46.0 INFLUENCE OF MICROSTRUCTURE ON THE OXIDATION BEHAVIORS OF REFRACTORY COMPLEX CONCENTRATED ALLOYS (RCCAS)

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This project initiated in Fall 2020. The research performed during this project will serve as the basis for a Ph.D. thesis program for Noah Welch.

46.1 Project Overview and Industrial Relevance

Refractory complex concentrated alloys (RCCA) are a subclass of refractory high entropy alloys (RHEA), that have five or less principal alloying elements in a near-equimolar composition [46.1]. Due to a unique combination of properties, these alloys show great promise for future use in advanced, high temperature, structural applications [46.2]. In addition to reported high-temperature compressive strength, the complex arrangement of atomic constituents provides a unique framework for the design of inherent oxidation resistance that is not readily accessible in conventional refractory alloys [46.2-46.4]. The complex arrangement of elements leads to formation of complex oxide structures, halting oxidation kinetics and thus leading to much slower oxidation rates [46.1-46.2]. A relationship between microstructural parameters (grain size, morphology, precipitates, etc.) and oxide structure will be established to provide a framework to engineer these alloys further.

RCCAs often form single phase BCC structures or BCC + Laves intermetallic structures, depending on the concentration of constituents [46.5]. Multiple compositions in the TaTiCr system— TaTiCr, Ta_2TiCr, Ta_4Ti_3Cr, and Ta_4TiCr_3 (at%)—will be analyzed to understand compositional contributions to microstructure and oxidation properties. From these analyses, a composition range with the most desirable properties will be determined. This will be followed by heat treatment, thermomechanical processing, and alloying additions to alter the microstructure and oxide structure.

A novel, bicombinatorial method for relating composition and oxidation behavior will be used after narrowing down the most promising compositional range. A compositionally graded, additive manufactured specimen will be heated using a Gleeble thermal-mechanical simulation system. This will establish a temperature gradient orthogonal to the composition gradient, allowing rapid assessment of oxidation properties in relation to composition.

Attributing their comparable density, impressive high-temperature oxidation resistance, and overall higher operating temperature regime, these alloy systems could potentially displace and outperform current high-temperature, oxidation-resistant alloys—such as nickel-based superalloys—in specific applications. Despite their potential, research is required to establish an equivalent knowledge base regarding fundamental properties and their underlying mechanisms, including, but not limited to, oxidation mechanisms and behavior.

46.2 Previous Work

Scientists at the Air Force Research Laboratory (AFRL) have made significant progress researching oxidation and mechanical behavior of several RCCAs systems, including Nb, Ti, Zr, Cr, Al, Mo, and others [46.1-46.2]. Work published by Dr. Oleg Senkov and Dr. Dan Miracle [46.1-46.2, 46.5-46.6] have been especially influential in elucidating the mechanical and chemical properties as well as the broader potential impact for many RCCA and RHEA systems.

A comprehensive database of properties, and microstructural information has been developed by Senkov, Miracle, et al., for over 370 RHEAs and RCCAs [46.7]. The most common structure observed in RCCAs is a single-phase disordered BCC structure [ref]. This disordered structure induces lattice strain and leads to exceptionally high strength and low ductility at room temperature [46.2]. Laves (C14 or C15) is the second most common phase,

generally associated with Cr, Mo, and Zr. From this information, and in conjunction with CALPHAD predictions, the TaTiCr system is expected to be composed of varying fractions of BCC+Laves, depending on specific composition ranges. Additionally, discussions with AFRL have shown that Ti additions effectively "invert" the microstructure from primary Laves to primary BCC. This is critical for the viability of a commercial alloy as the ductility can be increased considerably [46.3].

The oxidation behavior of NbTiZrCr specifically influenced the choice to pursue the TaTiCr system, as Ta has excellent oxidation performance and the relation between Ti and Cr has a significant effect on the Laves-BCC phase ratios. Further, Butler et al [46.4] compares the NbTiZrV and NbTiZrCr systems and it can be seen that the oxidation performance of the Cr alloy far exceeds that of the V alloy. The V alloy was completely oxidized after a 100 hour test and the Cr alloy had bulk material remaining and far less mass gain. Analysis of the oxide structure for both alloys show that several complex oxide structures form after long-term oxidation tests, with the Cr alloy exhibiting a mix of both simple and complex oxides. The complexity of these structures is attributed to the heightened oxidation performance due to halting the kinetics of oxide formation deeper in the bulk. However, due to the discrepancy between oxidation performance when both alloys exhibited complex oxide structures, there is a need to characterize and model the oxidation mechanisms at play.

