Surface Engineering of Annealed High Entropy Alloys Towards Thermodynamically Stable, Anti-Oxidation, Solar Selective Absorbers

Sheppard R. Somers
sheppard.r.somers.19@dartmouth.edu

Follow this and additional works at: https://digitalcommons.dartmouth.edu/engs88

Part of the Materials Science and Engineering Commons

Recommended Citation
https://digitalcommons.dartmouth.edu/engs88/1

This Thesis (Senior Honors) is brought to you for free and open access by the Thayer School of Engineering Project Class Reports at Dartmouth Digital Commons. It has been accepted for inclusion in ENGS 88 Honors Thesis (AB Students) by an authorized administrator of Dartmouth Digital Commons. For more information, please contact dartmouthdigitalcommons@groups.dartmouth.edu.
SURFACE ENGINEERING OF ANNEALED HIGH ENTROPY ALLOYS
TOWARDS THERMODYNAMICALLY STABLE, ANTI-OXIDATION,
SOLAR SELECTIVE ABSORBERS

by

SHEPPARD R SOMERS

Bachelor of Arts Honors Thesis

Thayer School of Engineering
Dartmouth College
Hanover, New Hampshire

Date: ________________________________

Approved: ___________________________

Jifeng Liu

____________________________________

Sheppard R Somers
Abstract:

High entropy alloys (HEA) as solar selective absorbers can be an important component in high-efficiency concentrated solar power (CSP) systems. Rather than trying to prevent the oxidation that can ruin current materials, we have harnessed oxidation to process HEA into a selective solar absorber that grows as a parabolic oxide at operating temperatures. The HEA used here is Fe$_{28.2}$Ni$_{18.8}$Mn$_{32.9}$Al$_{14.1}$Cr$_6$. Results of this research demonstrate that annealing processes of HEA can yield over 90% solar thermal efficiency by engineering the surface oxidation to be both physically and optically optimized for absorption. The rough surface topography coupled with the darkened and dulled surface of the oxide layer create the low reflectance samples applicable for use in concentrated solar power and elsewhere. Our most successful annealing process was annealing for 100 hours at 750 °C which lead to an irregular, bulbously textured and blackened surface with 93% thermal efficiency. During extended annealing at 750 °C the samples weight follows a square root function, meaning it is undergoing parabolic oxidation, which is generally protective at high temperatures as it thickens and limits diffusion to the surface (Li). The oxide is largely made up of Manganese oxide (Mn$_2$O$_3$) which has been used in creating absorbent coatings, but these coatings do not achieve the levels of thermal efficiency that annealed samples do (Eldred Lee, et al.). Overall, annealing provides a more efficient and more protective coating than other coatings have demonstrated, making the HEA a potential material for CSP application.
Acknowledgements

This project began in ENGS 24 my sophomore year with Professor Liu and Eldred Lee, Ph.D. candidate. Fiona Li taught the class, introducing me to material science for the first time, while Eldred Lee and Professor Liu guided our group on our high entropy alloy (HEA) oxidation project. I would like to extend my sincerest gratitude to these two professors and Eldred, as well as my group for the class project that started this journey for me: Mallory Byrd, Mia Kobs, and Lily Zhang. The section on carbon doped samples is based on the research we did for this project. Many thanks to Spencer Adams-Rand and Conor Rowan who wrote a Matlab script for calculating thermal efficiency that was altered and adapted for this project.

I would also like to thank Dr. Cullen, Eldred, and Can Xu for helping me learn all of the necessary tools to complete this project. Dr. Cullen has often rescued me when I feared I had broken the SEM or EDS, patiently working through whatever issue there might be and even staying late to work things out. For all of this I am extremely grateful. Eldred was always available to train me with the Spectrophotometer, FTIR, and XRD, answering my every question. I thank him for this and helping keep me prepared to work on this project. Can Xu has helped refresh me on the XRD, spectrophotometer, and FTIR, allowing the final push on this project to be successful. Than you to Regina Yan ’19 as well for turning off the furnaces whenever I could not be at Thayer.

Thank you to everyone, both mentioned and not mentioned here, for helping me along the way with this project.
Table of Contents

1. Introduction 1

2. Experimental 3
   2.1 Sample Preparation 3
   2.2 Annealing 4
   2.3 Measurements 5
      • Optical and Thermal Properties 5
      • Oxide Growth Rate 6
      • Oxide Characterization 7
   2.4 Observations 7

3. Results and Discussion 8
   3.1 Carbon Doping 8
   3.2 Single-Stage Annealing 11
   3.3 Two-Stage Annealing 12
   3.4 Oxide Composition 13
   3.5 Oxide Growth 20

4. Conclusions 21

Appendices 23

   I. Thermal Efficiency of all HEA samples 23
   II. Carbon Doped Samples SEM 24
   III. HEA Single-Stage Samples 26
   IV. Thermal Efficiency and Discussion of Two-Stage Samples 27
   V. EDS Cross Section and Best Result 28
   VI. Tools 32

References 34
Table of Figures

1. Picture of sample before and after annealing 4
2. Absorbance of an HEA, a carbon doped, and a two-stage sample 8
3. SEM: carbon doped and not doped comparison 8
4. SEM: Carbon doped sample oxide flaking 9
5. Absorbance of carbon doped samples 9
6. Thermal efficiency of single-stage samples 11
7. Absorbance with and without cooling for two-stage samples 12
8. Thermal efficiency of two-stage samples 12
9. XRD: cross section and best result 14
10. EDS: best result at different accelerating voltages 15
11. SEM: best result at different accelerating voltages 16
12. SEM: cross section two oxide areas 17
13. EDS: cross section 18
14. TGA: best result oxide growth 19
1. Introduction

