FIERF/FIA Final Report:

Exploration of New Forging Materials: High Entropy Alloys

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Executive Summary

The primary objective of this project is to explore high entropy alloys (HEAs) as a potential coating to extend the lifetime of H13 steel die heads. The four tasks for completing this objective are as follows:

1. Down-select from a wide range of HEAs to at least two to three candidate alloys that show promise given their room temperature microstructures.

Based on a literature review, two HEA compositions were selected: CrMoTaWZr and $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$.

2. Produce laboratory-scale specimens of the candidate alloys to measure the room temperature microstructure and elevated temperature tensile properties, and acquire H13 to serve as a baseline.

Queen City Forge (Rob Mayer) donated two H13 dies. Several flat discs were electro-discharged machined (EDM) from one of the dies. The H13 flat discs were then laser-clad with either CrMoTaWZr or $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA with variable power ranging from 400 W to 1100 W in increments of 100 W. Vickers hardness testing was performed and the microstructure for the CrMoTaWZr HEA and $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA were examined.

3. Subject subscale specimens to both long-term isothermal holds and thermal cycling to assess the stability of the microstructure and properties.

The CrMoTaWZr HEA was subjected to both long term isothermal holds and thermal cycling and showed both stable microstructure and mechanical properties.

4. Fabricate an H13 die with at least one HEA inset in the die to assess performance in conjunction with a forging partner (Queen City Forge Company: QCF). A die head clad with a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA at 800W was originally sent to QCF., but unfortunately the HEA layer proved to be too thin for testing. Therefore, die head was returned UNT for recladding. The recladding process involved completely removing the previous HEA layer and then applying four HEA layers, which were polished after each cladding pass. The newly cladded die head was sent to Queen City Forge for further testing.

Abstract

High entropy alloys (HEAs) represent a new class of materials that show great potential for application as new forging materials. HEAs are known for having superplastic behavior at forging conditions, phase stability at elevated temperatures, and excellent wear resistance. Using laser cladding, HEAs were coated onto sectioned samples of H13 tool steel die heads used in the hot forging process. Two different HEAs were clad onto the cut H13 tool steel samples, with variable power ranging from 400 W to 1100 W in increments of 100 W. Sample 1 and 2 had a composition of CrMoTaWZr and $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$, respectively. The samples were mechanically tested using Vickers hardness measurements and characterized using scanning electron microscopy (SEM) as well as x-ray diffraction (XRD). Samples were then subjected to thermal cycling and isothermal holds to assess phase stability of the cladded specimens. The heat-treated materials were then subjected to the same mechanical testing and characterization as the as-clad HEA samples. The results show that HEAs have phase stability at elevated temperatures as well as, high resistance to thermal cycling making them an ideal choice for a forging material.

Keywords: High Entropy Alloy, H13 Tool Steel, Hot Forging, Laser Cladding

Introduction

High entropy alloys (HEAs) are a new type of alloy system which often exhibit improved properties over traditional alloys [1]. Thus, HEAs are suited as potential replacement alloys to those currently used in the aerospace, automotive, and forging industries [2]. For example, HEAs have three advantages over current alloy systems: i) exhibit high tensile properties, ii) inhibit the formation and growth of precipitates at higher temperatures, and iii) show excellent corrosion resistance [3]. HEAs are defined by the formation of only a 1- or 2-phase simple disordered and slightly ordered solid solutions [4]. The reason for the formation of these solid solution phases is that the high configurational entropy of HEAs lowers the free energy of solid solution phases, especially at high temperatures [5]. H13 tool steel is a hot worked steel that is typically used in die heads for the hot forging process. However, after a prolonged period of use, the die heads can become damaged or fail due to wear, erosion, or thermal cycling from constant heating and thermal gradients in the hot forging process [6]. Laser cladding is a process that is often utilized in additive manufacturing to metallurgically bond a metal coating to a base layer using a laser. The laser is used to create a shallow melt pool of the base materials, with the coating material being introduced into the melt pool in the form of either powder or wire. Several studies [7-10] that have suggested using laser cladding of a metallic coating on H13 die heads as a method to extend their life cycle, as well as to reduce the cost of replacing the die heads. Jiang et al. [9, 10] used laser processing of TiC on an H13 die head using a similar method to this paper and saw an increase in erosion resistance and mechanical properties In a study using WC/Ni layering on H13 tool steel, Huang et al. [11] found that both the hardness and wear resistance increased on the clad layer, with the wear resistance increasing by as much as ten times. In the study presented here, we examine eight different laser power settings for depositing a CrMoTaWZr and a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA on the surface of a H13 steel die head to determine the best wattage for the most homogeneous adhesion of the HEA to the H13 steel die head. Scanning electron microscopy (SEM) was performed to provide microstructural insight into the cladded region, mixed region, and base metal. X-ray diffraction (XRD) was performed to identify the number of phases present in the HEA metal coating and compared with the H13 base metal. Vickers hardness testing was performed to determine if the cladded HEA produces an equivalent or higher hardness than the H13 base metal. Based on these results, we determine the optimum laser setting and composition for a CrMoTaWZr and a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA.