The NbTiCr system is also of major interest because of the lower density of Nb (8.4 g/cm^3) compared to Ta (16.6 g/cm^3) [46.5]. From CALPHAD predictions, NbTiCr and TaTiCr should exhibit similar phase fractions of BCC and Laves. Ternary phase diagrams of the TaTiCr system at 1200 °C and 298 °C were created using ThermoCalc software by Robert Puerling from Colorado School of Mines to compare simulated and actual phases present.

A bicombinatorial method for alloy development has been used previously by Dr. Brian Martin using a Laser Engineered Net Shaping (LENS) system to additively manufacture compositionally graded specimens combined with a Gleeble thermomechanical simulation system [46.8]. The LENS system can print compositionally graded specimens by programming different distributions of specific powder compositions along the build direction. The Gleeble system uses differential resistive heating to impose a temperature gradient onto the specimen rapidly. This technique allows for rapid assessment of properties along orthogonal compositional and temperature gradients. Applying a similar method to the current work will provide a unique way to assess microstructural effects on oxidation behavior in a specific compositional range for any desired RCCA system.

46.2.1 As-cast/HIP Ingots

Twelve ingots were prepared via arc melting at the Ames Laboratory Metals Preparation center. Three of each of the following compositions were prepared: TaTiCr, Ta$_2$TiCr, Ta$_4$Ti$_3$Cr, and Ta$_4$TiCr$_3$. To maximize homogeneity, the specimens were Hot Isostatic Pressed (HIP) at AFRL. Specimens were made via Electrical Discharge Machining (EDM) for Thermal Gravitational Analysis (TGA), compression test, and metallography. To maximize homogeneity, all ingots were sent to AFRL to be hot isostatic pressed after sectioning a small portion for comparison purposes of the microstructure after each stage to the as-cast condition. The ingots were held at 1400 °C for 3 hours at 30 ksi (~206 MPa). The as-cast condition compared to the HIP condition can be seen in **Figures 46.1-46.4**. Small sections were taken off the ends of each ingot to analyze as-cast microstructure using backscatter electron (BSE) imaging.

Figure 46.1: TaTiCr specimens, as-cast (Top) and after HIP at 1400 °C, 30 ksi for 3 hours (Bottom).

Figure 46.2: Ta$_2$TiCr specimens, as-cast (Top) and after HIP at 1400 °C , 30 ksi for 3 hours (Bottom).

Figure 46.3: Ta$_4$Ti$_3$Cr specimens, as-cast (Top) and after HIP at 1400 °C , 30 ksi for 3 hours (Bottom).

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Figure 46.4: Ta$_4$TiCr$_3$ specimens, as-cast (Top) and after HIP at 1400 °C, 30 ksi for 3 hours (Bottom).

46.3 Recent Progress

Ingots of the chosen compositions were sectioned off site using EDM to obtain samples with specific geometries. After EDM, specimens were pickled in a solution consisting of 20 mL Hydrofluoric acid, 20 mL nitric acid, 80 mL sulfuric acid, and 40 mL water. Specimens were left in solution until all surface damage was removed from the wire used for machining. Upon completion of pickling, a large amount of unmelted and unmixed tantalum could be seen remaining in the compression specimens (**Figure 46.5**). These will need to be remade making changes in the manufacture of the ingots to ensure this problem will not occur in future samples. The oxidation specimen surfaces are usable, however, and TGA experiments are being planned for the near future. Further, thermal-mechanical processing methods are being investigated to break up and disperse the Laves phase and assess oxidation behavioral differences between HIP and deformed structures.

