14.01	14.27

* T_m - the melting temperature

The analysis of the values presented in Table 2 reveals as follows:

- The alloy configuration entropy, ΔS_{conf} has values between 11.05 and 13.38 J/mol·K, which means that all three analysed alloys have high entropy;
- The experimental alloys have high densities, with values above 13 g/cm^3, meeting the necessary conditions for the manufacture of small-calibre penetrators; of these, the MoNiTaW alloy has the highest density value;
- The mixing enthalpy, ΔH_{mix}, is reduced for all alloys; none of them falls within the -11.6 to 3.2 kj/mol range (the closest value is featured by the MoNiTaW alloy). This means that no alloy forms only solid-type structures;
- The presence of intermetallic compounds in the structure is also evidenced by the criterion k_1^{cr}, where the $\Delta H_{IM}/\Delta H_{mix}$ values are higher than those specified in the literature [11].
- The valence electron concentration, VEC, has values between 6.33 and 7.75%, which results in the formation of solid solutions with both BCC and FCC phases.
- All four alloys have values of the derivative parameter, Ω, ranging from 1.1 to 3.6, but only for the MoNiTaW alloy the difference of the atomic radii, δ = 4.91%, is within the 4-6% range of values, the alloy predominantly forming solid solutions.

2.2 Heat treatments

After obtaining, the experimental alloys were subjected to heat treatments for homogenization: TT1 - homogenization at 1100 ºC for 24 hours, followed by slow cooling; TT2 – homogenization at 800 ºC for 4 hours followed by slow cooling. The heat treatments were performed in Nabertherm furnace, without protective atmosphere. After applying the first heat treatment, it was found that the alloys incurred severe oxidation effects with the occurrence of the disintegration and fragmentation phenomena. As a result, the heat treatment was resumed by lowering the holding value within the

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maximum temperature range of 800 °C, and reducing the holding time to 4 hours. The treated samples were analysed from a microstructural point of view, the results being compared with those obtained on samples without heat treatments [13].

3. Results

3.1 Microstructure
Samples were cut from the high entropy alloys specimens and were subjected to the metallographic preparation procedure (grinding with 320 to 600 sandpaper grit sizes and polishing with alumina powders with grain sizes between 6 µm and 0.3 µm). No chemical attack was applied, to prevent any influence on the chemical composition analyses.

The microstructural aspects and chemical composition analyses were carried out on the micro-zones, using EDS analyse. In the case of the 2HfMoNi2Ta alloy, the microstructure prior to the heat treatment exhibits Mo and Ta islands, which did not completely dissolve in the metal matrix of the alloy (Figure 2).

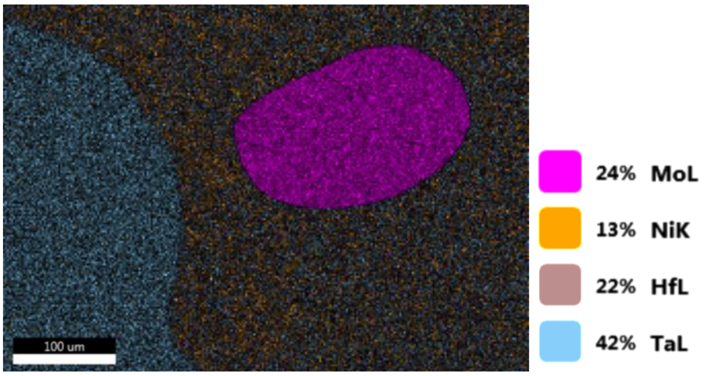


Figure 2. Microstructural analysis for the 2HfMoNi2Ta alloy.

After the homogenization heat treatment at 800 °C, the refractory chemical elements dissolved in the BCC HfMo and MoTa solid solution matrix [12]. Also has been observed the relatively uniform distribution of the Hf_xNi_y, Hf(Mo,Ni), $(Ni,Ta)_{6.5}$ intermetallic compounds and of the intermediate NiMo phases (Figure 3).

