THERMAL PROPERTIES OF $CrTaO_4$ AND $(CrTaTi)O_2$

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***Abstract* – The purpose of this study is to experimentally determine the coefficients of thermal expansion (CTE) for the complex oxides $CrTaO_4$ and $(CrTaTi)O_2$ in order to assess their suitability as protective oxides. Techniques such as Spark Plasma Sintering (SPS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), and dilatometry were used to prepare, characterize, and test the oxide specimens. A secondary phase of Ta_2O5 was found in both oxides by SEM and EDS analysis. The CTEs of $CrTaO_4$ and $CrTaTiO_2$ were found to be $5.9*10^{-6}$ and $5.6*10^{-6}$, respectively.**

INTRODUCTION

Due to advancements in aerospace technologies, there is a growing necessity for materials that can withstand extreme environments beyond the capabilities of traditional Ni-base superalloys (e.g., temperatures > 1000ºC)[1]. Refractory alloys have gained interest as they have much higher melting temperatures (> 1800ºC), retain high-temperature mechanical strength to significantly high temperatures, and avoid complex cooling schemes [1]. However, a challenge of employing refractory alloys is their extremely poor oxidation resistance, which previous research has found to be the main contributor to shorter lifetimes and severe degradation of mechanical properties[2]. The development of refractory complex concentrated alloys (RCCAs) and high entropy alloys (RHEAs) have enabled enhancements in the ability to balance both high-temperature strength and oxidation resistance, albeit for shorter periods of time. RCCAs have been shown to form more complex oxide species due to the reaction of simple oxides ($Cr_2O_3 + Ta_2O5 \rightarrow 2\ CrTaO_4$) that mitigate the presence of deleterious oxides (e.g., Nb_2O_5, Ta_2O_5), thus providing moderately protective oxidation resistance[1]. Additionally, Schellert et al. elucidated the protective influence of substitution on the cation sublattice in related complex oxides, specifically that substitutional additions of Ti into $CrTaO_4$ form rutile-structured $(Cr,Ta,Ti)O_2$ [2]. This oxide provides additional beneficial oxidation resistance that is ultimately attributed to the substitution of Ti^{4+} on Cr^{3+} sites in $(Cr,Ta,Ti)O_2$, which is hypothesized to reduce the oxygen vacancy concentration and thus enhance the oxidation resistance.

RCCAs containing Cr, Ta, and Ti are of interest for high-temperature structural applications due to the unique combination of properties they offer. Ta is quite dense (16.65 g/cm3) but has a high melting temperature (3017 °C) and offers significant high temperature strengthening potential, but poor oxidation resistance[2]. Cr and Ti have lower densities (7.19 and 4.5 g/cm3, respectively) and are known to form favorable oxides with Ta (e.g., $CrTaO_4$, $(Cr,Ta,Ti)O_2$) as well as classically protective yet volatile Cr_2O_3. Four alloys of varying composition in the ternary Ta-Ti-Cr system were recently studied by Welch et al[2]. Equiatomic TaTiCr was found to have the best oxidation resistance, which was attributed to the formation of a dense and compact oxide composed of complex oxides ($(CrTaTi)O_2$, $CrTaO_4$, and $TaTiO_4$) and Cr_2O_3 [2].

This work reports on experimental efforts to further characterize properties of $CrTaO_4$ and $(CrTaTi)O_2$, specifically their coefficients of thermal expansion.