Figure 46.5: Compression specimen with unmixed tantalum

46.3.1 As-Cast/HIP Microstructure

BSE images were taken using a scanning electron microscope (SEM) to compare microstructure morphology between each composition. As the composition deviates from the equimolar condition, phase segregation can be

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seen, progressing from **Figure 46.6** to **Figure 46.9**. After HIP, (Ta,Ti)Cr$_2$ Laves phase coarsening and matrix homogenization can be seen. Energy dispersive spectroscopy (EDS) was conducted to analyze phase compositions, seen in **Table 46.1**. In the HIP condition, TaTiCr consists of a Ti-rich matrix with coarsened Laves phase evenly dispersed throughout the matrix. Ta$_2$TiCr Consists of a Ta-rich matrix with coarsened Laves forming on grain boundaries and within grains. Ta$_4$Ti$_3$Cr consists of a binary Ti-Ta rich matrix with no observable Laves formation. Ta$_4$TiCr$_3$ consists of a Ta-rich matrix with Laves morphology refining from the as-cast dendritic structure. All phases were verified using x-ray diffraction, as discussed in the next section.
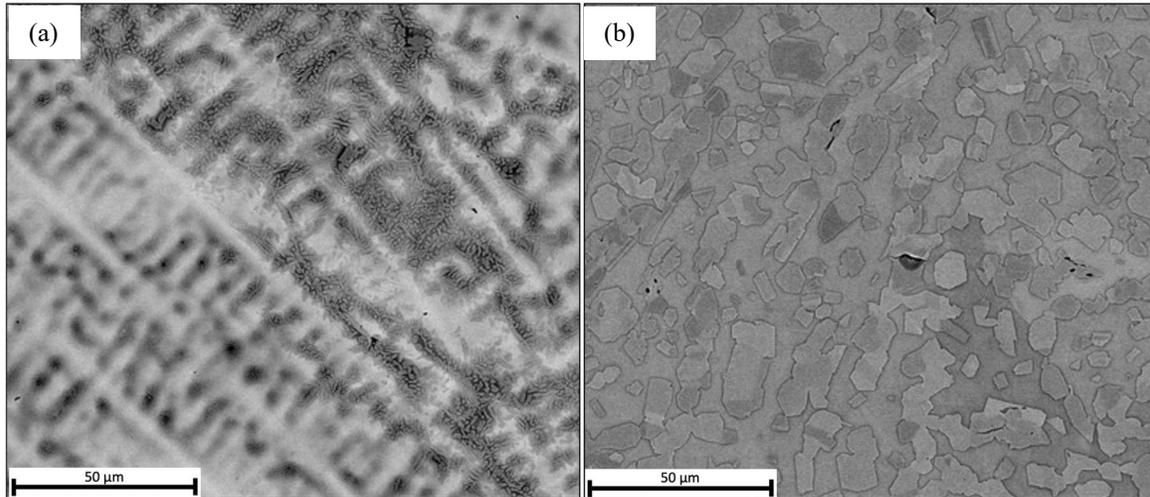

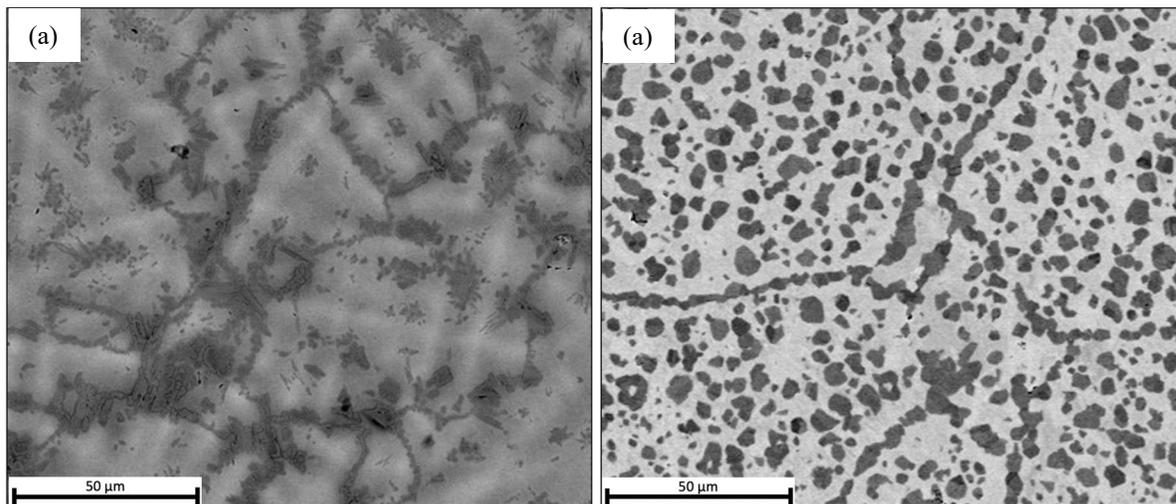Figure 46.6: As-cast (a) and HIP (b) TaTiCr microstructure.

