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Combinatorial alloy design for Refractory High Entropy superAlloys (RHEA)

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1. Introduction

Recent studies have been focusing on the development of hypersonic vehicles, turbine engines and Gen-IV nuclear structural materials which will bear extreme conditions in terms of simultaneous strength and toughness. Even though current advanced Ni-based superalloys have good performance in high temperature environment but still their high density which leads to high cost and melting point up to ~1300˚C were main obstacles. To solve that problem several alloys with higher melting points, such as W-based alloys, Co-Re- or Co-AlW-based alloys [1] have been studied. Notwithstanding the promising mechanical properties, mass production of these high density alloys is not efficient economically thus those materials remain as a disputable problem.

The up-to-date idea of High Entropy Alloys (HEA) has been popular. They defined HEAs as alloys where constituent elements (more than 5) were in the range of 5 and 35 at%. Additionally, the definition in terms of configurational entropy of mixing (CEM),

$$\Delta S_{conf} = -R \sum X_i \ln(X_i) \qquad (1)$$

which is equal to or higher than 1.5R was included. Here, X_i is the atom fraction of element i and R is the gas constant. A high CEM reduces the formation of intermetallic phases and facilitates the formation of solid-solution phases which significantly affect the microstructure and properties . According to Coreño-Alonso et. al. $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ should be anticipated as the criteria which facilitate to form high entropy stabilized solid solutions where Ω and δ are the value for predicting the solid-solution formation and the compressive effect of the atomic size difference in n-element alloy, respectively.

Yeh et. al. stated that the number of principal elements is bounded by 13 because there was little change in CEM. Therefore, the number of equal-mole alloy by choosing 13 arbitrary principal elements will be 7099:

$$C_5^{13} + C_6^{13} + C_7^{13} + C_8^{13} + C_9^{13} + \\ + C_{10}^{13} + C_{11}^{13} + C_{12}^{13} + C_{13}^{13} = 7099 \qquad (2)$$

On the other hand, if we choose unequal-mole alloys there would be an indeterminable number of possible combinations of HEAs[2]. Therefore, there is a need to determine and optimize the multiprincipal HEAs in terms of their mechanical and other properties in an efficient way using high-throughput synthesis such as the combinatorial approach. The combinatorial approach has been mostly applied in areas of material science such as thin films while it was originated from combinatorial chemistry by Nobel Prize winner, Merrifield [3]. Basic idea relies on synthesizing a library with varying concentration along certain range. In this paper, there was studied roadmap to this composition and further development by a combinatorial alloy design. Moreover, replacing constituent elements such as Ta with Cr in order to increase oxidation resistance was considered along with the density, price, neutron absorption cross section and their melting points.

2. A review of mechanical properties of several HEA

2.1. Properties of an earlier RHEAs

Along with the concept of HEAs, some promising refractory high entropy alloys (RHEA) have been studied as one of the candidates to replace Ni-based superalloys. At first four RHEAs NbTiVZr, $NbTiV_2Zr$, CrNbTiZr and CrNbTiVZr were tested by Senkov et al. Their common property is having low densities such as 6.52 g/cm^3, 6.34 g/cm^3 , 6.67 g/cm^3 , and 6.57 g/cm^3 , respectively. CrNbTiVZr had the most promising yield strength of these four alloys: at room temperature it was 1298 MPa and 615 MPa at T= 1073 K. However, at that particular temperature the other alloys could not be close to the half of the yield strength. Brittleness at room temperature of this alloy was compensated by increased ductility when the temperature was increased. [4]

2.2. Properties of recently developed RHEAs

Refractory elements such as Mo, Nb, Ta, Zr, Hf and Ti are the main targets in this study, including Al and Cr, so the focus will be on RHEA composed of these elements. Senkov et. al. mentioned about 4 earlier reported alloys such as HfNbTaTiZr and $CrMo_{0.5}NbTa_{0.5}TiZr$ which were modified to $Al_{0.4}Hf_{0.6}NbTaTiZr$ and $AlMo_{0.5}NbTa_{0.5}TiZr$ to see the Al effect when it is used instead of Cr [4]. According to those studies there was found that substitution of Al instead of Cr leads to higher microhardness (from 5.3 to 5.8GPa) and reduction of density from 8.23 g cm^{-3} to 7.40 g cm^{-3}. Likewise, microhardness and density reveal similar behavior in partial replacement of Hf with Al, from 3.8 to 4.9GPa and from 9.94 to 9.05 g cm^{-3}, respectively (Table 1). It must be acknowledged that low-density HEA is described as the density lower than that of steel which is 7.86 g/cm^3 [5]. On the other hand, cost of the alloys has been always an issue. Despite a good corrosion resistance and high melting point of Ta, it would not be economically beneficial to commercially produce a Ta-included alloy since Ta is much more expensive than Cr . For this reason, cheaper and the element with a compensable properties should be used such as Cr. Among the studies done by Senkov et. al. for further development AlMo$_{0.5}$NbTa$_{0.5}$TiZr can be the preeminent one in terms of its mechanical properties, namely, it has the highest H_v, the highest yield strength (T=1000˚C) and low density with a moderate melting point. Additionally, the combinatorial alloy design and substitution of Ta with Cr can be the one way to improve the properties of RHEA.