Concentrating solar power (CSP) is an alternative energy technology to photovoltaic cells that works by focusing sunlight on a receiver to heat some medium. The focused sunlight generates heat which is then used directly or to drive a heat engine to generate electricity. CSP’s advantage over photovoltaic cells lies in its ability to store energy in heat form and respond to the grid’s energy demands. CSP does require more maintenance as the mirrors have to be kept clean and large grid-scale systems are only appropriate in certain climates (“Power Tower System…”). CSP is not meant as an alternative or replacement for photovoltaic cells but as an addition to help fill the power need surge in the evening that photovoltaic cell energy production is misaligned with (Lee, Wu, et al.). This thesis investigates a potential alternative material for the receiver in a tower system of concentrating solar power.

Current tower systems of CSP have to limit their working temperature due to limitation in the receiver material’s physical properties above 600 °C (Lee, Wu, et al.). At temperatures above 600 °C, stainless steel begins to suffer creep and cracking, as well as accelerated oxidation (Lee, Wu, et al.). Nickel based alloys have been developed that are capable of operating above 600 °C, but they are cost prohibitive (Lee, Wu, et al.). This leaves grid-scale tower systems operating well below their theoretical temperature max of 900 °C, which in turn leads to lower system efficiency as higher operating temperatures lead to higher efficiency (Lee, Wu, et al.).

Concentrating solar power receivers require materials that have stable physical and optical properties at high temperatures. These materials often are selected for their physical properties at high temperature and then processed until they have sufficient optical properties. Professor Baker and his lab at Thayer School of Engineering has
created a high entropy alloy (HEA) that is cheaper than current nickel based alloys that is iron and manganese based and has the necessary physical properties at high temperatures to be used as a receiver in CSP tower systems (Lee, Wu, et al.).

In order to drive an efficient conversion from light to heat energy the material used in the receiver of a CSP system must be absorbent of light in the solar spectrum and limit emittance. The combination of high absorbance and low emittance means that the receiver is maximizing energy capture and minimizing energy loss; it means the receiver is thermally efficient. This alloy is not naturally absorbent, but must be processed to be solar absorbent for it to be applicable in CSP.

The receiver in a CSP system must also have some protection against harmful oxidation at the high operating temperatures. Oxide growth rates generally fall into three categories, linear, parabolic, and logarithmic. For CSP application parabolic oxide growth is ideal as it is protective at high temperature because the oxide layer limits diffusion of oxygen to the surface thereby limiting oxide growth (Li). There are some paints and coating commercially available right now that utilize manganese oxide to be absorbent, but these paints degrade after 300hrs at 750 °C (Lee, Wu, et al.). Controlled annealing of the HEA presents an efficient and simple solution to both of these challenges by using oxidation to improve performance rather than detract from it. The goal of this project was to create a coating of the HEA, with its own native oxide, that is both protective and over 90% thermally efficient. This goal is above the current state of the art and uses a cheaper alloy (Lee, Wu, et al.).

This research demonstrates that annealing the HEA can yield over 90% solar thermal efficiency by engineering the surface oxidation to be both physically and
optically optimized for absorption and protective oxide growth. The rough surface
topography coupled with the darkened and dulled surface of the manganese oxide based
oxide layer create low reflectance samples applicable for use in concentrating solar power
and elsewhere. Our most successful annealing process was annealing for 100 hours at 750
°C which lead to an irregular, bulbously textured and blackened surface with 93%
thermal efficiency. Manganese oxidation on the HEA forms a protective oxide at high
temperature as it has a parabolic oxide growth rate.

2. Experimental

2.1 Sample Preparation

The preparation procedure of oxidized HEA solar absorbers is relatively simple. HEA
samples are cast by Margaret Wu in professor Baker’s lab, cut using a diamond blade
saw, and polished up to 0.3 micrometer aluminum polish before being annealed. The
HEA alloy used was Fe$_{28.2}$Ni$_{18.8}$Mn$_{32.9}$Al$_{14.1}$Cr$_6$ in a two-phase form. Carbon doped
samples are also used which are single-phase and doped with 1.6% carbon. Carbon
samples are prepared in the same fashion as non-doped samples. The sample originally
are just Fe$_{28.2}$Ni$_{18.8}$Mn$_{32.9}$Al$_{14.1}$ with a FeMn-rich face-centered cubic (FCC) that
alternates with a NiAl-rich ordered body-centered cubic (BCC) (Lee, Wu, et al.). The
chromium is then doped into the sample and largely is partitioned to the FeMn phase
(Lee, Wu, et al.). Carbon doping then causes the alternating microstructures to become
randomly distributed and changes the ordered BCC to a body-centered tetragonal (BCT)
structure (Lee, Wu, et al.). Both the regular HEA and the carbon doped sample have yield
strengths of two to three times that of the current state of the art stainless steel (Lee, Wu,
et al.).

2.2 Annealing
Originally, the most successful samples were annealed in two stages, a stage being defined by a temperature and length of time, for example 2hrs at 500 °C. In the end, a sample, originally intended as a long-term exposure test, had the best performance after a single stage of annealing at 750 °C for 100hrs. It is important to note that each annealing process was performed using a ramp increase in temperature and at least a 12hr cooling period to return to room temperature in Thermo Scientific Thermolyne electric furnaces.