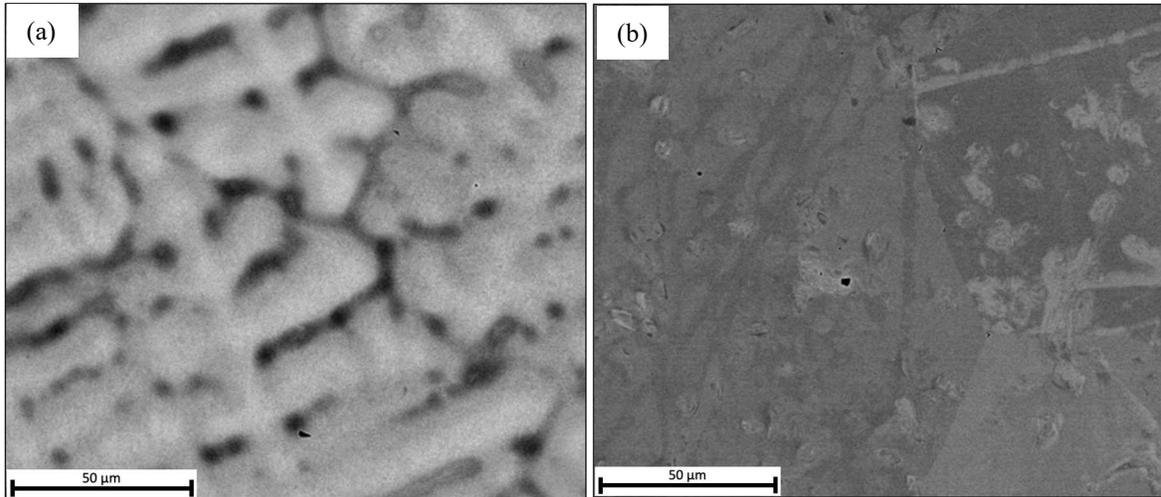Figure 46.7: As-cast (a) and HIP (b) Ta$_2$TiCr microstructure.

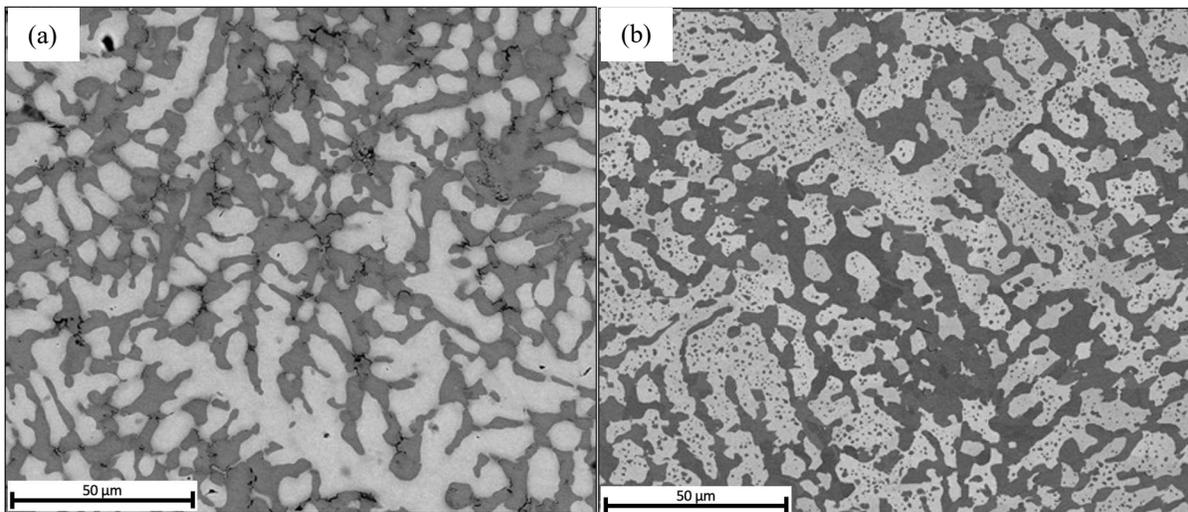Figure 46.8: As-cast (a) and HIP (b) Ta$_4$Ti$_3$Cr microstructure.

