Physical characterization of High Entropy Alloys through Differential Scanning Calorimetry and Nanoindentation.

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I. ABSTRACT

In recent years several accelerator facilities have been limiting their beam power output not due to constraint of the accelerators but by concerns on the survivability of their targets, which in turn has led to R&D efforts into new, more resistant materials. One of these novel materials are High Entropy Alloys, the main focus of the internship project. This paper details the activities performed during the CCI 10-week internship by the authors, as well as to discuss the results obtained from said internship. The project consisted of the physical characterization of 12 batches of High Entropy Alloys (HEAs); the methods used to analyze the materials were Nanoindentation, which allows to determine the elastic modulus of the material and its hardness, and Differential Scanning Calorimetry (DSC), allowing the determination of specific heat.

II. INTRODUCTION

A. Motivation

In recent years there has been an increase in the need for sturdier, more resistant materials in the field of High-Power Target systems since the current target materials have become a limiting factor for the intensity of the beam. Several modern targets at different high-energy facilities have failed while in service, diminishing the output of the desired products (be it pions, neutrinos or others) and raising concerns regarding future plans of more powerful accelerators. Some of the most challenging problems include thermal shock induced damage and radiation damage. To solve these problems, new materials have been researched and developed; some of these new possibilities include HEAs and nanofibers. The novelty of these materials has in turn created the need for testing their properties and their performance under the stresses they would find in an accelerator, although for this internship the focus resided on the HEAs.

As mentioned earlier, thermal shock induced damage is one of the main concerns of High-Power Target systems, it is caused by the compression generated by the expansion of a material surrounded by cooler material. The extent of the damage caused by thermal shock is dependent on the change in temperature, and the elastic module of the material, as it can be seen in the following equation:

$$\sigma = \sqrt{(\rho E)} \cdot \alpha \cdot L \cdot \frac{\Delta T}{\Delta t}$$

Equation 1. Thermal shock stress as a function of the change in temperature (1D).

Where σ is the stress, ρ is the density, E is the elastic modulus, α is the coefficient of thermal expansion, L is the length, ΔT is the temperature rise per pulse driven by the beam energy deposition and specific heat capacity, and Δt is the pulse length. This means that a medium with

high specific heat (c_p) can resist thermal shock damage better than a material with low c_p, the predicted specific heat values for HEAs make it a good candidate to use in an accelerator environment. HEAs have also shown high resistance to radiation damage in the literature, and it is theorized to be due to the disorder and mismatch of their lattice structure which generates a resistance to defect clustering and increases the opportunities for recombination of the material[1][2].

B. Background Information

a. High Entropy Alloys

High Entropy Alloys (HEA), Multi-Principal Element Alloys (MPEA), and Complex, Concentrated Alloys (CCA) are different names for an alloy that consists of multiple principal components (this is where the complex and multi-principal come from). In contrast to regular alloys that have one principal material, iron in the case of steel for example, with several secondary elements in small concentrations that give the alloy more desirable characteristics. All these terms, however, have different focuses, for example HEAs look for a more disordered atomic structure (entropy)[3]. The study focuses on HEAs due to some of the characteristics derived from their disordered structure which were explored more in depth under the Motivation section.

Fermilab in collaboration with the University of Wisconsin-Madison has produced 12 different HEAs divided in two generations, the first one consisting of four alloys, and the second of eight, although the measurements were intended to be performed on all 12 alloys. However, due to time constraints and delays caused by contamination of the crucibles, only the first generation HEAs were analyzed by the time this paper was submitted.

ID	AL	CO	CR	MN	TI	V
1.1	0.0	0.0	33.3	33.3	0.0	33.3
1.2	0.0	0.0	31.0	31.0	7.0	31.0
1.3	15.0	0.0	20.0	20.0	10.0	35.0
1.4	15.0	4.0	20.0	20.0	6.0	35.0
2.1	9.9	4.1	26.5	22.1	1.1	36.4
2.2	11.7	4.0	27.1	18.4	4.3	34.5
2.3	18.7	2.0	25.3	26.2	1.1	26.7
2.4	18.0	4.0	25.1	27.4	1.2	24.3
2.5	22.4	1.1	0.0	24.5	2.1	49.8
2.6	14.0	2.9	6.1	24.2	2.1	50.7
2.7	20.6	0.0	0.0	27.6	2.2	49.6
2.8	22.3	2.0	0.0	24.1	2.0	49.5