EXPERIMENTAL PROCEDURE

Coefficient of Thermal Expansion Study Procedure- $CrTaO_4$

A stoichiometric mix of Cr_2O_3 and Ta_2O_5 was placed into a cylindrical Nalgene container with zirconia (ZrO_2) milling media and placed on a ball mill for 24 hours. The blended and refined powder was then inserted into a 1-inch graphite Spark Plasma Sintering (SPS) die. SPS was performed on the sample resulting in a solid puck of $CrTaO_4$ with density 6.813 g/cm3, measured via Archimedes density. Compared to the calculated density of 7.572 g/cm3 from the Highscore software used for analysis, the sample has a relative density of 91.1 %. Due to the argon environment of the SPS chamber and the graphite die, a reducing environment was created. The puck was annealed in a stagnant air box furnace for 24 hours at 1500 0C to restore oxygen stoichiometry. A slow speed diamond saw was used to cut the puck into two smaller samples, one of which was then tested via X-Ray Diffraction (XRD) to determine crystal structure. This same sample was then prepared for Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). This sample was polished to 1µm, sonicated, and sputtercoated with gold and palladium. The specimen was then placed in the SEM to investigate composition and microstructure of the sample. Finally, dilatometry was performed on the second of the two samples to determine CTE. This sample was 14.120 mm by 4.806 mm by 3.734 mm. The peak temperature was set to 1200 ºC with heating and cooling rate of 5 ºC per minute. After dilatometry, sample density was measured to be 6.900 g/cm3. This slight and practically negligible increase in density is most likely due to the compression the sample experienced during dilatometry. Compared to the calculated density of 7.572 g/cm3 from the Highscore software used for analysis, the sample has a relative density of 90.0%.

Coefficient of Thermal Expansion Study Procedure- $(CrTaTi)O_2$

A stoichiometric mix of Cr_2O_3, Ta_2O_5, and TiO_2 was prepared. The sample preparation methods used follow those already described for $CrTaO_4$. Two dilatometry specimens were prepared. Specimen A measured 14.491 mm by 4.456 mm by 4.678 mm and specimen B measured 14.472 mm by 4.145 mm by 4.683 mm. Archemedes density was taken for both specimens, but as specimen A was the only sample used in this study, only the density for specimen A is reported here. The measured density of specimen A is 5.54518 g/cm^3. Dilatometry and characterization procedures follow those already described for $CrTaO_4$.

RESULTS

Coefficient of Thermal Expansion Study- $CrTaO_4$

I. SEM and EDS

SEM micrographs display the $CrTaO_4$ oxide puck to be slightly rich in Ta_2O_5. Figure 1 provides an overview of the bulk, as captured by the SEM's Everhart-Thornley detector (ETD). The micrograph contains white dispersions throughout the grey $CrTaO_4$ bulk that were found to be Ta_2O_5. EDS area analysis on a dispersion spot confirms the $CrTaO_4$ puck to be rich in Ta_2O_5. The micrograph of a selected dispersion and subsequent EDS analysis are included in Figure 2.

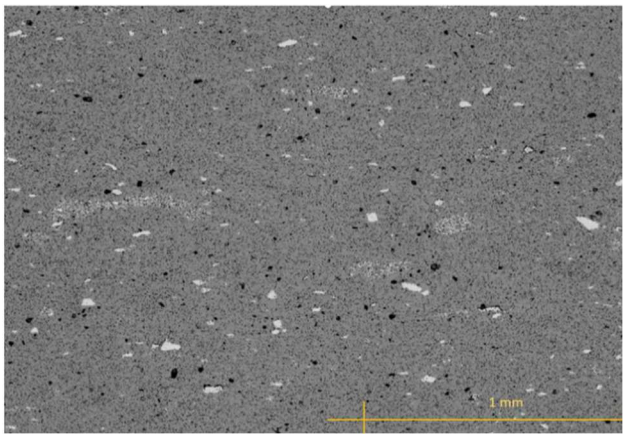
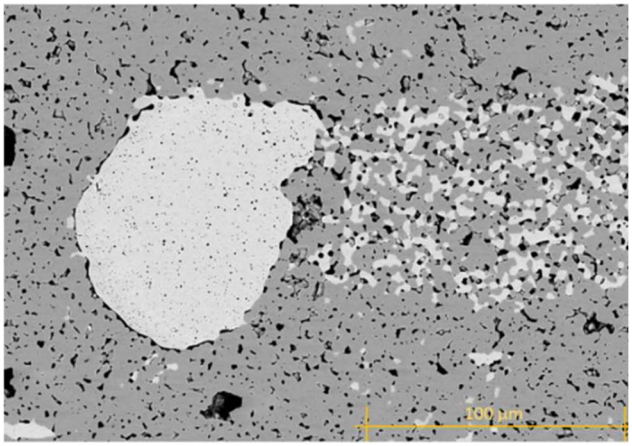


