A Thesis Presented to

The Faculty of Alfred University

Compositional Testing of Refractory High Entropy Alloys

to Provide Oxidation Resistance in Air at 1000°C

by

Thomas G. Brewer

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Under the Supervision of:

Chair:

Dr. Kun Wang, Assistant Professor of Materials Science and Engineering

Committee Members:

Dr. Alexis Clare, Professor of Glass Science and Engineering

Dr. William LaCourse, Professor of Glass Science and Engineering

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Abstract

The refractory high entropy alloy that consists of refractory and oxidation-resistant elements is a rather new material that has shown excellent resistance to oxidation at both high temperatures and long periods of time. However, an abundance of research has not been conducted to examine all the potential chemical combinations that could provide such oxidation resistance due to the large compositional space. For this research, six high entropy alloys of the theorized chemical compositions: WTaNbTiAlCr, WTaNbTiAlCrMo, WNbAlTiCr, WTaNbAlCr, WMoNbAlTi, and WMoNbAlCr were created to examine the oxidation resistance that different sequences of elements provided. A powder metallurgy process was utilized to form all the samples. High energy planetayr ball milling was used to uniformly mixed or even prealloyed powders, which would allow for high densification and full alloying of the powders during the spark plasma sintering process (SPS). Post sintering and polishing, as fabricated microstructure, hardness, elastic modulus, and phase identification were investigated to rule out any samples with undesirable properties. Upon review of X-ray diffraction (XRD) and scanning electron microscopy(SEM) results, the samples comprised of WTaNbTiAlCr, WNbAlTiCr, and WMoNbAlTi were the only samples to form a single densified phase. Subsequently, oxidation tests of 2, 12, and 24 hours at 1000°C were conducted on separate sample specimens. A single composition, WTaNbTiAlCr, provided the best oxidation resistance along every timeline, while the two other samples showed severe/full oxidation at 12 and 24 hours.

Keywords: Refractory high entropy alloy; Powder metallurgy; High temperature oxidation

Introduction

A refractory high entropy alloy (RHEA) is defined as a material comprised of at least 5 metal elements, which are mixed in equal molar proportions^[9]. This novel class of materials has primarily been investigated for its use in high temperature, potentially radioactive, and chemically abrasive environments^[4]. Previously, nickel-based (Ni-based) superalloys were used as the primary material in these types of destructive environments^[4,10]. A Ni-based superalloy contains upwards of 10 elements, some of which are classified as refractory heavy metals, because of their location on the periodic table^[4,10]. However, these nickel-based superalloys also contain elements like carbon, boron, and other non-metals that increase the number of elements present, and do not boost mechanical properties^[4,10]. The primary elements found RHEA and Nibased superalloys separate the two. A RHEA will typically contain large amounts of elements like Ta, Nb, W, and other elements in the refractory heavy metal section in equimolar proportions, while Ni-based superalloys only contain fractional percentages of these elements^[5].

RHEAs demonstrate properties that make them a suitable replacement for Ni-based superalloys. First, RHEAs have a very high mechanical hardness^[11]. Mechanical hardness refers to how much energy it takes to indent the surface of a material. The second favorable property of RHEAs is their thermal properties. RHEAs have very high melting and softening temperatures, which provides creep resistance, with respect to other metal-based materials^[4,5,7,8]. Creep is the stationary deformation of a material at high temperatures and needs to be considered given the high temperature environment in which these materials will be used^[9]. Most RHEAs will exhibit these thermal properties, however, the material composition can be changed to favor lower melting temperature, which would cause creep resistance to fall and the softening temperature to

also decrease^[7]. For the purpose of this thesis, predicted high melting point RHEA compositions will be used.

One theoretical use for these materials is in jet engines^[7]. The typical materials used in the "hot side" of the turbine are the Ni-based superalloys^[10]. However, the modern engine has pushed this material to its temperature limit^[7]. The refractory high entropy alloy's melting temperature and creep resistance provides room for improvement in these engines. Another promising property found with the RHEA is its ability to resist oxidation at very high temperatures in air, which is needed for a material that is to be exposed to extreme temperatures in an oxidation favored environment^[4,8].

Although various oxidation-resistant RHEAs have been reported, novel RHEAs with superior oxidation resistance at high temperatures eed to be found. For this reason, multiple refractory high entropy alloys will be constructed and examined for their oxidation resistance. Oxidation occurs when oxygen diffuses into a material and causes grain growth, lattice distortions, and the displacement of existing atoms in the crystal structure^[4]. In refractory high entropy alloys, the oxygen will bond to various elements, causing significant phase changes and compromising the structural integrity of the material^[8]. Oxidation of the high entropy alloy is seen when the material is held at a very high temperature, at least 800°C for a long time period^[4,8,9,12]. Materials with excellent oxidation resistance will withstand temperatures in excess of 1000 °C for 24 or more hours^[4,8,9,12].