Table 1. Elemental compositions for all 12 HEAs by atomic %.

b. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermal analysis technique that consists of heating a sample and a reference (which is an empty sample carrier) following a temperature program, which typically includes heating, cooling, and isothermal holds, and measuring the energy flow of both the sample and the reference. This method allows for the determination of specific heat (c_p) and small or big changes in the phase (solid, liquid) of the sample[4]. The DSC was mainly used to obtain the c_p of the 12 HEAs.

c. Nanoindentation

Indentation is a mechanical testing procedure that consists of making small indentations at different loads on the surface of a material and record the behavior of the substance over the load increase. Nanoindentation is the same technique with the difference that it is applied on micron to nano scales, using a diamond tip that is extremely small and using relatively low loads. The data obtained from this test alongside the Oliver-Pharr method allows for the determination

of hardness (H), and elastic modulus (E) of the sample[5]. The first gen HEAs have already been tested so the efforts of this internship fell onto the eight second-gen HEAs, particularly on how and if their properties change after irradiation. This part of the project was mainly handled by another intern, Ned Sigler, so the details and results of the nanoindenter will be mostly an overview of his work.

III. METHODOLOGY

This section is intended to be a general description of the workflow needed for these machines rather than in-depth, step-by-step account of the utilization of the instruments.

A. DSC 404 F3

The first step to take when using this tool is to stablish a temperature program that will reach the temperatures the experiment requires, in the case of this project the temperature program is as follows:

Nr	Type	°C	K/min	Time	pts/min	pts/K	STC	P1	P2	PG
1		25.0					☐	☐	☑	☑
2		40.0	5.000	0:03:00	75.00	15.00	☐	☐	☑	☑
3		40.0		0:15:00	20.00		☐	☐	☑	☑
4		600.0	20.000	0:28:00	200.00	10.00	☐	☐	☑	☑
5		600.0		0:10:00	100.00		☐	☐	☑	☑
6		610.0					☐	☐	☑	☑

Figure 1. Temperature program for HEAs testing from the Proteus analysis software.

This program allows us to check how the HEAs react under similar temperatures they would experience in an accelerator environment.

The next step is to take baseline (a baseline test is a run of the experiment without any of the samples that measures the difference in energy flow between the two crucibles to later subtract that difference from the actual test) measurements until the repeatability of the baseline

measurement is assured (less than .5 μV difference between measurements), it takes at least two runs, but might be more depending on the possibility of dust particles or other contaminants. Once the baseline is established, the program is run with a sapphire disc whose mass very similar to the mass of the HEA sample. It is important to take this measurement since the results from the sapphire will be used to obtain the c_p of the HEA with a comparison technique. The next step consists of running the test on the HEA, once the test has finished the analysis of the data can start and it is done on the analysis software provided by the machine manufacturer, the c_p values can be obtained using the ratio method that uses the following equation[6]:

$$C_p^s(T) = \frac{m_R \Delta V_S(T)}{m_s \Delta V_R(T)} C_p^R(T)$$

Equation 2. c_p determination through the ratio method.

Where $C_p^s(T)$ is the specific heat of the sample as a function of temperature, m_R and m_S are the masses of the reference and the sample respectively, $\Delta V_s(T)$ and $\Delta V_R(T)$ are the voltage difference between the sample and reference curves and the baseline, and finally $C_p^R(T)$ is the specific heat of the reference dependent on temperature. For one measurement it usually takes eight hours since the baseline and sapphire tests must be repeated every time the furnace is turned off for several hours to ensure an accurate reading.