Two stage samples were tested after annealing with and without a cooling period in between stages. Samples without cooling in the middle were annealed at the first temperature until the first length of time passed at which point the furnace ramped up to the second temperature. Samples that underwent annealing with a cooling break were left to cool to room temperature in the furnace before the furnace ramped up to the second temperature for the specified amount of time. Samples annealing without a cooling break yielded more desirable results, see figure 7 for the comparison of spectrophotometer measurements. The main investigation originally centered around samples annealed for equal times at each temperature, but as mentioned above the most successful sample came from single stage, long term annealing.

2.3 Measurements

Optical and Thermal Properties
Measurement of the samples centered around determining the thermal efficiency derived from the reflectance and emittance data. Thermal efficiency is calculated with equation 1 and is the measure of success for a sample. Equation 1 is essentially the absorbance of the solar spectrum, termed final absorbance in this paper, in the first term and the energy loss to due emittance, termed final emittance in this paper, in the second term. In other words, the first term is the fraction of solar energy collected and the second term is the fraction of energy lost to thermal radiation (Lee, Wu, et al.). The integrations are necessary to calculate how much of the available solar energy is being absorbed and what energy is lost to black body radiation at 1000 times solar concentration. This formula is the same used in Professor Liu and Eldred Lee’s previous research. The description published by Eldred Lee, et al. in SPIE is as follows:

\[
\eta_{\text{therm}} = FOM = \frac{\int_0^{\infty} (1-R(\lambda))I(\lambda)d\lambda}{\int_0^{\infty} I(\lambda)d\lambda} \cdot \frac{1}{C} \int_0^{\infty} (1-R(\lambda))B(\lambda,T)d\lambda = \alpha_{\text{solar}} - \varepsilon \sigma T^4 C_{\text{solar}},
\]

This calculation was completed using a Matlab script originally written by Spencer Adams-Rand and Conor Rowan for Professor Liu that was adapted for this project. Reflectance data was collected using a spectrophotometer and the emittance was collected using a Fourier-transform Infrared Spectroscopy (FTIR) with an integrating sphere. From FTIR and Spectrophotometer data the absorbance, emittance, and thermal efficiency of each sample is calculated.
The spectrophotometer records reflectance, R, across wavelengths from 300 to 2500 nm. From this, absorbance, A, is calculated as:

\[ A = 1 - R \]  

This absorption data is then matched to solar spectrum intensity data to calculate the solar spectrum absorption. This gives the actual absorbance percentage of energy from the solar spectrum of radiation and is shown in the first term of equation (1).

FTIR data is used to calculate emittance due to black body radiation by mapping the FTIR data to black body radiation at 700 °C or 1000 times solar concentration. This is done in a similar way to the spectrophotometer data; the blackbody radiation intensity by wavelength is used to create a weighted average of the emittance that is the actual blackbody emittance of the sample. This represents the energy loss after it has already been absorbed. The solar thermal efficiency is then calculated by subtracting the emittance from the solar absorbance yielding a final thermal efficiency percentage. All three of these metrics are percentages.

**Oxide Growth Rate**

In order to characterize the type of oxide growth and determine if it is stable and protective thermogravimetric analysis is used. The TGA measures the mass of the sample over an annealing cycle. A sample was annealed for 100hrs at 750 °C for TGA analysis. There are three general types of oxide growth rates, linear, parabolic, and logarithmic (Li). Linear oxide growth is not protective and involves the oxide flaking off as it grows, so it does not form a protective, diffusion limiting layer (Li). Parabolic oxide growth leads to a thick oxide layer that is protective at high temperatures as it limits diffusion to the surface (Li). Logarithmic oxide growth forms a protective oxide layer at lower
temperatures, but not at the high operating temperatures of CSP tower systems (Li). The goal for HEA is that it follows parabolic oxide growth so that it is stable at the CSP tower system’s operating temperature.

**Oxide Characterization**

X-ray diffraction (XRD) is used in determining the elements and phases present in the oxide layer and the sample. The XRD measures the intensity of reflected (diffracted) x-rays across incidence angles and uses the pattern of peaks measured to match the sample with existing information about various materials’ peak patterns. This yields the elements and compounds present, as well as estimations of their mass percentage in the sample.

### 2.4 Observations

Observations are the non-quantitative information collected about the samples which included imaging with the scanning electron microscope (SEM) and element identification with energy dispersion spectroscopy (EDS). The SEM was used to gain an understanding of the surface topography of each sample and how it impacted absorbance as well as gather clues about how the oxide grows. Imaging from the SEM spans from 40x to 10kx magnification. As previously stated, samples with rough surfaces and bumpy topography capable of capturing photons and a dark matte surface to limit reflectance.

EDS is used to determine the elements present in the oxide layer, both on the whole and in specific regions. The EDS does not report conclusive quantitative results, but can be used to compare relative amounts of the elements between areas in the sample. This is used in determining which elements are creating the majority of the oxide layer.

### 3. Results and Discussion
3.1 Carbon Doping

The introduction of carbon to HEA speeds annealing and allows a consistent oxide layer to grow at lower temperatures, see figure 3 for SEM images comparing carbon and non-carbon doped samples after 2 hours at 500 °C. The difference in oxidation is often apparent to the bare eye, as non-carbon doped samples are still shiny and lack a complete oxidation layer. Because of increased oxidation, carbon doped samples have greater absorbance after lower temperature annealing, as shown in figure 2. Figure 2 also shows that the 2-stage annealed sample is more effective than either single stage sample, likely due to its time at the higher temperature.