Figure 1: $CrTaO_4$ Bulk Micrograph



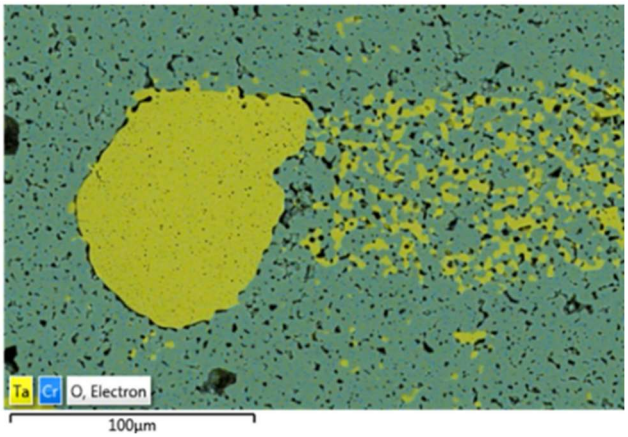


Figure 2: Micrograph and EDS of Ta_2O_5 dispersion

II. XRD

Figure 3 shows $CrTaO_4$ peaks in blue and excess peaks representing Ta_2O_5 in grey. It is worthy to note that there was a direct reference card in the Highscore software used to process this XRD data, which was provided by Krylov E.I et. al [4] .Figure 4 shows an XRD spectrum of the rutile structure, which is consistent with the peak pattern shown in Figure 3 [5].

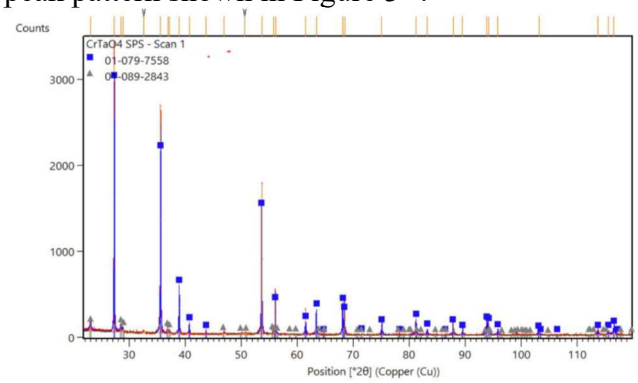


Figure 3: XRD spectra for $CrTaO_4$

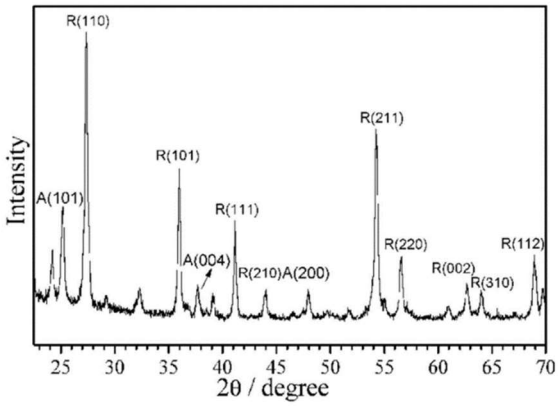


Figure 4: Common XRD pattern of a rutile structure

III. Dilatometry

The linear CTE of $CrTaO_4$ was found to be $5.9*10^{-6}$/ºC by dilatometry as shown in Figure 5. This result is consistent with coefficients of other rutile oxides, which are typically on the order of 10^{-6} /ºC.