Figure 46.9: As-cast (a) and HIP (b) Ta$_4$TiCr$_3$ microstructure.

Table 46.1: Phase composition information for each alloy

| | | Elemental fraction (at%) | | |
		Ta	Ti	Cr
Ta_4TiCr_3	Matrix	59.25	19.13	21.19
	Laves	38.54	6.19	55.27
TaTiCr	Matrix	28.31	59.99	11.71
	Laves	28.84	13.75	57.42
Ta_2TiCr	Matrix	48.66	25.55	25.79
	Laves	28.73	23.98	47.29
Ta_4Ti_3Cr	Matrix	58.17	33.29	8.08
	Laves	-	-	-

46.3.2 X-Ray Diffraction Data

X-ray diffraction (XRD) experiments were conducted on the mounted samples to verify phase information and collect lattice parameter information. From the data in **Figure 46.10**, it can be seen that each composition except for Ta_4Ti_3Cr contains BCC+Laves structures. Additionally, Ta_4TiCr_3 was also observed to contain small amounts of retained C14 Laves, a hexagonal phase expected to form at high-temperatures in this system. The lattice parameters for each phase and composition can be seen in **Table 46.1.** These values are logical considering the lattice parameters for BCC Ti and Ta (2.816 Å, and 2.877 Å, respectively). It was concluded that the slow kinetics are responsible for the retained C14 phase and non-equilibrium phase fractions observed.
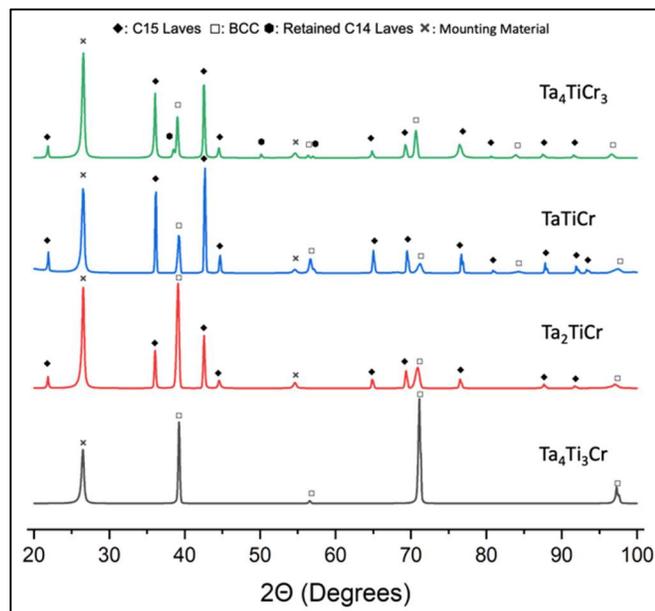

Figure 46.10: X-ray diffraction data for the four compositions.

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Table 46.2: Lattice parameters of phases, Å

	Ta_4TiCr_3	TaTiCr	Ta_2TiCr	Ta_4Ti_3Cr
C15 Laves	7.047	7.024	7.036	-
BCC	3.264	3.243	3.254	3.247

46.4 Plans for Next Reporting Period

Next reporting period,
- Initial DSC tests will be completed, providing background oxidation information
- Thermal-mechanical processing will be utilized to disperse Laves phase and measure influence on oxidation behavior
- Influence of dilute alloying additions will be investigated
- Oxide structure will be analyzed via SEM/TEM

46.5 References

[46.1]   D.B. Miracle, O.N. Senkov (2017). A critical review of high entropy alloys and related concepts. Acta Materialia. Volume 175.

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[46.7]   S. Gorsse, M.H. Nguyen, O.N. Senkov D.B. Miracle, (2018). Database on the mechanical properties of high entropy alloys and complex concentrated alloys. Data in Brief. Volume 21.

[46.8]   B. Martin, Development of a Novel, Bicombinatorial Approach to Alloy Development, and Application to Rapid Screening of Creep Resistant Titanium Alloys, (2017). Graduate Theses and Disstertaions. Iowa State University.