Figure 2: Absorbance of pure and doped after 9hrs at 500 °C compared to pure annealed 2hr

Figure 3: Carbon doped (left) and no carbon doping (right) both annealed for 9hrs at 500 °C. The carbon doped sample (left) annealed much more than the non-carbon doped sample
Despite the better performance after annealing at 500 °C, carbon doped samples show indications of oxidizing too rapidly at 750 °C. The rapid oxide growth leads to flaking, a disadvantage in long term annealing and deployment. SEM imaging reveals a cyclical growth of the oxide layer in carbon doped HEA samples (HEAC) where protrusions form on the surface creating a rough, towered, bulbous surface that is soon swallowed up in a smoother oxide layer before new protrusions grow on top again. This multi-stage process of growth is consistent with the optical results, shown in figure 5, and our understanding of rough surfaces creating more points of incidence and therefore more absorbance than flatter surfaces. Appendix II: Carbon Doped Samples demonstrates the oxide growth pattern as observed in SEM images. As the oxide layer

![Figure 4, HEA 15hr 750 °C, oxide flaking off](image)

**Figure 4, HEA 15hr 750 °C, oxide flaking off**

![Air Annealed HEA-C 1hr to 6hrs](image)

Air Annealed HEA-C 1hr to 6hrs

![Air Annealed HEA-C 8hrs to 20hrs](image)

Air Annealed HEA-C 8hrs to 20hrs

**Figure 5: Absorbance of various carbon doped samples annealed at 750 °C.**
grows to swallow its own peaks, the surface sometimes flakes or cracks, either because of contamination or because of excess surface compression, see figure 4 and the images in Appendix II. This flaking and cracking gives the opportunity to see below the newest oxide layer to what is below, confirming our hypothesis that the oxide grows to cover its own peaks. The carbon doped samples demonstrate high absorbance, showing the potential of oxidation as a method of creating an absorbent coating. Ideally, the oxide growth could be stalled in its rough, peaky, bulbous stage thus allowing an incident ray to make a greater number of contacts with the surface. The cyclical nature of the oxide growth, the flaking at CSP operating temperatures, and optical performance is also not promising for long term stability at the high operating temperatures.

Due to the concerns about stability, investigation in this paper continues with non-carbon doped samples in the hopes that oxidation would be more controlled without the doping. Carbon doped samples could be explored more fully in future investigations of two stage carbon doped samples and oxidation growth rate and stability analysis. The carbon doped samples do have a different microstructure than the undoped samples, changing from alternating body-centered cubic (BCC) and face-centered cubic (FCC) to randomly distributed FCC and body-centered tetragonal (BCT). It is unclear how this directly affects oxidation, but may be an important part of making the oxidation more protective for carbon doped samples. If the oxidation at 750 °C can be slowed, carbon doping may make the annealing process cheaper if it does not require such high temperatures. In the meantime, not doping with carbon slows the oxide growth enough to limit flaking and create a relatively stable oxide layer.
3.2 Single-Stage Annealing

Single-stage annealing initially proves the concept of annealing for improved optics yielding initial findings on how the oxide forms and what oxide formations are the best solar absorbers with carbon doped samples. Single stage annealing of the carbon samples does not demonstrate the required oxide stability in samples. Single-stage annealing was initially intended only for longevity tests, but these longer-term tests (greater than 48hrs) yield the most efficient sample. The thermal efficiency, absorbance, and emittance of the long-term annealed samples are shown in figure 6. A sample annealed for 100hr at 750 ºC had 93% solar efficiency. The next best single stage annealing result achieved 85.1% thermal efficiency by annealing at 500 ºC for 48 hours. The 100hr 750 ºC sample exceeds the project’s goal of 90% thermal efficiency.

Intended as longevity tests, the single-stage samples lack a consistent annealing time progression, making it difficult to draw any concrete conclusions about what oxide growth patterns in single stage annealing lead to effective samples. In general, annealing time for single stage samples seems to be correlated with better thermal efficiency. As mentioned above, the most successful single stage annealed HEA sample (100hr 750 ºC) achieved 93% thermal efficiency, reaching the 90% efficiency goal.

Figure 6: HEA single stage thermal efficiencies, the 48hr samples are carbon doped.
3.3 Two-Stage Annealing

Two-stage samples are annealed at two different temperatures and times and demonstrate improved stability and absorbance over the single-stage samples (excluding the 100hr 750 °C sample). Annealing in two stages allows the possibility of cooling in between the two stages. Annealing without cooling time between the two stages leads to the better absorbance, as shown in figure 7 which shows the results of two samples annealed for 2hrs at 550 °C and 750 °C, one cooled in the middle and one immediately ramped up to 750 °C. The sample that continued immediately to 750 °C shows better optical properties. Given this, the remainder of the two-stage samples are annealed continuously in two stages with no cooling. Ultimately, two stage annealing yields similar results to the long-term, high-temperature, single-stage annealing process.

The main investigation into two-stage annealing used equal time at 500 °C and 700 °C. The times were 2, 3, 4, 5, and 6hrs. The thermal efficiency of these 5 samples is

![Figure 7: Absorbance of 2hr 550 °C 2hr 750 °C with and without a cooling break](image)

![Figure 8: Thermal efficiency, absorbance, and emittance for selected two-stage samples.](image)
shown in figure 8, while the absorbance and emittance graphs are included in Appendix 4: Two-Stage Samples Calculations. The two-stage samples each show similar oxide structures under the SEM. The images are included in Appendix IV: Two-Stage Samples. As annealing time increases small protrusions on the surface each become more clearly defined, making the surface more bulbous and bumpy which improves absorbance and thereby efficiency.