The oxidation resistance of the RHEA is due to the wide variety of atoms in the unit cell. In many cases, the corners of the unit cell will contain different atoms^[4]. Given the different atomic sizes each atom possesses, the oxygen atoms will have a hard time passing into the unit cell. This is the reason that a single-phase material is desirable with the refractory high entropy

alloys. The single phase means that the crystal structure is uniform across the material, so the diffusion rate of oxygen into the unit cell will not change over the surface area of the material^[4,9]. Another factor to which the slow oxidation of the material can be attributed is the lattice distortion of each unit cell^[4]. The changing atomic radii at the corners of the unit cells will cause a non-symmetric unit cell. In short, this means that instead of being a perfect rectangular or hexagonal prism, the unit cell will potentially have irregular dimensions, but will retain a perfect stacking order^[4]. Even though there is a high degree of disorder within the unit cell parameters, the elements within the structure do not produce much strain on one another^[4]. As reported in previous works, the strain on the nearest neighbor atom is normally less than or equal to 5%^[4]. With a high degree of distortion within the unit cells, refractory high entropy alloys still form into simple crystal structures.

The unique and desirable mechanical properties found in refractory high entropy alloys can be attributed to the crystal structure. The combination of elements would typically not be thought to be compatible to form a fully crystalline structure of simple order given the high degree of disorder these elements have when mixed together. However, as seen in many experiments, these five or more heavy refractory metals will bond together to form a single-phase crystal structure. The primary structures formed by these HEA's are body centered cubic (BCC), face centered cubic (FCC), or hexagonal close packed (HCP)^[1,9]. The three different structures can be seen in Figure 1^[3]. These structures are known to be three of the simplest crystal structures, which is unique for a compositionally complex material to form in such a low energy system. The unit cells as previously mentioned will become strained with the increase in elements, but the large number of elements per these unit cells contribute to the advanced properties seen in HEAs^[1,4,5,7-9]. Typical materials will be governed by the primary element in

the unit cell, however, in HEAs, there is no primary element present, so material properties are less predictable^[4]. The bonding, within each unit cell, is typically accurately investigated through the use of advanced spectroscopy methods or transmitting electron microscopy. For the purpose of this experiment, since oxidation resistance will be the primary study, the specific crystal structure of the elements is not analyzed, but rather the composition is analyzed to see if a single phase will form.



Figure 1. BCC, FCC, and HCP unit cell diagrams

Synthesizing these refractory high entropy alloys can be very difficult due to the high melting points of the metal elements. One common fabrication method is called Powder Metallurgy, or PM for short. The process allows for a high mixing entropy to take place, because of the large number of complex elements present, so this is where refractory high entropy alloys achieved their name. First, powder metallurgy starts with high purity elemental metal powders. The metals need to be measured out so each element will be in an equimolar relationship with one another, and then they can be poured in a tungsten carbide jar with different sized tungsten carbide milling balls. The powder has entered the stage known as "ball milling." Ball milling creates a uniform particle size and distribution, throughout the powder, by a griding action initiated through various directions of rotation. The PM process is of the utmost importance, since a nonuniform particle size, will not allow the metals to densify or completely alloy. The last stage in the powder metallurgy process is the sintering method, which is normally conducted through spark plasma sintering (SPS)^[1].

Different sintering methods have been investigated in the past experiments conducted on refractory high entropy alloys. However, methods are either too slow, so they will lead to large formations of oxide within the sample, or they have to utilize a constant vacuum, which becomes a very expensive process for large materials^[8,12]. A fast process that utilizes multiple sintering techniques and does not require expensive machinery needs to be utilized. For these reasons, spark plasma sintering has been studied and used for many refractory high entropy alloy experiments^[1,8]. SPS utilizes pressure and heat to form a solid, densified material in a short period of time. The SPS process can be seen in Figure 2, which provides a diagram for the sintering process of a powder via SPS^[6]. The heat comes from electrically charging a die that contains the powder, simultaneously, the powder is compressed^[6]. Once the powder is compressed to the desired force, the material is held there for a predetermined period of time, which is controlled by the sample mass and die size. The methodology used in spark plasma sintering produces minimal oxidation and allows for a high degree of densification with the applied pressure^[1,8,12].



Figure 2. Spark Plasma Sintering process

The processes behind fabricating refractory high entropy alloys have had a lot of success. With those principles demonstrating favorable results, the different compositions of the HEAs need to be investigated to see which element combinations form desirable properties. Compositions, as stated are traditionally in equimolar proportions. However, the atomic percentages of elements can vary from 5 to 35%, which can change the equimolar proportion^[1]. Elements that are typically found in refractory high entropy alloys are aluminum (Al), tungsten (W), tantalum (Ta), titanium (Ti), niobium (Nb), chromium (Cr), molybdenum (Mo), and vanadium (V)^[1,4-5,7-9,11-12]. The addition, subtraction, or substitution of one of these elements from a HEA composition will change both the mechanical and chemical properties of the bulk material.

For the purpose of this research, compositions containing W, Ta, Ti, Al, Nb, Cr, and Mo were examined. Vanadium based compositions were not be examined as more literature exists on HEAs containing this element^[9]. Six and seven component HEAs will be examined to study how the addition of more elements will affect both the phase formation and the oxidation resistance, as well as to provide insight into a new and potentially favorable type of refractory high entropy alloys. Refractory high entropy alloys are still a novel research topic, so literature has yet to look deeply into all of the compositions possible^[4]. Some of the alloys examined will have been published, but this work attempts to form a single-phase material for all compositions and analyze the oxidation behavior of the various compositions using standard PM and oxidation parameters.