B. iMicro Nanoindenter

The first, and fairly important, step is to prepare the sample, which includes polishing the surface of the material to obtain as much as a planar surface as possible, with the last polishing substance using 20 nanometers colloidal silica beads, and ensuring that the sides of the sample are as parallel to each other as achievable since the instrument is highly sensitive and small

variations in the surface roughness or a slight slant of the top will cause irregularities on the results. Once everything is prepared the samples are loaded into the machine, and, with the help of a digital microscope, the places on which the indentations are going to be placed are selected, alongside the force and depth the prove is going to perform. After those parameters are selected the test can be started, it usually takes 1 hour 20 minutes to execute 25 indentations, and the machine is usually left to run overnight to prevent the usage of onsite tools, the passing of cars or any other source of vibration (it is worth noting there is a construction site next to the laboratory the experiment is run in) to affect the results. Afterwards the results can be analyzed using the Oliver-Pharr method and continuous stiffness measurements (CSM) to determine properties as a function of depth.

IV. OTHER ACTIVITIES

As the subtitle suggests, this section will consist of all other miscellaneous activities performed during the internship that do not directly relate to the main project, in other words, not related to the nanoindentation nor the DSC. These tasks consisted mostly of sample preparation for other experiments or procedures such as SEM, which were not in the hands of the interns.

The first- and most-time consuming activity was sample polish, which consisted in cutting the material to the desired size to later fix it into a plate with an adhesive substance called crystal bond and then run the sample through different grits of sandpaper, starting at 80-grit all the way to 1200-grit. The polish would then be mostly performed through chemical reactions and colloidal silica suspensions that allowed for surface scratches smaller than 20 nanometers. This procedure prioritized a mirror-like finish that facilitated light reflection and allowed for the grains in metallic samples to be seen. Some of the materials that were prepared this way are Titanium 64, Copper, Graphite, Tungsten and the eight different compositions of the HEAs.

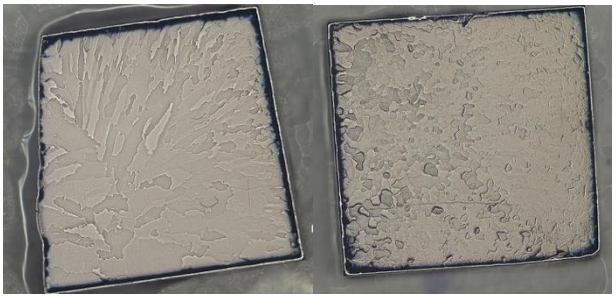

Illustration 1. Visible grain structure after polishing; HEAs 2.3 left and 2.7 right.

During the intervals between tests and sample preparation, a procedure for the use of the DSC 404 F3 was written, this manual describes the proper use of the machine and the steps that must be followed to obtain a measurement, a baseline, as well as how to (re)calibrate the furnace's temperature and enthalpy measurements.

V. RESULTS AND FUTURE WORK

A. Results

a. DSC

The first task to be completed during the internship consisted in recalibrating the machine's enthalpy and temperature measurements. To do this several reference elements (in this case In, Sn, Bi, Al, and Au) must be taken beyond their melting point to measure at which temperature the phase change occurs. After obtaining the temperature and enthalpy of the phase change these measurements are taken into the calibration software provided by Netzsch that generates a calibration curve that brings the obtained values closer to the actual values. The calibration curves and the corrected values can be seen in the following figures:

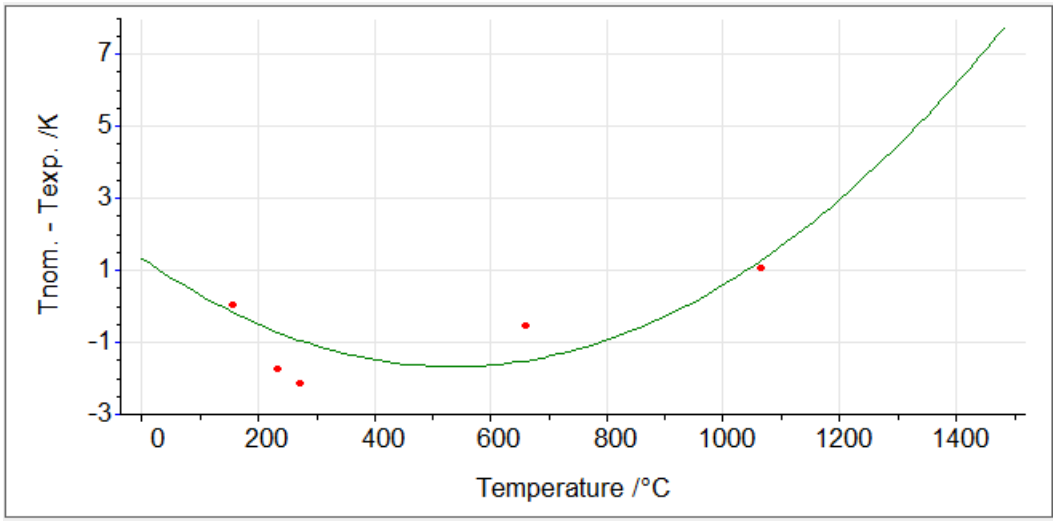

Figure 2. Temperature calibration curve generated by Proteus software.