3.4 Oxide Composition

The oxide composition is determined using both XRD and EDS analysis, which shows that the oxide layer is largely manganese oxide (Mn$_2$O$_3$). The oxide has variable surface topography, both within the same sample and across multiple samples, but EDS mapping of the bumpy surface show that the manganese has consistent spread across the oxide, shown in figure 10. It is important to note that these EDS scans should not be taken as a quantitative measure of the elements present but as relative indications of what is present, e.g. 67% oxygen in figure 10 should only be taken to mean that there is a higher count of oxygen showing up with a 5kV accelerating voltage than with 30kV (Cullen). The other elements that are matched have a relatively even distribution. Maps for each element are included in Appendix V: EDS Cross-Section and Best Result. An accidental cross section was obtained when the 12hr 750 °C 12hr 23 °C x7 sample snapped in half during SEM mounting, providing a rough cross section to further analyze the oxide layer. (The 12hr 750 °C 12hr 23 °C x7 was intended as a test of the daily heating and cooling cycle of 12 hours hot and 12 hours ambient temperature that the HEA might experience when deployed for one week.)
The XRD results from the 100hr 750 ºC and the 12hr 750 ºC 12hr 23 ºC x7 samples both show large amounts of three forms of manganese oxide, sometimes with some iron atoms replacing a couple manganese atoms. The compounds identified were manganese iron oxide \((\text{Mn}_{0.983}\text{Fe}_{0.017})_2\text{O}_3\), manganese oxide \((\text{Mn}_2\text{O}_3)\), and bixbyite-c (which is also manganese iron oxide). Essentially, the oxide layer is made up of some amorphous materials that were not identified by the XRD and manganese iron oxide, with varying amounts of iron replacing manganese atoms in the oxide. Aluminum chromium iron 2 was also identified in the 100hr 750 ºC sample. The two phase weight percentage pie charts for these samples are shown in figure 9.

The EDS was utilized on an un-annealed sample, the 100hr 750 ºC, and a rough cross section of the 12hr 750 ºC 12hr 23 ºC x7 sample. For the 100hr 750 ºC sample the EDS was done with two varied accelerating voltages for the SEM, 5kV and 30kV. The two resulting images for the EDS scan are shown in figure 10 along with the SEM images at the respective voltages shown in figure 11. These SEM images are not exactly the same area used in the mapping, but are representative of it. They are used because the EDS did

---

**Figure 9:** The XRD results for the 100hr 750 ºC sample (left) and 12hr 750 ºC 12hr 23 ºC x7 sample (right). Both samples are largely manganese oxide with varying amounts of iron atoms mixed in.
not capture high quality images due to the high beam intensity necessary to read the counts from the samples which blurs the images.

The accelerating voltage of the SEM is related to how large the interaction volume is. The interaction volume is the volume in the sample that image is actually being generated from. When the accelerating voltage is higher the electrons from the SEM have more energy and thus penetrate deeper into the surface on average before bouncing a signal up to the detector, this means a lower accelerating voltage will give a image from the very surface of the material while a higher accelerating voltage will report more of the underlying structure in the oxide. The higher accelerating voltage will also give a sharper image as there is a stronger signal to record.

Figure 10: EDS maps of the 100hr 750 °C at 5 kV (left) and 30 kV (right) accelerating voltages. The lower accelerating voltage shows more oxygen, possibly because it is scanning the upper level of the oxide, but mainly because 5 kV is more effective at measuring oxygen due to its electron shell energies.
While the accelerating voltage definitely impacts the interaction volume for the EDS, since it is just another reading from the SEM, the main driver of the reported higher levels of oxygen in the 5kV image is a result of electron shell energy levels. The EDS is most accurate at identifying elements when the accelerating voltage is at least 2 times but not more than 20 times the K-shell energy level of the atom (Cullen). (This short hand calculation ignores the units and works when the energy level of the atom is in keV and the accelerating voltage is in kV.) This means that when the accelerating voltage is 30kV the EDS has trouble recognizing oxygen atoms as their K-shell energy is only 0.523keV but is successful at identifying the metals whose K-shell energy levels are between 5keV and 8keV (“Periodic Table”). This means that while the varied result showing predominantly oxygen in the manganese sample at 5kV and predominantly manganese at 30kV (figure 10) may be partly due to the interaction volume, it is mainly driven by the requirements for the EDS to most accurately identify an element. The EDS and XRD data

**Figure 11:** SEM images of the 100hr 750 °C sample with an accelerating voltage of 5kV (left) and 30kV (right). The different accelerating voltages for the SEM show different detail levels of the surface with the 5kV providing extreme detail of the very top of the surface and the 30kV showing more of the underlying structure and a sharper image.
do both indicate that the oxide is largely manganese oxide.

The cross section is not the same quality as a cross section that might have been obtaining using the transmission electron microscope (TEM) for its cutting and lift out functionality. The snapped cross section does allow us to observe the cross section without any smearing or degradation, despite not providing a flat, smooth surface. It is hard to determine exactly where the oxide starts and the alloy ends in some areas of the cross section. The EDS results indicate that the oxide layer is largely made up of Mn, confirming the XRD results and the results from the top EDS scan in figure 10.