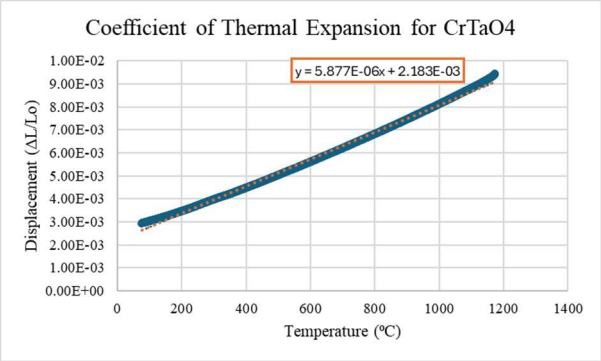


Figure 5: Dilatometry heating curve for $CrTaO_4$ with linear regression equation result

Coefficient of Thermal Expansion Study- $(CrTaTi)O_2$

I. SEM and EDS

Figure 6 provides a compositional bulk micrograph of $(CrTaTi)O_2$. Similarly to $CrTaO_4$, the micrograph contains white dispersions of excess Ta_2O_5 throughout the $(CrTaTi)O_2$ bulk, but at a higher phase fraction. This is confirmed by EDS analysis of a smaller area of interest. The area of interest is shown in Figure 7 as captured by the ETD detector. A backscatter (BSE) image of this area is provided in Figure 8 for clarity. The EDS for this area of interest and the resulting EDS maps are provided in Figures 9 and 10. It is clear that the large white dispersions are a secondary phase of Ta_2O_5.