Experimental Procedure

A) Synthesis:

Refractory high entropy alloys of the chemical compositions: WTaNbTiAlCr,

WTaNbTiAlCrMo, WNbAlTiCr, WTaNbAlCr, WMoNbAlTi, and WMoNbAlCr were to be fabricated using a powder metallurgy process. The different compositions will be named and identified according to Table I and will be referred to as such for the remainder of this thesis.

Composition	Name
WTaNbTiAlCr	Sample A
WTaNbTiAlCrMo	Sample B
WNbAlTiCr	Sample C
WTaNbAlCr	Sample D
WMoNbAlTi	Sample E
WMoNbAlCr	Sample F

Table I. The compositions and respective names are listed below

The powder metallurgy process starts with calculating the necessary mass of each given element that will be added to the milling jar. This experiment will be using elements in an equimolar percentage, so all of the elements will be contributing an equal part to the whole material. The calculations for each element can be conducted in Microsoft Excel (Excel v.2203) as shown by the reference in Table II. Each composition was calculated the same way, but different number of elements may be present. Each sample was calculated to have 10 grams of powder going into the milling process. Each element was weighed separately using a AG204 Delta Range® scale (Mettler Toledo, USA), which accurately weighed samples to the 0.1mg, and then was poured into the milling vessel. When attempting to achieve equimolar ratios, precision was of the utmost importance, so recording masses to the 1x10⁻⁴ decimal place is necessary.

WTaNbTiAlCr					
Material A	Atomic Mass	Amount	Material	Percent in	Amount for
	(g)		Weight	Material	10g
W	183.84	1	584.54	31.45%	3.1450
Та	180.95	1		30.96%	3.0956
Ti	47.87	1		8.19%	0.8189
Nb	92.91	1		15.89%	1.5895
Cr	51.99	1		8.89%	0.8894
Al	26.98	1		4.62%	0.4616
				Total =	10.0000g

Table II. Excel calculations used to determine equimolar elemental masses for Sample A

Milling of two different samples was conducted simultaneously. Two samples needed to be made at the same time to ensure a balance of the ball milling machine. Tungsten carbide jars with tungsten carbide milling balls of different sizes ground and blended the powder to ensure equal particle size and distribution. The PQ-N2 Planetary Ball Mill (Across International, USA) was set to mill at 200rpm for 2 hours and would reverse direction every 30 minutes. Upon completion and cooling, the powders were extracted from the milling jars. The powders could then be loaded into spark plasma sintering (SPS) dies.

Spark plasma sintering dies were lined with carbon paper around the inside and then two wafers were put on each die. The carbon paper ensured that no bonding between the metal powders and graphite die would occur. Figure 3 displays the dies used in SPS. Each powder was sintered using a Spark Plasma Sintering Furnace (FCT Systeme GmbH, Germany) set to press at 27kN, the ram of 50°C/min, an overall time of 30 minutes, and a nominal sintering temperature of 1350°C.



Figure 3. SPS dies

B) Sample Preparation:

Completion of sintering requires samples to be polished. All samples must be prepared with a mirror polish in order to accurately test them later on. Diamond grinding plates of US grits 180, 320, and 600 were utilized to remove any carbide that formed on the sample's surfaces. Upon carbide removal, mirror polishing of the bulk material took place using an EcoMet 3 variable speed grinder-polisher (Buehler, USA). US grits, of 400, 600, 800, 1200, and 2000, were used in the order listed to work each sample to a mirror polish. Each sample was rotated 90° about every 30 seconds to ensure that all preliminary grinding marks were removed, and a flat level surface was obtained.

C) Analysis Methods:

The refractory high entropy alloys formed needed to have phase identification conducted firstly. X-ray diffraction, XRD, was accomplished using a D2 Phaser (Bruker, USA) and copper radiation of wavelength 1.54Å. The scanning parameters were kept constant for each sample and were as follows: scanning angles 10-90°20, step size 0.0283, divergence slit width of 1mm, and 10.0mA/30kV generator. Results would be analyzed using Diffrac.eva (Bruker, v.6.0) coupled

with PDF-4+ (ICDD, 2022) for peak analysis and Topas (Bruker, v.6.0) for multiple peak overlaying.

Scanning electron microscopy, SEM, utilizing a JEOL 6061 (JEOL, Japan) coupled with energy dispersive spectroscopy, or EDS, allowed for pictures of the microstructure and elements to be taken and analyzed. Images were taken at different magnifications depending on the focusing behavior of the SEM. Generally, scanning parameters utilized entailed a potential of 15kV, a spot size of 60nm, and a working distance of 11mm. On some samples, especially those containing Mo, the potential was increased to 20kV to obtain better data. Backscattered electron, or BSE, and secondary electron, or SE, views were used to study the presence of more than one phase and topography respectively. Topography analysis would reveal the overall densification and porosity of the samples. EDS maps were taken on a paused backscattered image. The map conditions varied in order to detect all of the present elements as some were at the lower limit of the detector's range. EDS maps were analyzed to see the dispersion of elements throughout the sample. The formatting of all SEM and EDS images was accomplished through ImageJ (NIH, v.1.53q).