![Figure 12: Cross section of the 12hr 750 °C 12hr 23 °C x7. Thin, more defined oxide section (left) and thicker, more irregular oxide section (right)](image)

The cross-section sample was a fortuitous accident that allows a relatively clean cross section of the oxide sample. Unfortunately, the 12hr 750 °C 12hr 23 °C x7 sample does not have the thickest oxide layer. The oxide layer is visibly irregular and not as continuous on the surface as other samples are. The cross section reflects some of this irregularity with one very thin section of the oxide and one thicker section, see figure 12. The thin section is approximately 2.3 μm thin, while the thick section is approximately
23.6 µm thick. These thicknesses are based on the average of six measurements taken from the SEM images. The difference in the fracture pattern is not a simple grain direction difference; the image on the left with the thin oxide is a contaminant, a part of the alloy that was not properly mixed with the rest so the thickness is a result of the oxide growing on different alloy substrate. The left, contaminant, thin section is a largely chromium section that is visible to the naked eye in the sample. This contaminant also likely led to the easy breaking of the thin sample.

The cross section of the 12hr 750 ºC 12hr 23 ºC x7 sample EDS results from both the spectrum and the mapping functionality are shown in figure 13 where (a) shows the area scanned, (b) is the overlaid map of all the identified elements, (c) is the map of manganese, (d) is the map of iron, and (e) is the graph of the actual peaks observed over the image area.

Again, the software’s percentage estimates should only be taken for their relative...
values compared to other samples or scan areas. The mapping clearly indicates a concentration of Mn in the oxide layer and a general lower concentration of other elements. The maps of manganese and iron are presented in figure 10(c) and 10(d) to illustrate this, the other element specific maps are in Appendix V: EDS: Cross-Section.

The manganese is the element driving the alloy oxidation during the annealing and should be further investigated to better engineer both the alloy and the annealing process. At other temperatures, other elements may be the primary oxidizers leading to different optical results. If different elements drive oxidation at lower temperatures, it might change whether the method is applicable to both small and large scale CSP systems where operating temperatures vary greatly. Lowering the amount of Mn might also help make the oxidation layer more of a protective layer, allowing the annealing process in the lab to create a stable layer that will not change in performance while deployed. At the same time, Lee notes in the MSR presentation that “Mn & O abundance indicates that there are transition metal oxides with d-shells that contribute to electronic band transitions, therefore enhancing optical properties” (Lee, Wu, et al.). This means that experimenting with other elements should center around transition elements.

In the future, a cleaner cross section should be obtained using the TEM to cut a cross section to be analyzed with EDS. This would

Figure 14: TGA measured mass over 100hr at 750 °C, note the data impurity has been removed for curve fitting.
provide the higher level of clarity into the oxide structure and composition, possibly showing different layers to the oxide or providing other insights into the oxide layer.

### 3.5 Oxide Growth

The TGA analyzed one sample’s weight increase as it oxidized over 100hrs at 750 °C, showing that the oxide growth parabolic as it fits a square root function. The graph of weight over time at 750 °C is shown in figure 14. In further investigations, it will be prudent to analyze the optical performance of the samples for longer annealing times to determine whether the oxide growth needs to be controlled or if longer annealing, i.e. during use in CSP, leads to stable optical performance, thereby diminishing the need to create a protective or slower growing oxide.

The 12hr 750 °C 12hr 23 °C x7 served as an initial check of the performance after annealing that mimicked what deployment in a CSP tower system might look like, twelve hours heated during the day and twelve hours cool overnight for seven days. This sample showed comparatively little oxide growth to what a sample annealed continuously for 84hr at 750 °C might show, but also had lower optical performance. This result is encouraging and in line with what was found during two-stage annealing, that cooling in the middle-lowered performance and oxide growth. It is an indication that daily operation may not cause damaging oxidation. A final check of annealing for 100hrs followed by the 12hr daily pattern should help determine the applicable nature of this HEA alloy and the annealing process to automatically generate a solar selective absorption coating.

### 4. Conclusions

The automatic generation of a solar selective absorbing layer is a promising solution to increase efficiency in CSP and decrease cost with the cheaper HEA alloy. The annealing process shows potential with this feasibility study demonstrating greater than 90%
thermal efficiency and 93% solar absorbance. Though the oxide layer is not completely characterized nor is the relationship between time, temperature and optical performance completely defined, the study has demonstrated an effective process. Annealing brings a sample from ~30% efficiency to over 90% efficiency.

The annealing process could help increase efficiency in tower systems of concentrating solar power. The research hopefully will serve as motivation to better understand the oxide growth to further optimize the result. This is just a promising beginning of the investigation. This processing holds the potential to be a single-treatment, long-term method of increasing the solar absorbance of HEA alloys making them applicable in CSP systems.