	Substance	Temp. nom. /°C	Temp. exp. /°C	Mathematical Weight	Temp. corr. /°C
1	In	156.6	156.6	10.000	156.4
2	Sn	231.9	233.7	1.000	233.0
3	Bi	271.4	273.6	1.000	272.6
4	Al	660.3	660.9	1.000	659.4
5	Au	1064.2	1063.2	1.000	1064.5

Figure 3. Real values, experimental values, and corrected values for Temperature Calibration by Proteus software.

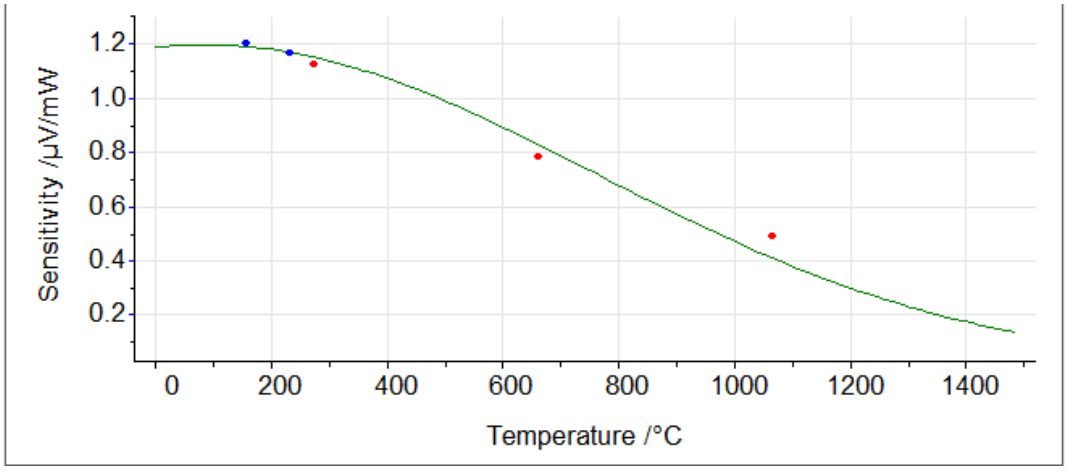

Figure 4. Enthalpy calibration curve generated by Proteus software.

As mentioned previously, time constraints and some contamination incidents delayed the characterization by a fair amount, leaving only the possibility to evaluate three HEAs of the first generation. The results for the first 3 compositions of the HEAs show a higher-than-predicted specific heat values, the greatest difference showed by the 3rd alloy (composition $Al_{15}Cr_{20}Mn_{20}Ti_{10}V_{35}$) with its experimental values being larger than the prediction by 25-50%; the other alloys in comparison were bigger by 7-16%. It is worth noting that the tested samples had been oxidized in a previous test and there is work underway to confirm these results with pristine samples.