Table 1. Density, *p* microhardness, H_v, yield strength and melting point of the produced and parent alloys. [5]

Alloy	H_v *(GPa)*	Density (g/cm^3)	Mechanical properties at RT	Mechanical properties at high temperature	
NbMoTaW	4.46	13.75	E_c=220±20GPa σ_y =1058MPa σ_m=1121MPa ε_p =1.5% ε_c=2.1%	T=1073K σ_y=552MPa ε_c>25%	T=1273K σ_y=548MPa σ_m=1008MPa ε_p=16% ε_c>25%
VNbMoTaW	5.42	12.36	E_c =180±15GPa σ_y =1246MPa σ_m=1270MPa ε_p=0.5% ε_c=1.7%	T=1073K σ_y=846MPa σ_m=1536MPa ε_p=16% ε_c=17%	T=1273K σ_y=842MPa σ_m=1454MPa ε_p=14% ε_c=19%
TiCrZrNbMo$_{0.5}$Ta$_{0.5}$	5.3	8.02	σ_y=1595MPa σ_m =2046MPa ε_c=5.0%	T=1073K σ_y=983MPa σ_m =1100MPa ε_c=5.5%	T=1273K σ_y=546MPa σ_m =630MPa ε_c>50%
TiZrNbHfTa	3.8	9.94	σ_y =929MPa ε_c>50%	T=1073K σ_y=535MPa ε_c>50%	T=1273K σ_y=295MPa ε_c>50%
NbTiVZr	3.3	6.52	σ_y=1105MPa ε_c>50%	T=1073K σ_y=187MPa ε_c>50%	T=1273K σ_y=58MPa ε_c>50%
CrNbTiVZr	4.7	6.57	σ_y=1298MPa ε_c=3.0%	T=1615K σ_y=535MPa ε_c>50%	T=1273K σ_y=259MPa ε_c>50%
AlMo0.5NbTa0.5TiZr	5.8	7.40±0.08	E_c =178.6GPa σ_y=2000MPa σ_m =2368MPa ε_c=10%	T=1073K E_c =80GPa σ_y==1597MPa σ_m=1810MPa ε_c=11%	T=1273K E_c =36GPa σ_y=745MPa σ_m=772MPa ε_c>50%
TiZrMoHfTa	5.4	10.24	σ_y=1600MPa ε_c=4%	T=1073K σ_y=1045MPa ε_c=19%	T=1273K σ_y=855MPa ε_c>30%
TiZrNbMoHfTa	5.0	9.97	σ_y =1512MPa ε_c=12%	T=1073K σ_y=1007MPa ε_c=23%	T=1273K σ_y=814MPa ε_c>30%
TiZrNbMoHf	-	8. 70	σ_y=1719MPa σ_m =1803MPa ε_c=10.12%	T=1073K σ_y=825MPa σ_m =1095MPa ε_c>60%	T=1273K σ_y=635MPa σ_m =6654MPa ε_c>60%
Al0.4Hf0.6NbTaTiZr	4.9	9.05	σ_y=1841MPa σ_m =2269MPa ε_c=10%	T=1073K σ_y=796MPa σ_m =834MPa ε_c=50%	T=1273K σ_y=298MPa σ_m =455MPa ε_c=50%

3. Methods and Experimental Procedure

3.1. Combinatorial alloy library

In section 2 of Gert Persson Report No. 153/2016 by Thomas and Sarmad, there was mentioned that even though RHEAs have high melting points, they have high density problem which can be a limitation in some areas of application, particularly high cost of the materials. Thus, there is a need to add more alloying elements to lessen their density or to obtain more ductility [5].