Immediate future research could focus on longer term testing of samples, better characterization of the oxide layer, and investigating slowing oxidation for carbon doped samples. It is important that longer term annealing tests are performed as they may yield even more efficient results and they will determine whether the oxide is truly protective in an applicable way. More complete characterization of the oxide layer, including a clean cross section to determine whether the oxide has any layering or variety, would aid in better engineering the oxide of this alloy, but also in further understanding what characteristics of this HEA make it a good solar absorber when annealed. For instance, since the manganese oxide is the main oxide perhaps, other alloys with a greater proportion of manganese might perform even better or lower the alloy cost. In regard to the alloy itself, the sample will have to be optimized for both physical and optical properties at the same time, as annealing can alter some of its physical properties (Lee, Wu, et al.). Finding the balance between physical and optical properties will involve an
analysis of the full needs and the importance of each characteristic for the material’s application in CSP. Continuing with cost, if the carbon doped samples can be slowed in their oxide growth they may be cheaper to anneal as they require lower temperature annealing. Lower temperature annealing might also have a smaller effect on the physical properties. These are just some of the questions that could be investigated next that will help drive the feasibility research done here towards application.
## Appendix I: Thermal Efficiency of all HEA samples

### All Samples – Sorted by Thermal Efficiency

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final Absorbance</th>
<th>Final Emittance</th>
<th>Thermal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>100hr 750C</td>
<td>93.63%</td>
<td>0.51%</td>
<td>93.12%</td>
</tr>
<tr>
<td>6hr 500C 6hr 700C</td>
<td>92.60%</td>
<td>3.53%</td>
<td>89.07%</td>
</tr>
<tr>
<td>2hr 550C 2hr 750C (no cooling)</td>
<td>90.32%</td>
<td>3.65%</td>
<td>86.66%</td>
</tr>
<tr>
<td>3hr 500C 3hr 700C</td>
<td>89.60%</td>
<td>3.46%</td>
<td>86.14%</td>
</tr>
<tr>
<td>5hr 500C 5hr 700C</td>
<td>88.96%</td>
<td>3.58%</td>
<td>85.37%</td>
</tr>
<tr>
<td>48hr 500C</td>
<td>87.63%</td>
<td>2.47%</td>
<td>85.15%</td>
</tr>
<tr>
<td>2hr 500C 9hr 700C</td>
<td>88.47%</td>
<td>3.45%</td>
<td>85.02%</td>
</tr>
<tr>
<td>2hr 550C 2hr 750C (with middle cooling)</td>
<td>87.95%</td>
<td>3.51%</td>
<td>84.44%</td>
</tr>
<tr>
<td>9hr 500C 32hr 700C</td>
<td>87.83%</td>
<td>3.76%</td>
<td>84.07%</td>
</tr>
<tr>
<td>9hr 500C (carbon doped)</td>
<td>87.62%</td>
<td>3.60%</td>
<td>84.02%</td>
</tr>
<tr>
<td>6hr 500C 15hr 700C</td>
<td>87.30%</td>
<td>3.68%</td>
<td>83.62%</td>
</tr>
<tr>
<td>4hr 500C 4hr 700C</td>
<td>86.98%</td>
<td>3.36%</td>
<td>83.62%</td>
</tr>
<tr>
<td>2hr 500C 2hr 700C</td>
<td>86.45%</td>
<td>3.32%</td>
<td>83.13%</td>
</tr>
<tr>
<td>6hr 500C 24hr 700C</td>
<td>85.85%</td>
<td>3.50%</td>
<td>82.36%</td>
</tr>
<tr>
<td>12hr 750C 12hr 23C x7</td>
<td>81.93%</td>
<td>1.33%</td>
<td>80.60%</td>
</tr>
<tr>
<td>24hr 500C 24hr 700C</td>
<td>83.52%</td>
<td>3.77%</td>
<td>79.75%</td>
</tr>
<tr>
<td>48hr 700C</td>
<td>82.60%</td>
<td>3.50%</td>
<td>79.10%</td>
</tr>
<tr>
<td>9hr 500C</td>
<td>74.51%</td>
<td>2.00%</td>
<td>72.50%</td>
</tr>
<tr>
<td>Unannealed</td>
<td>33.51%</td>
<td>-0.18%</td>
<td>33.69%</td>
</tr>
</tbody>
</table>
Appendix II: Carbon Doped Samples SEM

HEAC 5hr 750 °C distinct irregularities begin

HEAC 6hr 750 °C sharper, more uneven surface forms

HEAC 8hr 750 °C, surface becomes more bulbous

HEAC 10hr 750 °C, irregularities begin to merge

These images were collected as part of ENGS 24 with my group Mia Kobs ’19, Mallory Byrd ’19, and Lily Zhang ’18 for the class project. They are included here to demonstrate why this thesis research focused on un-doped samples, as the carbon doped samples anneal rapidly, leading to surface cracking and flaking.
HEAC 12hr 750 °C, ribbed layer is formed

HEAC 15hr 750 °C, upper layer flakes showing irregular under layer

HEAC 20hr 750 °C, another ribbed upper layer forms

HEAC 15hr 750 °C, oxide flaking off
Appendix III: HEA Single-Stage Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final Absorbance</th>
<th>Final Emittance</th>
<th>Thermal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>100hr 750°C</td>
<td>93.63%</td>
<td>0.51%</td>
<td>93%</td>
</tr>
<tr>
<td>48hr 500°C</td>
<td>87.63%</td>
<td>2.47%</td>
<td>85%</td>
</tr>
<tr>
<td>48hr 700°C</td>
<td>82.60%</td>
<td>3.50%</td>
<td>79%</td>
</tr>
<tr>
<td>9hr 500°C</td>
<td>74.51%</td>
<td>2.00%</td>
<td>73%</td>
</tr>
<tr>
<td>9hr 500°C (carbon doped)</td>
<td>87.62%</td>
<td>3.60%</td>
<td>84%</td>
</tr>
</tbody>
</table>