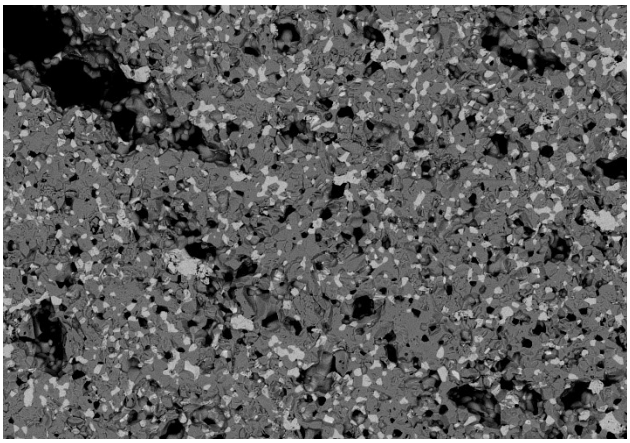


Figure 6: Compositional bulk micrograph of $CrTaTiO_2$

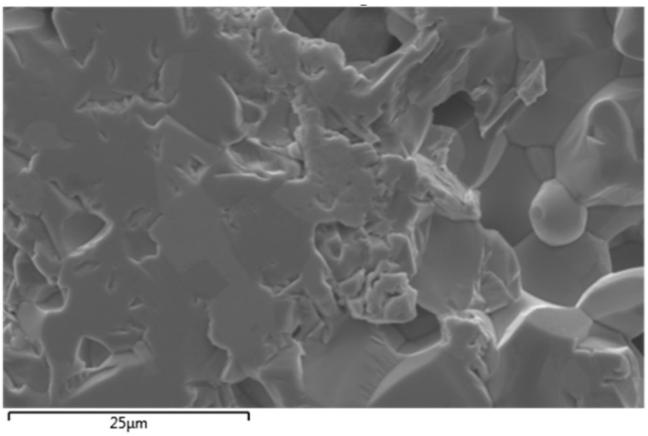


Figure 7: Micrograph of area of interest within $(CrTaTi)O_2$ puck

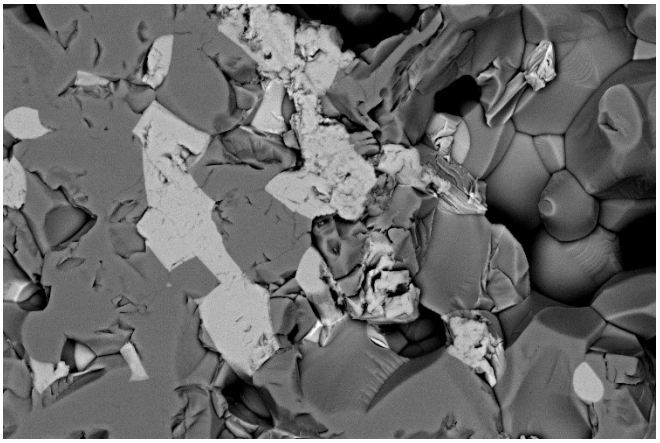


Figure 8: Compositional micrograph of area of interest within $(CrTaTi)O_2$ puck

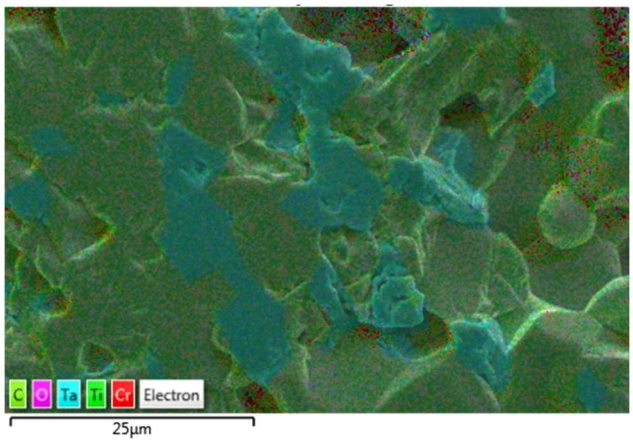


Figure 9: Layered EDS map of area of interest within $(CrTaTi)O_2$ puck

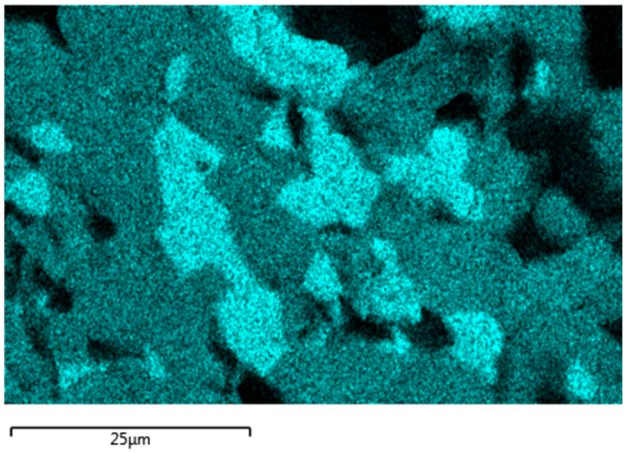


Figure 10: EDS map of Ta_2O_5 present in area of interest

In order to further investigate the composition of these inclusions, EDS point scans were conducted. Figure 11 displays the results of an EDS point scan done on the grey sample bulk. It shows a relatively even composition of Cr, Ta, and Ti as expected. This indicates the successful synthesis of $(CrTaTi)O_2$. Any trace amounts of gold (Au) or palladium (Pd) found via EDS are attributed to the sample coating required for SEM of nonconductive samples.