Upon completion of microstructure and phase identification, the calculation of mechanical properties could be investigated. Samples were investigated for their hardness using a LEEB LHVS-1000z (Chongqing Leeb, China) as well as their elastic modulus using a TDS 2002B (Tekronix, USA) oscilloscope. The hardness readings were taken using a force of 0.2kgf and a 15s indentation time. Elastic modulus readings were calculated using the transverse signal time recorded. The formula for this calculation is shown in Equation 1 below:

$$v_{transverse} = \sqrt{\frac{E}{\rho}}$$

where $v_{transverse}$ is the velocity of the transverse wave, *E* is the modulus of elasticity, and ρ is the density of the material^[2]. The testing only reveals transverse wave time to travel through the material and back to the detector, so some smaller calculations are needed to obtain the transverse wave velocity. The thickness of the samples was measured, and then utilizing the time divided by the number of peaks recorded, the velocity was found. The density was recorded utilizing mass and volume calculations.

D) Oxidation:

Oxidation was the primary focus of this experiment and would only be conducted on single-phase samples. Before oxidation experiments could take place, each sample was to be cut into 4 pieces of roughly the same dimensions, and a small piece, roughly 80mg, which was to be taken for use in thermogravimetric analysis (TGA). Mirror polishing had to be conducted again on all surfaces including the cross section surfaces, as it would allow for accurate surface area calculations. Surface area calculations were made in Solidworks (Dassault Systemes, 2020) by extruding sketches that corresponded to the small sample sections. Initially, a piece of each of the single-phase samples would be investigated at lower oxidation temperatures to visually study their oxidation response. These samples were exposed to temperatures of 800°C and 900°C for 2 hours each in a Barnstead 48000 Furnace (Barnstead Thermolyne, USA). If both of those preliminary tests appeared to show favorable results, the same samples were then exposed to a temperature of 1000°C for 2 more hours. The sample(s) that showed the most oxidation resistance would be tested at 1000°C for 2, 12, and 24 hours with each test using a different piece of the sample^[12].

Upon successful oxidation completion, samples were then investigated using XRD, SEM, and EDS to analyze the oxide layers that formed. The sample(s) that visually showed the least

oxidation would be cold mounted in 5:1 clear epoxy/resin. The cold mounting procedure took place over a time period of 36 hours. The samples from the 2, 12, and 24hr tests were put in separate epoxy molds, with the sample placed vertically, and combined with epoxy/resin to cover the top of the specimen. The molds were allowed to dry and then the cross-section surface of the samples was mirror polished. Since the epoxy was non-conductive, silver sputter coating was employed for 30 seconds on each sample using a Cressington 108 Sputter Coater (Cressington Scientific Instruments, UK). SEM and EDS images were then taken for each cross-section sample, which allowed for the accurate measurement of the oxide layer thickness.

The sample(s) that had their cross sections analyzed also underwent thermogravimetric analysis, or TGA. TGA was conducted on a small roughly 80mg sample for 24 hours utilizing a SDT Q600 DSC-TGA (TA Instruments, DE, USA). Surface area calculations of the small sample piece were made in Solidworks using the same procedure as before. The mass of the sample was initially recorded by the TGA instrument and then updated every 5.04 seconds. The test was set to run for 24 hours and hold a constant temperature of 1000°C, which will allow for a comparison to other oxidation data. The TGA data collected enables an accurate mass versus time plot to be obtained.

Results and Discussion

A) XRD Results of the as-Fabricated RHEAs:

After sintering and polishing, samples appeared as a button shape and with a shining surface as can be seen in Figure 4. All samples appeared the same, and no visible difference could be detected between the polished surfaces. Small differences in diameter were calculated but are not pertinent to the data.



Figure 4. Sample D is shown for reference as to the overall shape of all samples.

The first test that ran after sintering and polishing was XRD. XRD results utilized a solid sample holder and needed not further preparation of the material given the small constructed sizes of the samples. Data for samples A, B, and C can be seen in Figure 5. Sample A showed very favorable results with a large peak around $37^{\circ}2\theta$, as seen in Figure 5(a), which was found to have every element present and in phase equilibrium with each other, thus indicating the BCC structure. Given that HEAs are still of the novel classification, the PDF 4+ database does not contain specific cards for these materials yet. Also, in sample A oxides of each element were found along with some impurities of silicon carbide, most likely residual surface contaminants from polishing. The presence of oxides will show up in almost every sample because oxygen was absorbed/dissolved into the metal elements during the ball milling process. This oxygen later reacted with the elements to form metal oxides. Sample B's data did not show a single-phase material. As seen in Figure 5(b), there is a distinct phase of AlTaTi as marked by the blue square, which adds an additional phase to the primary BCC phase. Overall, Sample B does not show favorable results for obtaining a single phase. However, Sample C shows an overwhelming single-phase BCC material in Figure 5(c). The XRD data showing a single-phase material for samples A and C is later supported by SEM and EDS images and maps.