100hr 750 °C sample at 2kx and 5kV accelerating voltage on the left and 30kV on the right. The 5kV image shows the very fine details of the surface, while the 30kV penetrates deeper into the oxide layer showing the underlying peaks.
### Appendix IV: Two Stage Samples Calculations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final Absorbance</th>
<th>Final Emittance</th>
<th>Thermal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>6hr 500 6hr 700</td>
<td>0.923</td>
<td>0.035</td>
<td>0.888</td>
</tr>
<tr>
<td>3hr 500 3hr 700</td>
<td>0.896</td>
<td>0.035</td>
<td>0.861</td>
</tr>
<tr>
<td>5hr 500 5hr 700</td>
<td>0.890</td>
<td>0.036</td>
<td>0.854</td>
</tr>
<tr>
<td>4hr 500 4hr 700</td>
<td>0.870</td>
<td>0.034</td>
<td>0.836</td>
</tr>
<tr>
<td>2hr 500 2hr 700</td>
<td>0.865</td>
<td>0.033</td>
<td>0.831</td>
</tr>
</tbody>
</table>

The 6hr sample shows the best optical properties and there appears to be a cyclical pattern between annealing time and efficiency. The cyclical pattern was also present in the carbon doped samples and could mean that the oxide grows in stages. The two-stage annealing process shows promise, especially in its potential to improve annealing rates for samples that anneal too quickly, like the carbon doped samples. The experimentation with two-stage annealing was the most successful annealing process up until the very end when the 100hr sample proved to be the most efficient and therefore successful.
Appendix V: EDS Cross Section and Best Result

12hr 750 °C 12hr 23 °C x7
<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>26.55</td>
<td>45.55</td>
<td>829.35</td>
<td>7.77</td>
<td>0.0900</td>
<td>1.1089</td>
<td>0.3057</td>
<td>1.0000</td>
</tr>
<tr>
<td>O</td>
<td>27.18</td>
<td>35.00</td>
<td>1654.57</td>
<td>8.75</td>
<td>0.0592</td>
<td>1.0721</td>
<td>0.2031</td>
<td>1.0000</td>
</tr>
<tr>
<td>Al</td>
<td>4.69</td>
<td>3.58</td>
<td>1153.80</td>
<td>7.60</td>
<td>0.0148</td>
<td>0.9700</td>
<td>0.3255</td>
<td>1.0021</td>
</tr>
<tr>
<td>Ca</td>
<td>2.34</td>
<td>1.20</td>
<td>1162.77</td>
<td>1.63</td>
<td>0.0222</td>
<td>0.9504</td>
<td>0.9566</td>
<td>1.0420</td>
</tr>
<tr>
<td>Cr</td>
<td>3.19</td>
<td>1.26</td>
<td>1258.44</td>
<td>1.61</td>
<td>0.0303</td>
<td>0.8596</td>
<td>1.0123</td>
<td>1.0930</td>
</tr>
<tr>
<td>Mn</td>
<td>24.34</td>
<td>9.13</td>
<td>8065.55</td>
<td>1.14</td>
<td>0.2139</td>
<td>0.8432</td>
<td>1.0174</td>
<td>1.0245</td>
</tr>
<tr>
<td>Fe</td>
<td>8.89</td>
<td>3.28</td>
<td>2663.41</td>
<td>1.07</td>
<td>0.0778</td>
<td>0.8585</td>
<td>0.9997</td>
<td>1.0200</td>
</tr>
<tr>
<td>Ni</td>
<td>2.82</td>
<td>0.99</td>
<td>667.29</td>
<td>2.18</td>
<td>0.0233</td>
<td>0.8714</td>
<td>0.9300</td>
<td>1.0210</td>
</tr>
</tbody>
</table>
Best Result: 100hr 750 °C
Appendix VI: Tools

Diamond Saw

An Isomet\textsuperscript{tm} 4000 Linear Precision Saw was used to cut the samples from the pucks that are cast. It was used at 2500 rpm and a cut rate of 2.5 mm/min.

Spectrophotometer

The Jasco V-570 UV/VIS/NIR Spectrophotometer was used to collect reflectance data which was then used to find absorbance. Spectrophotometer data was visualized and analyzed using Matlab and the slightly adapted script originally developed by Spencer Adams-Rand and Conor Rowan for Professor Liu.

FTIR

The Jasco FT/IR-4100 Fourier Transform Infrared Spectrometer (FT/IR-4100 LE) was used to collect emittance data. FTIR data was also visualized and analyzed using Matlab and the slightly adapted script originally developed by Spencer Adams-Rand and Conor Rowan for Professor Liu.

SEM

The SEM used is a TESCAN Vega3. It was used always under high vacuum mode, generally with an accelerating voltage of 30kV or 5kV, a working distance of 10mm, a beam intensity of 10, magnification between 40x and 10kx, and a scanning speed of 4 for most images. These were changed when EDS observations were being made.

EDS

An EDAX Ametek Octane Plus model was used in conjunction with the TESCAN Vega3 for EDS measurements. The EDS data was collected and visualized using APEX software from EDAX. The EDS was used with a dead time between 30 and 35, which meant that the beam intensity as well as the speed/resolution scale had to be adjusted to
meet this requirement. Generally, the mapping function of the EDS was the most useful for this project.

**XRD**

A Rigaku 007 X-Ray Diffractometer was used for X-Ray diffraction measurements. The XRD data was analyzed using Jade, as well as the open source phase database.

**TGA**

A Pyris Diamond Thermogravimetric/Differential Thermal Analyzer was used for oxide growth rate measurement. The TGA has to be calibrated before beginning the annealing and measurement cycle. The TGA was used over a 100hr period of annealing at 750 °C.
References