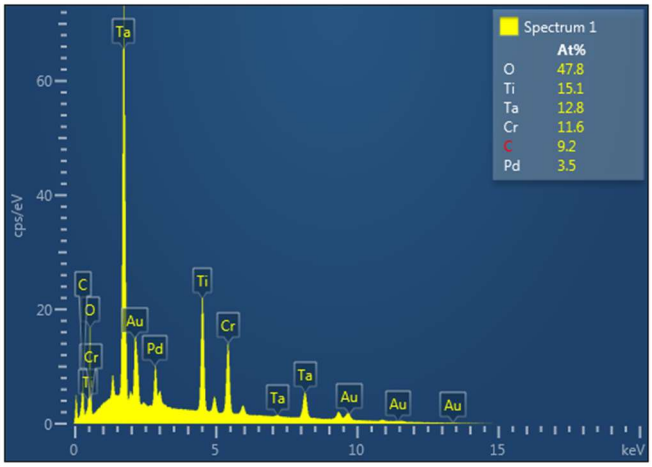


Figure 11: EDS point scan of grey specimen bulk

An EDS point scan was also conducted on one of the white phases. The spot was found to be consistent with Ta_2O_5 with almost no Cr or Ti present. These results are provided in Figure 12. It is clear that Ta_2O_5 is a secondary phase of this $(CrTaTi)O_2$ puck under the selected processing conditions.

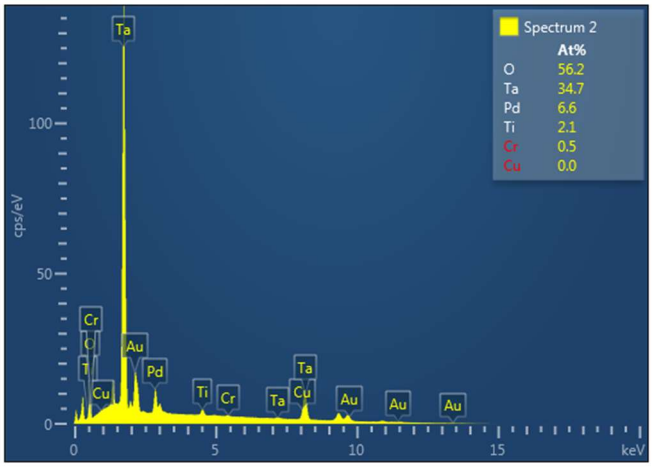


Figure 12: EDS point scan of white Ta_2O_5 dispersion

II. XRD

It is important to note that results reported in this section are the product of a different $(CrTaTi)O_2$ synthesis made prior to the

creation of the oxide puck used for the previous section.

Figure 13 displays $(CrTaTi)O_2$ peaks in blue and excess peaks representing Ta_2O_5 in green. It is worthy to note that there was a direct reference card in the Highscore software used to process this XRD data, which was provided by Mani et. al [5]. This pattern is once again consistent with a rutile structure, as provided in Figure 4. Thus, it is reasonable to assume that linear CTE of $(CrTaTi)O_2$ will also be on the order of 10^{-6}.

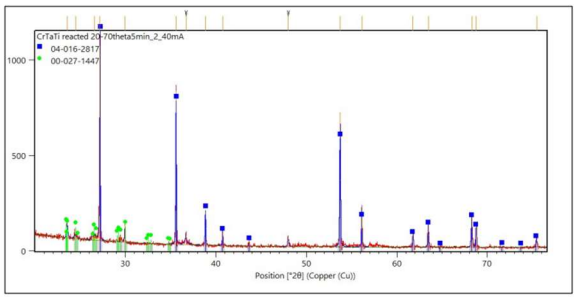


Figure 13: XRD spectra for $(CrTaTi)O_2$

III. Dilatometry

The linear CTE of $(CrTaTi)O_2$ was found to be $5.6*10^{-6}$/ºC by dilatometry as displayed in Figure 14. This result is consistent with coefficients of other rutile oxides, which are typically on the order of 10^{-6}.