Figure 5. a) Sample A XRD single-phase pattern b) Sample B XRD multi-phase pattern c) Sample C XRD single-phase pattern

XRD results of samples D, E, and F can be seen in Figure 6. Sample D, in Figure 6(a), shows a mixture of sub-phases in addition to the main BCC phase. This data is also supported by SEM and EDS images. Multiple impurities are also present within the material as can be seen by the carbon oxide formations around the main phase peak at 37°20. Cr, Nb, Ta, and W form a secondary phase present at 57 and 86°20. Sample E, seen in Figure 6(b), contains the same elements at every peak with no variation other than minor titanium oxide indicating the

formation of single-phase BCC. The peaks are equally spaced and of decreasing intensity, so they are repeating the first peak as the scan rotates through. Lastly, Figure 6(c), displays the XRD results of sample F's XRD scan. It shows very unfavorable results for the desired singlephase testing. Some of the Cr and W formed in carbide around the main BCC peak,



Figure 6. a) Sample D XRD multi-phase scan b) Sample E single-phase scan c) Sample F

multi-phase scan

B) SEM/EDS of the as-Fabricated RHEAs:

SEM and EDS images/maps were taken on every sample to study the microstructure and confirm XRD results. Sample A, like every other sample to follow, was viewed using secondary electron imaging and backscattered electron imaging.SE showed the topography of the sample, which would reveal if the sample fully densified. BSE imaging utilizes a different detector that allows for the viewing of different phases. As seen in Figure 7, sample A formed a densified single-phase material. The backscattered image in Figure 7(a) shows the presence of a slight phase change, but as further analyzed with EDS, this image will correlate to an oxide.



Figure 7. BSE (a) and SE (b) images of sample A taken after initial sintering was conducted

EDS mapping of every sample enabled the viewing of how different elements ended up dispersing. Oxide materials formed in sintering will appear as heavy pockets of a single element in one area. As seen in Figure 8, sample A shows excellent dispersion of elements throughout the bulk of the material. Some titanium and aluminum oxide are present in the material, but these are unavoidable by-products of the powder metallurgy method. All six elements present are evenly dispersed throughout the remainder of the sample.



Figure 8. Preliminary EDS map of sample A

Sample B when viewed using secondary and backscattered imaging proved the presence of multiple phases as seen in the XRD pattern. The backscattered image clearly shows multiple different shades of grey, which indicate a known phase change. The secondary image shows a high degree of densification, as not many pores are present, and a granulated topography is not seen.



Figure 9. BSE (a) and SE (b) images of sample B

The EDS mapping of sample B, as seen in Figure 10, displays the multiple phase regions as seen in the backscattered image of sample B in Figure 9. Cr and Al fail to be equally dispersed throughout the material. The map of chromium and titanium distinctively show where the sample is lacking chromium but is rich in titanium. These titanium-rich regions also do not line up with any features in the BSE image that would be indicative of oxidation. Furthermore, Mo, W, Ta, and Nb are equally dispersed in these Ti-rich regions, which proves multiple phases are formed. Aluminum does show dark, Al-rich, regions, but these correspond to known oxides present in the sample.



Figure 10. EDS mapping completed on sample B, displaying multiple phases

Sample C, which showed a single-phase material upon XRD analysis, is verified as such through examination of its SEM images in Figure 11 and EDS map in Figure 12. The BSE image, as in Figure 11(b), most notably shows a whiteish region in the lower right, extending upwards towards the middle of the sample. This area was investigated further through EDS, as no other phases were found in XRD. The topography of this sample is a little rougher with a large void in the lower left of Figure 11(b), but the sample has densified fully.



Figure 11. BSE (a) and SE (b) images of sample C

The EDS map of sample B shows that the whiteish area present in the BSE image is in fact a tungsten-rich area of the material. However, all other elements are present in this region which means that overall, a single-phase has still formed. The dispersion of all elements and the very small concentration of Al/Ti-oxides makes sample C desirable.



Figure 12. The complete EDS map of sample C after initial sintering

Sample D was further examined using SEM and EDS to determine if the sample was in fact multiple phases. Upon SE and BSE imaging of the surface, seen in Figure 13, Sample D was in fact multi-phase. The BSE image in Figure 13(a) clearly shows 3, possibly 4, phases. The phases are defined by light to moderate color change. The black spots in the image correspond to either oxidized regions or pores. The materials were mixed using the same parameters as all other samples, so this combination of elements, as produced in this experiment, does not yield a single-phase material. The SE views show that sintering densified the sample, but different phase regions can be seen. To pick up differences in material composition, from SE imaging, the sample has to have very clearly distinct phases, and this is portrayed in Figure 13(b).



Figure 13. Sample D's secondary (b) and backscattered (a) images after sintering

EDS mapping of sample D, as seen in Figure 14, shows a non-uniform distribution of elements. Niobium and chromium formed in their own rich phases that were lacking tungsten and tantalum. Aluminum appears to be the only element that formed uniformly throughout the sample. This composition is the same as sample A, however it does not contain titanium. Titanium appears to be the element that allows for all the elements to bond to one another. Without Ti, the sample is left in multiple phases.



Figure 14. EDS map of sample D portraying multiple phases

Sample E shows an excellent single-phase material as seen in the SE and BSE images of Figure 15. The sample shows some whiteish areas, Figure 15(a), just like sample C, but overall, the sample is single-phase. These areas were initially believed to be tungsten just like in sample C, and this was confirmed by the EDS map seen in Figure 16. The SE image in Figure 15(b), shows some voids, which were most likely caused by carbide formations in sintering, but in all, a high densification is present in this material too.