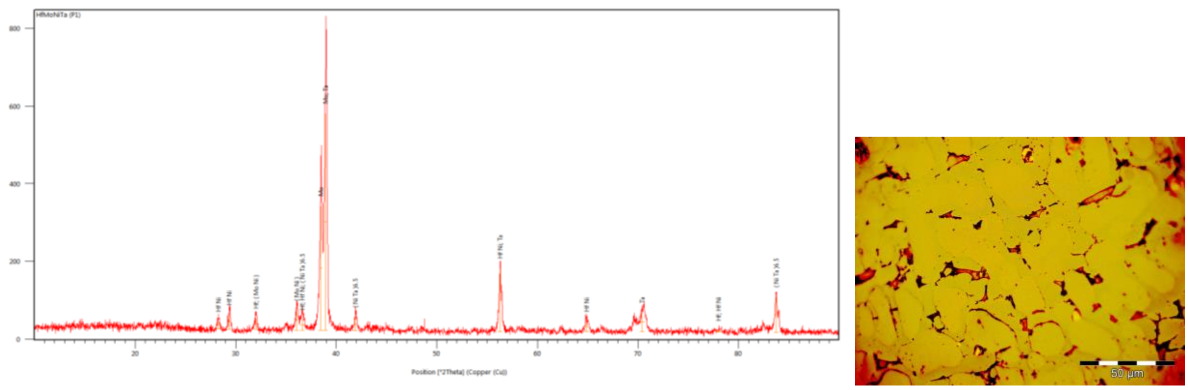
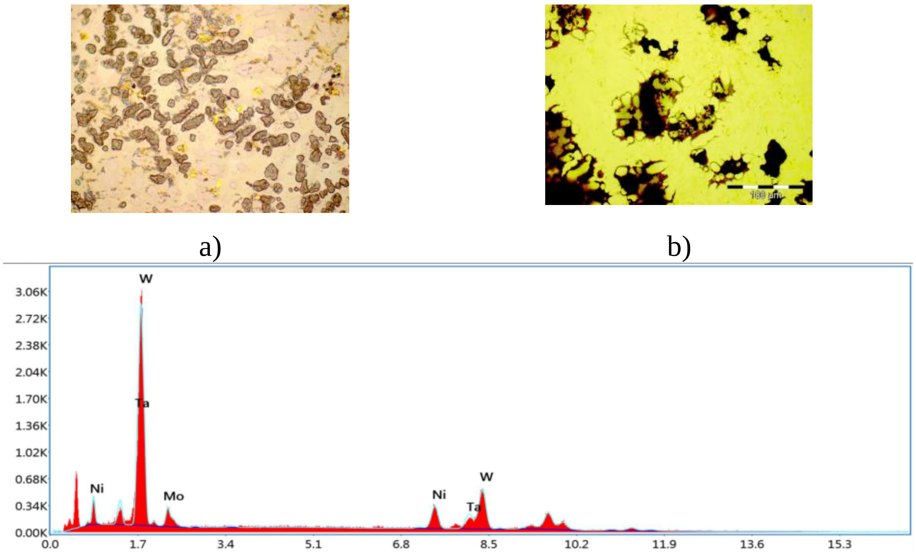


Figure 3. The diffractogram and the microstructure of the 2HfMoNi2Ta alloy following heat treatment.

As cast, the HfMoNiTaW alloy contains 2 types of solid BCC solutions (MoTa and MoW), intermediate phases (NiMo and NiTa), and Hf_xNi_y intermetallic compounds (Figure 4a). After applying the homogenization heat treatment at 800 °C for 4 hours and slow cooling, internal oxidation effects occurred in the dendritic microstructure, impacting the microhardness value (Figure 4b).