As it was mentioned, the combinatorial technique can be applied as shown in Figure 1 in the form of a triangle. Since Al and Cr has an effect on decreasing the density of an alloy significantly, and Mo has high melting point, they are chosen to be the variables. For the sake of calculation convenience and HEA concentration limit of each constituent element is 35 at%, these variables were varied from 0 to 36 (at%). However, the others are fixed near 20at% (21.33at%) relying on the concentrations chosen in the references [4]. There are total 28 samples along the points of the triangle. To ensure efficiency, out of 28 samples 18 compositions which contain 0 as a component will be studied later to be able to see the effect of each element. All the targeted alloys satisfy the solid-solution formation rule-10th sample has δ=6.66% which is not significant- and have lower densities than 7.86 g/cm^3 as shown in Table 3.

Table 2. Combinatorial library with variables and fixed elements in at%.

Alloy #	Al(at%)	Cr(at%)	Mo(at%)	Nb(at%)	Ti(at%)	Zr(at%)
1	24	6	6	21.33	21.33	21.33
2	18	6	12	21.33	21.33	21.33
3	12	6	18	21.33	21.33	21.33
4	6	6	24	21.33	21.33	21.33
5	18	12	6	21.33	21.33	21.33
6	12	12	12	21.33	21.33	21.33
7	6	12	18	21.33	21.33	21.33
8	12	18	6	21.33	21.33	21.33
9	6	18	12	21.33	21.33	21.33
10	6	24	6	21.33	21.33	21.33

3.2. Experimental Procedure

Firstly, the powders of Al, Cr, Mo, Nb, Ti and Zr were weighted according to the table 2. Then they were compacted by hand press and arc melted. In addition, calculation of theoretical densities and densities of produced alloys were compared.

For the analysis, prepared samples were cut by diamond cutter, then polished for the next stages of an experimental procedure to observe their microstructure by XRD and SEM. Vickers hardness test were planned as well.

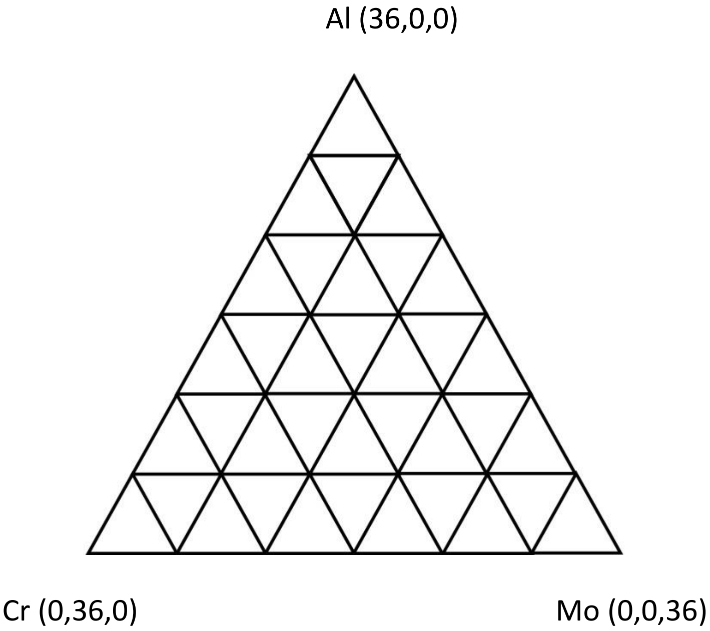

Figure 1. Combinatorial alloy design for RHEAs

Table 3.Respective CEM, delta, omega and density of alloys

Alloy #	CEM	δ (≤ 6.6%)	Ω(≥ 1.1)	density
1	13.87	4.443	1.389	5.916
2	14.30	4.571	1.894	6.317
3	14.30	4.689	2.695	6.72
4	13.87	4.8	4.299	7.126
5	14.30	5.34	1.906	6.146
6	14.56	5.432	2.823	6.553
7	14.30	5.517	4.782	6.964
8	14.30	6.061	2.896	6.383
9	14.30	6.128	5.331	6.798
10	13.87	6.66	6.038	6.628

4. Conclusions

The development of advanced superalloys, such as $AlMo_{0.5}NbTa_{0.5}TiZr$ was discussed in this study by producing the combinatorial alloy library along with the substitution of Ta with Cr. The vacuum arc melting will be used to synthesize desired compositions. Al, Mo, Cr are thought to be possible elements to be varied which can improve mechanical properties in a harsh environment. Therefore, there is a big opportunity to get the best values thanks to combinatorial approach.

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