Figure 15. BSE (a) and SE (b) images post sintering

The EDS mapping of sample E most notably shows equally dispersed compositions. A tungsten rich area is present where the whiteish spots in the material were located, but just like in sample C, this area is still part of the single-phase that comprises the material. All elemental compositions are equally dispersed and do not show voids indicative of a phase change. Ti/Al-oxides are present, but like every other material with one or both of these elements, oxidation occurs when sintering.



Figure 16. Sample E EDS map taken on a BSE image

Sample F was the last sample to be imaged and examined through SEM and EDS. The SE and BSE images of the sample can be found in Figure 17. As seen, sample F is clearly multiphase as initially found in the XRD data. In Figure 17(a), sample F, when viewed using the backscatter electron detector, clearly shows 4 different phases which are characterized by a change in color. Again, the black spots correlate to either pores or oxidated regions. The SE image shows a material that is not perfectly densified but does not contain a large number of pores. The sample has microcracked regions where it appears two phases did not fully bond together and are marked with arrows in Figure 17. These microcracks separate the very dark regions from the light grey regions in Figure 17(a).



Figure 17. BSE (a) and SE (b) of sample F

The EDS data seen in Figure 18 clearly shows how the combination of elements in sample F does not form a single-phase, or even a fully bonded multi-phase material. Niobium and tungsten will not form a stable single-phase together with any other elements present. Aluminum oxidized some during sintering, just like every other sample, but it also seems to be somewhat evenly dispersed. Uniform chromium is different from what would be expected. Typically, Cr and Mo were the elements that posed to be an issue in the other samples examined. However, in this sample, Cr and Mo are evenly dispersed throughout the material.



Figure 18. EDS map of sample F post sintering

C) Mechanical Property Testing:

The hardness and elastic modulus were found using the methods outlined in the experimental procedure section. The hardness of each sample, despite the phase changes in different samples, provided a range of 1.901GPa. The hardness values were converted from Vickers Hardness units to GPa upon testing to be comparable unit wise with the elastic modulus calculations. The hardness and elastic modulus data were graphed for each sample and can be seen in Figure 19. Hardness values were converted to GPa by multiplying the obtained Vickers Hardness (Hv) value by 0.009807 GPa/Hv. The hardness of each sample is relatively high for a metal classification, but the elastic modulus is within the expected range for metals^[11]. These properties show that RHEAs provide mechanical properties that make them suitable for structural materials.



Figure 19. Bar graphs of mechanical hardness and elastic modulus for each sample in GPaD) Oxidation Testing Results:

Samples A, C, and E were the only single-phase materials present out of all six samples, so these were the only ones to undergo oxidation testing. Firstly, all of the samples were divided into

quarters and attempted to cut. Since the samples had such a high hardness and a relatively low thickness, they were hard to cut without fracturing. Four pieces were obtained from each sample to use for oxidation. The picture of samples after cutting is shown in Appendix Figure A2. Initially, one piece of each sample underwent oxidation at 800, 900, and 1000°C for 2 hours. Upon visual inspection, all three samples showed oxidation resistance. The cross section surface, after cutting, was mirror polished, and the surface areas of the remaining three pieces of samples A, C, and E were measured. Table IV displays the measured surface area in mm² and μ m².

The oxidation experiment was conducted on every sample simultaneously. Visual inspection after the 2-hour test at 1000°C showed little oxidation on each sample. At 12 hours and 1000°C, Samples C and E were showing significant and oxidation, while Sample A displayed very little oxidation. At 24 hours samples C and E became worse with sample E fracturing down the middle part due to over-expansion. Sample C became even more saturated with oxygen, while sample A picked up a very small oxide coating. The mass gain and oxygen saturation of each sample is given in Table III. Actual sample pictures at all different oxidation times can be seen in Appendix A.

Table III. Surface area, mass before oxidation, mass after oxidation, mass gain, and oxygen saturation are displayed for samples A, C, and E for 2, 12, and 24 hours of oxidation at

Sample	Surface Area Before (mm^2)	Surface Area Before (µm^2)	Mass Before (g)	Mass After Oxidation (g)	Mass Gain (mg)	Oxygen Saturation (mg/ μ m^2)
A(2hr)	132.73	1.33E+08	0.6988	0.70450	5.7	4.29E-08
A (12hr)	64.60	6.46E+07	0.5872	0.60100	13.8	2.14E-07
A (24hr)	198.56	1.99E+08	0.9765	1.01770	41.2	2.07E-07
C (2hr)	172.93	1.73E+08	0.7019	0.72280	20.9	1.21E-07
C (12hr)	145.77	1.46E+08	0.62	0.67880	58.8	4.03E-07
Ċ (24hr)	148.86	1.49E+08	1.1053	1.35020	244.9	1.65E-06
E (2hr)	103.05	1.03E+08	0.4012	0.41670	15.5	1.50E-07
E (12hr)	115.52	1.16E+08	0.4579	0.49520	37.3	3.23E-07
E (24hr)	136.60	1.37E+08	0.4683	0.52200	53.7	3.93E-07

1000°C

The oxide layers for all three samples were viewed and analyzed using XRD, SEM, and EDS. The three different oxidized pieces of sample A were examined using the same scanning parameters as before, but these scans were overlayed onto one another to study phase shifts. As seen in Figure 20, the peaks of the oxide layer became more prominent as time progressed, but there were no displacements. Ti, Nb, Cr, and Ta appear to have formed the majority of the oxide at all three oxidation times, as shown by the three large peaks. The minor peaks show non-dominant phases of tantalum tungsten oxide, tantalum aluminum oxide, and aluminum chromium niobium oxide. The lack of intensity changes between the different timelines shows that the oxide formation is not rapid, and the material provides oxidation resistance.