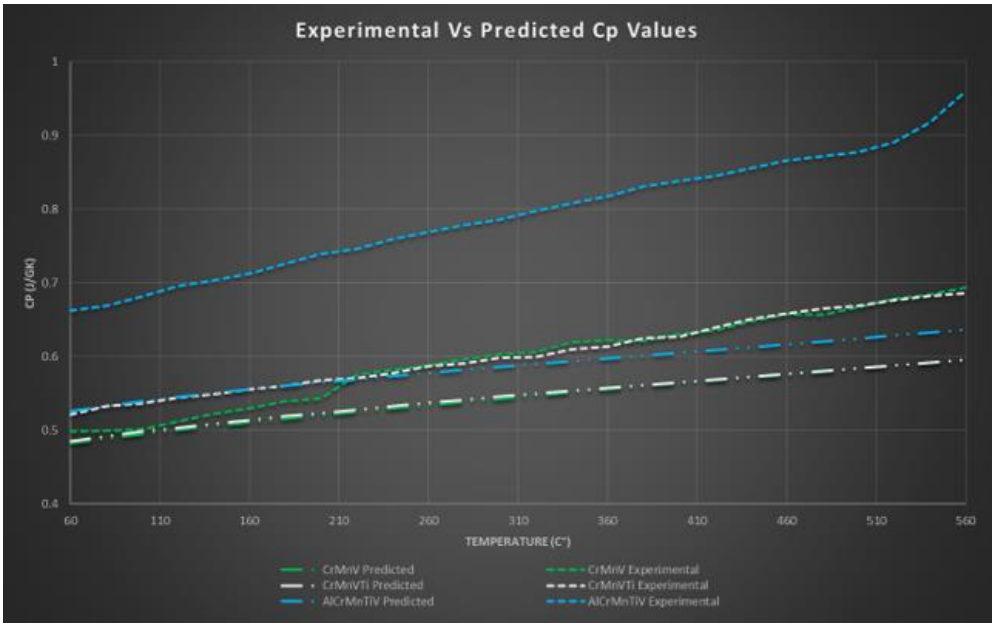

Figure 5. Experimental vs Predicted c_p values for the three tested compositions.

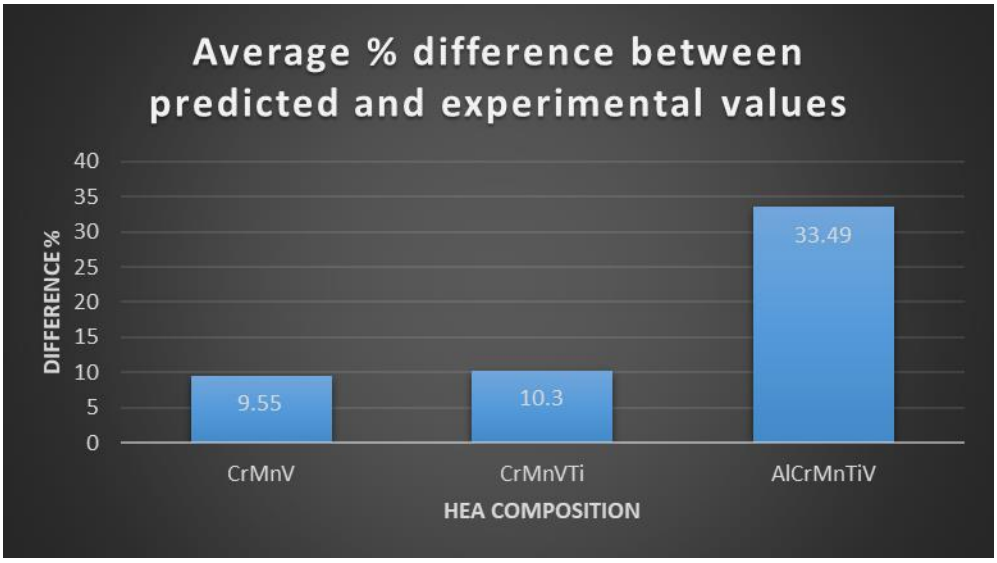

Figure 6. Average % difference between predicted and experimental values for the tested HEAs.

b. Nanoindentation

As it was mentioned near the beginning of this paper, the nanoindenter was handled by Ned Sigler so this section will be an overview of his results. After testing all the materials with different indentation depths (300 nm, 500 nm, and 1 μm) to check for the repeatability of the results, it was determined that the 1 μm indentation had the least standard deviation as can be seen in tables 2-3, and was selected for further testing, the results are based upon the data obtained from this depth using CSM.

STANDARD DEVIATION ELASTIC MODULUS

SAMPLE	300nm	500nm	1000nm
2.1	10.2000	7.1560	2.0340
2.2	6.3120	4.4070	2.1210
2.3	12.2930	5.3240	3.7650
2.4	3.2500	4.8020	1.8600
2.5	12.1100	10.3690	2.1040
2.6	2.3610	3.2830	5.4860
2.7	6.2770	4.2830	3.9480
2.8	5.0490	6.5710	2.8120
AVERAGE	7.2315	5.7744	3.0163

Table 2. Standard Deviation for Elastic modulus at different indent depths.