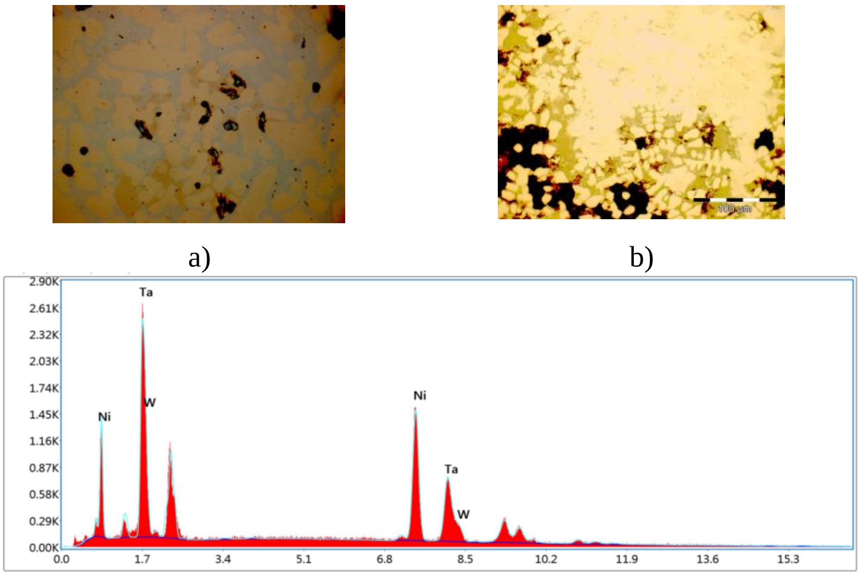


a) b)

c)

Figure 4. The microstructure of the HfMoNiTaW alloy: a) before the heat treatment; b) after the heat treatment; c) the spectrum of elements.

In the case of the MoNiTaW alloy, the dendritic microstructure is more homogeneous starting with the cast state, containing solid solutions of MoTa, MoW, and NiTa and WNi intermediate phases. After the heat treatment, the oxidation effects occur on the marginal areas of the mini-ingot (Figure 5b).



a) b)

c)

Figure 5. The microstructure of the MoNiTaW alloy a) before the heat treatment; b) after the heat treatment; c) the spectrum of elements.

3.2 Mechanical tests

3.2.1 Tensile tests. The compression tests in quasi-static regime revealed high values of the mechanical tensile strengths and very low elongations (0.024 - 0.03%). The values of the mechanical characteristics determined were as follows:

- Yield strength: 1400MPa for MoNiTaW; 1650MPa for 2HfMoNi2Ta; 1850MPa for HfMoNiW;
- Tensile strength: 2050MPa for MoNiTaW; 2150MPa for 2HfMoNi2Ta; 2350MPa for HfMoNiTaW.

3.2.2 Microhardness. In order to highlight the effects of heat treatments, there were conducted hardness tests before and after the application thereof (Table 3). All the 3 analyzed alloys underwent hardness decreases following the heat treatment.

Table 3. Microhardness $HV_{0.2}$ values of experimental high entropy alloys.

	Before heat treatments	**After heat treatments at 800°C/4h/slow cooling**
2HfMoNi2Ta	615	541
HfMoNiTaW	637	602
MoNiTaW	618	527

4. Conclusions

The analysis of the chemical composition values determined on micro-zones (EDS) revealed that certain high melting temperature elements (Mo, Ta, Hf) did not completely dissolve in the metallic matrix, remaining in the form of macro islands with various rounded shapes, surrounded by the highly alloyed solid solution.

The application of heat treatments to high entropy alloys can produce either hardening effects or increased plasticity and tenacity, depending on the heating temperature, the actual duration of holding at those temperatures and the cooling mode. In the case of the HfMoNiTaW, 2HfMoNi2Ta and MoTaNiW alloys, portions of the materials which did not completely melt in the first production can be dissolved in the solid solutions during the homogenization heat treatment.

After the homogenization heat treatment at 1100 °C followed by a 24-hour holding and by slow cooling, there was found that the alloys also incurred severe oxidation effects with the occurrence of the disintegration and fragmentation phenomena. The heat treatment performed at 800 °C followed by a 4-hour holding and by slow cooling caused the homogenization of the microstructure and the dissolution of the macro-islands formed during the melting process in the VAR equipment. This heat treatment allows obtaining a good homogenization of the chemical composition while generating a decrease in the microhardness, from a maximum value of 637 $HV_{0.2}$ to a minimum value of 527$HV_{0.2}$.

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Acknowledgements
This paper was supported by a grant from the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0875 – 20/2018 (HEAPROTECT).