The SEM and images of sample A after these three different oxidation tests are seen in Figure 21. Figure 21(a) and 21(b) show a dark area in the center where the oxidation has not fully formed after 2hrs, as demonstrated by the coarse and non-uniform distributed oxide layer. The 12-hour test shows a much smoother, fully formed oxide layer as seen in Figure 21(c) and 21(d). The BSE image, Figure 21(c), provides a clear views to see the multiphase oxide layer, but also that this oxide layer has cracks running throughout it. The oxide layer has not formed a complete shell here. After 24 hours of oxidation, the sample has a much smoother oxide layer as seen, but unequal growths of the layer are present as a void has opened up in the material as seen by the large black spot in Figure 21(e) marked by an arrow.



Figure 21. 2hr oxidation BSE (a) 2hr oxidation SE (b) BSE 12hr oxidation (c) 12hr oxidation SE (d) 24hr oxidation BSE (e) 24hr oxidation SE (f) of sample A

The EDS maps of oxide layers of sample A can be seen in Figures 22, 23, and 24. Each EDS map shows a completely dispersed oxide layer with every element present. One element does not form a rich phase in certain areas. In the 2-hour sample A map, Figure 22, there is an area in the center of the BSE image where titanium looks to be dominant, however, this is some of the alloy surface showing through, so a better detection of elements is present. The actual before and after images of sample A can be seen in Appendix A.



Figure 22. EDS map of sample A after 2 hours of oxidation



Figure 23. EDS map of sample A after 12 hours of oxidation



Figure 24. EDS map of sample A after 24 hours of oxidation

Samples C and E as can be seen by the XRD patterns, in Figure 25, for 2, 12, and 24 hours, form three distinct oxide phases. Instead of having two different oxides forming and making a larger single-phase oxide, sample C has formed three completely separate phases. The same phenomenon is true for sample E. Sample E has two large peaks with many surrounding minor peaks, showing that multiple oxide phases are present in the material. Oxides also matched to every peak on samples C and E, so there is a full coating of oxide even after 2 hours of high-temperature exposure.



Figure 25. Sample C (b) and sample E (c) XRD scans after 2, 12, and 24hr of oxidation

Sample C when viewed through SEM and EDS, showed full oxidation of the surface at all different times as displayed in Figure 26. The oxide layer appeared almost as large growths that did not form smoothly on the surface of the sample. The layers of oxide formed as seen in BSE images Figure 26(a), 26(c), and 26(e) are all multiphase as characterized by the grayscale color changes in the material. The SEI images, Figure 26(b), 26(d), and 26(f) all display a nondensified, rough oxide layer that appears to be thick. Cross-sectional views of this sample were not possible as the material turned very brittle upon oxidation and the oxide layer was not bonded to the surface of the material well at 2 and 12 hours. After 24 hours, sample C had grown severely in size and appeared to be almost completely comprised of oxides. Appendix A displays actual images of Sample C before and after all oxidation tests.



Figure 26. BSE 2hr (a) SE 2hr (b) BSE 12hr (c) SE 12hr (d) BSE 24hr (e) SE 24hr (f) SEM

data of sample C after oxidation

EDS maps for sample C are found in Figures 27, 28, and 29. The maps for each different oxidation period all show the same data. All elements that were present in the bulk material have formed oxides. In each different map, there are titanium-rich and aluminum-rich regions of oxidation that are not overlapping. The aluminum-rich regions appear more at 12 hours of oxidation.



Figure 27. EDS mapping of sample C after 2 hours of oxidation



Figure 28. EDS mapping of sample C after 12 hours of oxidation



Figure 29. EDS mapping of sample C after 24 hours of oxidation

Sample E SEM images, displayed in Figure 30, show full oxidation of the surface of the material much like sample C. The oxide layer appears to be thick, as there is dimensionality to it when viewed through secondary imaging methods, and the layer contains multiple phases, as shown in the backscattered images. The image quality is not perfect as surface charging has distorted some features in images of Figure 30(c) and 30(d), but what remains clearly displays an encompassing, multi-phase oxide layer.



Figure 30. BSE 2hr (a) SE 2hr (b) BSE 12hr (c) SE 12hr (d) BSE 24hr (e) SE 24hr (f) SEM data of sample E after oxidation

EDS maps obtained from the different oxidized samples of sample E show a very detailed texture to the surface of the samples as seen in Figures 31, 32, and 33. Notably, on every EDS map of sample E, molybdenum would not be picked up by the detector. The potential was increased to 20kV, and the spot size was moved up and down, but none of the three samples would show molybdenum. This could be due to the detector having a sensitivity of 1% for elemental compositions, Mo could have sublimated at or below the 1000°C, or Mo could be blanketed by another element. After 2 hours of oxidation, the sample has some Al-rich and Ti-rich regions, but overall, the sample shows complete oxidation. The 12-hour sample shows some W-rich regions and not Al or Ti-rich regions which is a deviation from the 2-hour results. After 24 hours of oxidation, there is Ti-rich, Al-rich, and W-rich phases present in the material. Across all three timelines, niobium stayed evenly dispersed in the material according to the EDS maps.



