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Combinatorial Techniques for Oxidation Resistant Refractory High Entropy Alloys (RHEA)

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1. Introduction

Recent development and screening of new alloys that can be applicable in a high-temperature environment, especially in aerospace engineering, power-generation industry and Gen-IV nuclear structural materials have been a hot issue. For example, the inlet temperature of the high pressure turbine blades is the highest temperature area in jet engines. Current Ni-based superalloys can be exposed to around 1150°C which is 90% of their melting points. Even though there are thermal barrier coatings or sophisticated cooling systems, the decreased efficiency and performance must be reconsidered [1]. Thus there is a demand for materials with simultaneous strength, low density and good oxidation resistance at ambient temperatures without any extra coatings and cooling systems.

Generally, most of the alloys are based on the main element with a small addition of the others to improve their properties. Additionally, the scope of the conventional alloys is being expanded with up-to-date alloys, so-called high-entropy alloys (HEA). They are composed of at least 4 and bounded by 13 elements each in the range of 5 and 35at% [2]. Possession of high configurational entropy of mixing suppresses the formation of intermetallic phases and enables to form solid-solution phases by which one can manipulate the properties of the alloys. If HEA are consisted of refractory elements i.e., group IV (Ti, Hf, Zr), V (V, Nb, Ta) and VI (Cr, Mo, W) due to their promising mechanical properties at extreme environment, oxidation resistance and the other features *refractory high-entropy alloys* (RHEA) can be a new player in high-temperature applications. However, their high density and high neutron absorption cross section are the main problems in commercializing these RHEA. On top of that, there are an indeterminable number of the combinations of possible HEAs [2]. Therefore, there must be found an efficient way to approach above-stated complications.

It should be acknowledged that the alloy $AlMo_{0.5}NbTa_{0.5}TiZr$ in a recently published work by D.B.Miracle and O.N.Senkov has still been considered as the most distinguished alloy with relatively low density (7.4g/cm^3) and attractive mechanical properties [3]. In this study, $AlMo_{0.5}NbTa_{0.5}TiZr$ is taken as a reference. Since Ta has very high cost, high density and high neutron absorption cross section, it was replaced by Cr. Additionally, it is generally accepted that Cr addition will boost oxidation resistance of the alloys. Furthermore, a combinatorial approach was involved to produce a library of alloys which included Al, Cr, Mo, Nb, Ti and Zr.

2. A review of RHEA

2.1. Motivation for the RHEA

Since refractory elements possess very high melting point, above 2000°C, they can be utilized for the high temperature applications, such as structural materials for the Sodium Fast Reactors. Additionally, refractory elements have small atomic size difference which one of the criteria to form solid-solution HEA. It must be acknowledged that by addition of Al and Cr - both of them have similar atomic size with refractory elements - oxidation resistance of refractory high entropy alloys will be enhanced and they will result in light-weight RHEA.

2.2. Mechanical properties of RHEA

It must be pointed out that most of the data are related to hardness or compressive properties but for tensile tests there are very little information hence directions for the future work are clearly shown. Among many alloys, $NbTiV_2Zr$ has the least microhardness (3.0 GPa) and $AlMo_{0.5}NbTa_{0.5}TiZr$ has the largest one (5.8 GPa) [3]. As for the compression properties, table 1 shows the comparison of different alloys between room temperature and high temperature as well. When the temperature is very high compressive yield stress, σ_y, decreases dramatically, especially around 1000 K for most of the alloys. On the other hand, the alloys which contain W, namely MoNbTaW and MoNbTaVW retain excellent strengths at 1273K but they have high density problem. The importance of density (p) is coming from the selfloaded stress in rotating parts of the industrial applications. In addition, low density HEA are the alloys which have a lower density than that of steel (7.8g/cm^3)[5]. Therefore, specific yield strength, σ_y/p, is considered as one of the significant factors in characterizing the particular alloy [3].

It is worth to say that, most of the already fabricated alloys like $Al_{0.4}Hf_{0.6}NbTaTiZr$, $AlMo_{0.5}NbTa_{0.5}TiZr$ and $Al_xNbTaTiV$ (x=0 to 1) have some advantages (enough room temperature ductility) over currently existing superalloys (Haynes®230, INCONEL® and MAR-M 247®). However, recently developed RHEA with only compressive properties are not reasonable to compare with superalloys which possess properties like sufficient tensile ductility, fracture toughness, oxidation resistance, creep and fatigue strengths [3]. Thus, there are more studies to be conducted in the near future.