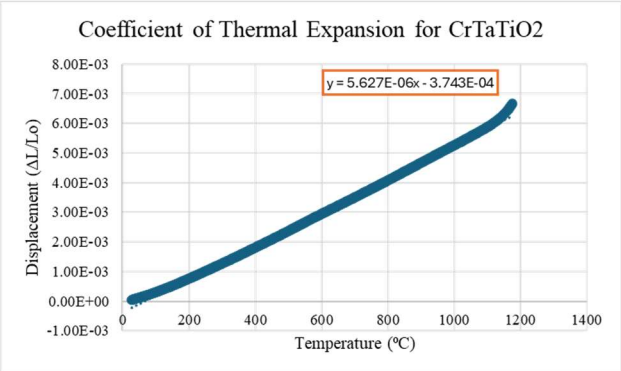


Figure 14: Dilatometry heating curve for $(CrTaTi)O_2$ with linear regression equation result

DISCUSSION

SEM and EDS

I. $CrTaO_4$

The excess Ta_2O_5 present in the $CrTaO_4$ puck could be a result of: volatilization of Cr_2O_3 during oxide formation, a measurement error when creating the powder mixture, a processing issue, or an unknown catalyst for secondary phase formation. Future work will investigate the phase fraction of $CrTaO_4$ to excess Ta_2O_5.

II. $(CrTaTi)O_2$

The SEM images collected of $(CrTaTi)O_2$ very clearly show a multi-phase structure. This is consistent with the XRD spectra in Figure 13.

XRD

$CrTaO_4$ and $(CrTaTi)O_2$

The XRD spectra in Figures 3 and 13 confirm the successful synthesis of rutile oxides $CrTaO_4$ and $(CrTaTi)O_2$. The spectra show an excess of Ta_2O_5, which is consistent with the Ta_2O_5 dispersions present in the SEM micrographs.

Dilatometry

CTEs of $CrTaO_4$ and $(CrTaTi)O_2$ were found to be $5.9*10^{-6}$/ºC and $5.6*10^{-6}$/ºC, respectively. This is a reasonable result as compared to other oxides of a rutile structure, such as the oxide TiO_2 which has a CTE range of $(8.4\text{-}11.8)*10^{-6}$/ºC.

The effect the secondary phase of Ta_2O_5 has on the CTE of $(CrTaTi)O_2$ is currently unknown. The CTE of Ta_2O_5 was found to be 3.786*

10^{-6}/ºC by Brown et. al. which is considerably smaller than the experimental CTE of $(CrTaTi)O_2$[6]. The difference in CTEs could cause internal stresses or uneven expansion. It is worthy to note that secondary phase formation may be due to processing conditions such as the synthesis temperature used during SPS, thus future investigations will involve varying processing conditions.

CONCLUSION

The CTEs of $CrTaO_4$ and $(CrTaTi)O_2$ were found by dilatometry to be $5.9*10^{-6}$/ºC and $5.6*10^{-6}$/ºC, respectively. SEM and EDS characterization helped to identify the presence of a secondary phase of Ta_2O_5 in each oxide. XRD results confirmed the successful synthesis of both oxides as well as the presence of excess Ta_2O_5. The cause of the secondary phase formation is unknown, but will be investigated in future work.

CONCURRENT STUDY AND FUTURE WORK

A concurrent study is being conducted by Hunter Schonfeld and Patrick Hopkins at the University of Virginia to determine the melting temperatures of $CrTaO_4$ and $(CrTaTi)O_2$. Preliminary results show the melting temperatures of both oxides to be approximately 2100 ºC.

Future work related to this research includes the use of ImageJ to determine the area fraction of the secondary Ta_2O_5 phase in micrographs of $CrTaO_4$ and $(CrTaTi)O_2$. It is also intended to use hot stage XRD to authenticate the CTEs determined by dilatometry. Additionally, studies to determine the effects of the secondary Ta_2O_5 phase on CTE will be conducted. Oxygen diffusivity will be determined once pure phases are synthesized.

ACKNOWLEDGMENTS

I would like to acknowledge Dr. Elizabeth Opila for her constant support and guidance throughout this project. I would also like to acknowledge the training and support I received from Cameron Miller and Clark Luckhardt that made this research possible. Hunter Schonfeld's contributions to a melting temperature study for these oxides cannot be overstated, and will be included in a future publication.

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