Figure 31. EDS map of sample E after 2 hours of oxidation



Figure 32. EDS map of sample E after 12 hours of oxidation



Figure 33. EDS map of sample E after 24 hours of oxidation

E) Cross Section Investigation:

Since sample A proved to be the only sample to show oxidation resistance at all three times, it was subjected to cold mounting and cross-sectional polishing. The cross-sectional SEM images of this sample obtained allowed for the oxide layer thickness to be calculated. The images used and the measurement areas can be seen in Figure 34 with corresponding markings. Arrows pointing outward indicate the oxide layer formation direction, line segments indicate measured thickness areas, and a double headed arrow indicates the interfacial region between the oxide and alloy substrate. The oxide layer was measured in four places, as seen in Table IV, on each piece, of Sample A, to get an average value of oxide thickness.

The oxide layer when forming will cause a phase change directly below it as more oxygen starts to permeate the material. This interfacial region is known to have a direct phase change over the alloy substrate because BEC images show a difference in color. Upon inspection of EDS images, Figures 35, 36, and 37, the interfacial region can be seen to have some oxygen saturation, but a clear cutoff is visible where the alloy substrate starts again. Once inside the alloy substrate, the single-phase, equally dispersed elements are visible. The BSE images seen in the EDS maps are the same ones used in Figure 34, so oxide layer and interfacial region markings are transposable.



Figure 34. BSE 2hr (a) SE 2hr (b) BSE 12hr (c) SE 12hr (d) BSE 24hr (e) SE 24hr (f) SEM cross-sectional images, of sample A, with measurement marks after oxidation

			24 hour	
Measurement	2 hour (μm)	12 hour (µm)	(µm)	
1	5.301	80.026	138.853	
2	8.868	75.551	186.013	
3	10.929 59.996		135.659	
4	9.28 86.661		97.129	
Average=	8.5945	75.5585	139.4135	

Table IV. Measured oxide layer thicknesses on the corresponding cross-sectional samples



Figure 35. EDS maps of the cross section of sample A, after 2 hours of oxidation



Figure 36. EDS maps of the cross section of sample A, after 12 hours of oxidation



Figure 37. EDS maps of the cross section of sample A, after 24 hours of oxidation

As sample A was the only sample to show oxidation resistance after every test, TGA testing was only conducted on the small piece of this sample. TGA data of sample A, after 24 hours of oxidation at 1000°C are seen in Figure 38. The sample initially had a mass of 81.66000mg and after 24 hours, the sample only weighed 84.9168mg, which is an overall mass gain of 3.25668mg. The initial calculated surface area of this sample was 28.94mm². When comparing the mass gain per unit surface area, the sample shows $0.1125 \frac{mg}{mm^2}$ or $1.125*10^{-7} \frac{mg}{\mu m^2}$.



Figure 38. TGA mass gain versus time graph of Sample A

Conclusion

The investigation of compositional changes in refractory high entropy alloys proved to be a effective method in searching for a sample composition that has great oxidation resistance in air at 1000°C. Mechanical property analysis conducted on the six different RHEAs showed that the materials can provide suitable hardness and elastic modulus values. Phase examination of the six different compositions showed three favorable samples to test for oxidation. Upon conclusion of 2-, 12-, and 24-hour oxidation testing, one sample, sample A, showed great oxidation resistance. The WTaNbTiAlCr equimolar composition proved to be an effective combination that had minimal oxide layer growth. The oxide layer took until the 12-hour mark to make a uniform shell around the material, and by 24 hours, the material only saw an average oxide layer thickness of 139µm. TGA testing of sample A also showed very favorable results for the oxygen mass gain to surface area, providing results of $0.1125 \frac{mg}{mm^2}$ or $1.125*10^{-7} \frac{mg}{\mu m^2}$. The results of this thesis show that refractory high entropy alloys potentially have the ability to be both oxidation resistant and provide desirable mechanical properties.

Suggestions for Future Work

The results seen throughout this thesis showed that refractory high entropy alloys can be formed into a single phase and can provide oxidation resistance while retaining suitable mechanical properties. The work here only covered equimolar compositions, so more research is needed to study the changes that will occur when some elements are in different ratios than 1:1. The powder metallurgy process used in the fabrication of these refractory high entropy alloys could be quite expensive and time intensive for large volume materials, so more sintering methods should be examined.

Appendix A



Figure A1. Powder metallurgy milling process tungsten carbide canister and balls



Figure A2. Samples A (a), C (b), and E (c) cut samples with ideal cut lines



Figure A3. Sample A (a) sample C (b) sample E (c) pieces for oxidation



Figure A4. Sample A (a) sample C (b) sample E (c) after 2-hour oxidation



Figure A5. Sample A (a) sample C (b) sample E (c) after 12-hour oxidation



Figure A6. Sample A (a) sample C (b) sample E (c) after 24-hour oxidation



Figure A7. Cold mounted pieces of sample A after 2hr (top) 12hr (center) 24hr (bottom)



Figure A8. Before (a) after (b) 24-hour oxidation sample A TGA specimen of

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