Table 1. Density, *p* microhardness, H_v, yield strength and melting point of the produced and parent alloys. [3]

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%
NbTiV$_2$Zr	3.0	6.38	σ_y=918MPa ε_c>50%	T=1073K σ_y=240 MPa ε_c>50%	T=1273K σ_y=72MPa 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%
AlMo$_{0.5}$NbTa$_{0.5}$TiZr	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%
Al$_{0.4}$Hf$_{0.6}$NbTaTiZr	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 design and library

At the beginning of this work, properties of the preeminent candidate, AlMo$_{0.5}$NbTa$_{0.5}$TiZr, was taken into account. As previously mentioned, Cr replaced Ta that causes several issues in real applications. Then for our constituent elements, Al, Cr and Mo, are varied in the range of 0at% to 40at% excluding those which do not obey compositional definition of HEA [3]. The reason behind this variation is that to observe properties such as oxidation resistance (i.e. Al and Cr) and to improve melting point (i.e.Mo, though it is relatively expensive, it can be employed) of the alloys systematically. Thus in the combinatorial triangle there are a total of 12 alloys which qualify HEA definitions (Table 2&Fig. 1). As for now, in Figure 2, there is presented microhardness of 12 new alloys. It is obvious that increase of Al and decrease of Cr led to higher microhardness than the reference alloy (>5.8GPa).

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

	Variables			Fixed		
Alloy #	Al(at%)	Cr(at%)	Mo(at%)	Nb(at%)	Ti(at%)	Zr(at%)
1	30	10	0	20	20	20
2	30	0	10	20	20	20
3	20	20	0	20	20	20
4	20	10	10	20	20	20
5	20	0	20	20	20	20
6	10	30	0	20	20	20
7	10	20	10	20	20	20
8	10	10	20	20	20	20
9	10	0	30	20	20	20
10	0	30	10	20	20	20
11	0	20	20	20	20	20
12	0	10	30	20	20	20

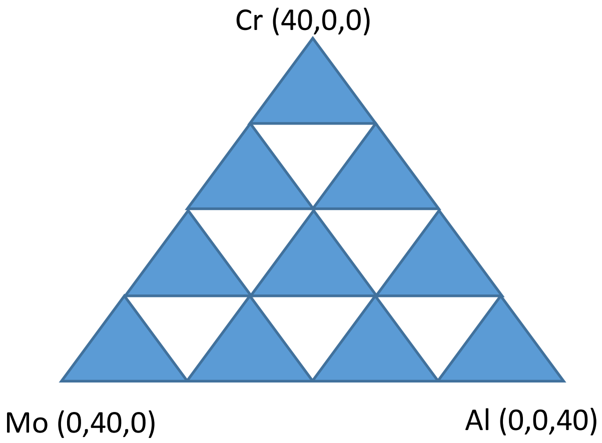

Figure 1. Combinatorial alloy design for RHEAs

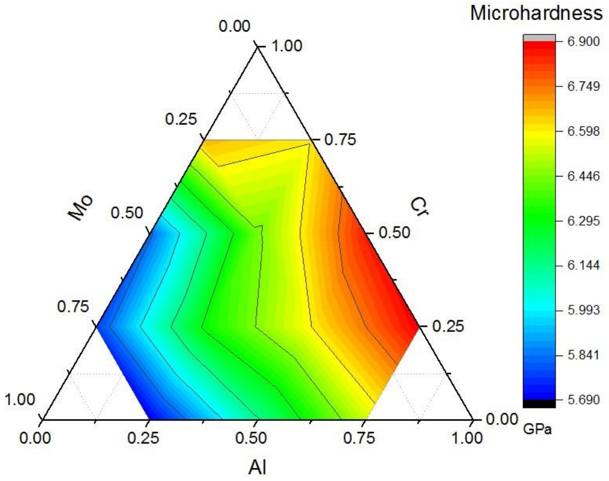

Figure 2. Microhardness ternary contour for the RHEA. (It was assumed that the data were normalized (x+y+z=1 or 100)

3.2.Experimental Procedure

Firstly, the granules of Al, Cr, Nb, Ti and foils of Mo, Zr that have high purity (>99%) were melted in vacuum arc melting furnace (DAIA Vacuum, Japan) for around 5 minutes each with flipping over the samples in order to get more homogenized microstructures in accordance with previous works [4]. The vacuum chamber was filled with Ar gas and constituent metals were put on the copper cavity along with Ti sponges as an oxygen getter because of its high chemical affinity to oxygen. Afterwards, XRD, SEM and Vickers hardness tests were conducted. Next step was annealing the samples at 1200°C for 24h. Then the oxidation test with conditions of 1100°C and 1200°C in a static air to imitate environment of the nuclear structural materials was carried out.

4. Conclusions

The combinatorial alloy design will facilitate to give an overview of different properties of newly developed alloys. An efficient and high-throughput screening is necessary to evaluate characteristics of lately fabricated alloys among many combinations. Thus, in this work, by utilizing the vacuum arc melting furnace a total of 12 alloys were fabricated to be able to assess their mechanical properties and oxidation resistance by the combinatorial approach. At last, increasing the content of Al and decreasing the amount of Cr and Mo can lead to a refractory high entropy alloy with higher microhardness.

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