STANDARD DEVIATION HARDNESS			
SAMPLE	300nm	500nm	1000nm
2.1	0.4468	0.3478	0.1034
2.2	0.3371	0.2338	0.1074
2.3	0.4741	0.1967	0.1243
2.4	0.1550	0.2249	0.0654
2.5	0.5500	0.4081	0.0559
2.6	0.1012	0.1403	0.2535
2.7	0.2600	0.0947	0.1431
2.8	0.2218	0.2776	0.1150
AVERAGE	0.3183	0.2405	0.1210

Table 3. Standard Deviation for Hardness at different indent depths.

In the following chart the different HEAs compositions were plotted according to their hardness (H) and elastic modulus (E).

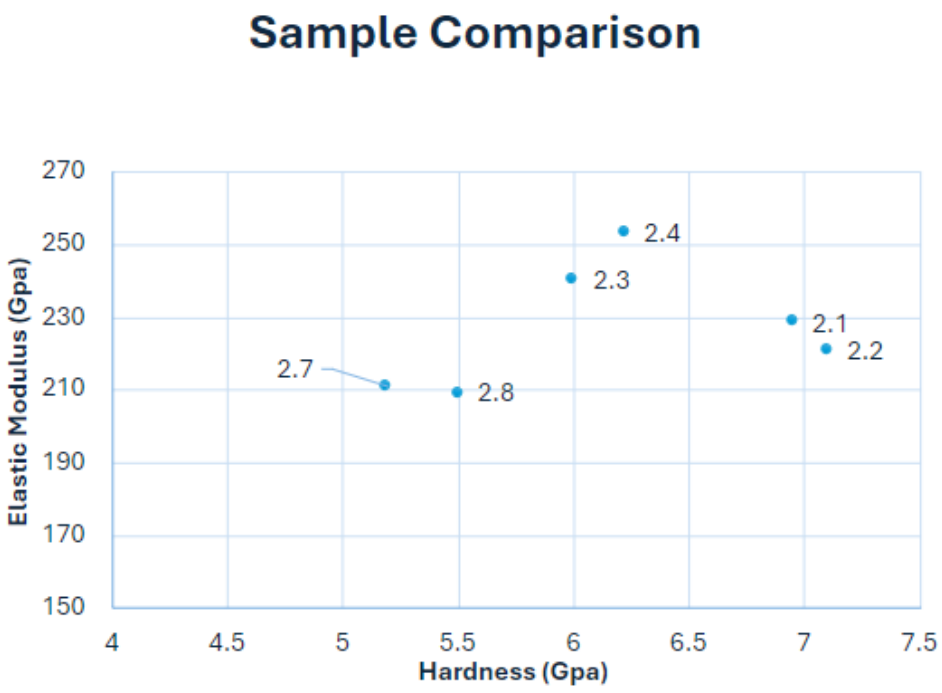

Figure 7. Elastic Modulus vs Hardness for 6 different HEAs compositions.

COMPOSITION	AVERAGE HARDNESS (GPA)	AVERAGE MODULUS (GPA)
2.1	6.95	228.57
2.2	7.10	220.67
2.3	6.00	240.24
2.4	6.22	253.06
2.7	5.19	210.944
2.8	5.5	209

Table 4. Numerical values for Hardness and Elastic Modulus.

B. Future Work

Due to the time constraints of the project only 3 of the 12 HEAs compositions were tested using the DSC, leaving 9 HEAs for future experimentation. Furthermore, the characterization after irradiation is still pending for both the DSC and the nanoindenter. The HEAs will be irradiated with 36MeV Argon and 4.5 MeV V to the estimated damage levels of the future HEA windows. The nanoindenter will test any hardening or embrittlement derived from the radiation damage while the DSC will measure any change in c_p which will help calculate the radiation-induced defects' formation energies. The field of HEAs is vast and unexplored; it offers new solutions to current challenges and might be the answer to future problems as well, more research and development of these novel materials might lead to unexpected, more exciting outcomes.

VI. AKNOWLEDGEMENTS

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