Objective and Tasks

The primary objective of this project is to explore HEAs as a potential coating to extend the lifetime of H13 steel die heads. The four tasks for completing this objective are as follows:

1. Down-select from a wide range of HEAs to at least two to three candidate alloys that show promise given their room temperature microstructures.

2. Produce laboratory-scale specimens of the candidate alloys to measure the room temperature microstructure and elevated temperature tensile properties, and acquire H13 to serve as a baseline.

3. Subject subscale specimens to both long-term isothermal holds and thermal cycling to assess the stability of the microstructure and properties.

4. Fabricate an H13 die with at least one HEA inset in the die to assess performance in conjunction with a forging partner (Queen City Forge).

Experimental Procedures

A used H13 steel die head donated by Queen City Forging Company was sectioned using electrical discharge machining (EDM) to form circular cross sections with a thickness of ~3 mm as shown below in Figure 1.

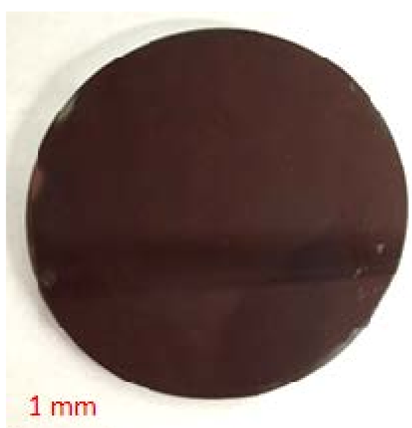


Figure 1. Cross-sectional optical image of a H13 steel sample from a die head after EDM.

These H13 steel samples were then coated with either a CrMoTaWZr or a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}$-$Ni_{24.2}Ti_{16.1}$ HEA powder mixture. The CrMoTaWZr and $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA powder mixtures was created by adding the appropriate atomic percentages of each element, which was then mixed by continuous rolling by placing the powders in a plastic container and setting it on two steel rollers for 24 hours followed by further mixing with a water-based binder and reducer to form a paint-like mixture, which was subsequently applied to the H13 steel sample. The HEA sample with powder mixture paste was then laser clad onto the H13 steel sample with variable power ranging from 400 W to 1100 W in increments of 100 W. Figures 2-3 show H13 steel samples after cladding with each section labeled based on laser power for the CrMoTaWZr and $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA, respectively. The cladding parameters are as follows: a translational speed of 100 mm/s, an overlap between laser passes of 0.2 mm, and a laser beam diameter of 0.6 mm.

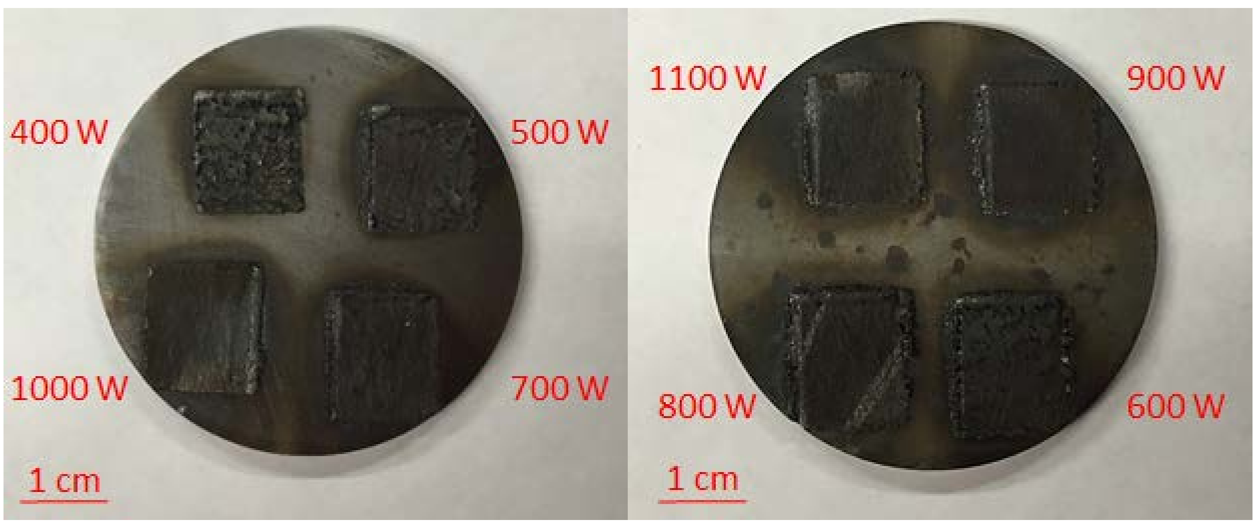


Figure 2. Optical images of H13 steel samples from a die head showing squares where CrMoTaWZr HEA has been laser clad to the surface at eight different power settings ranging from 400 W to 1100 W in increments of 100 W.

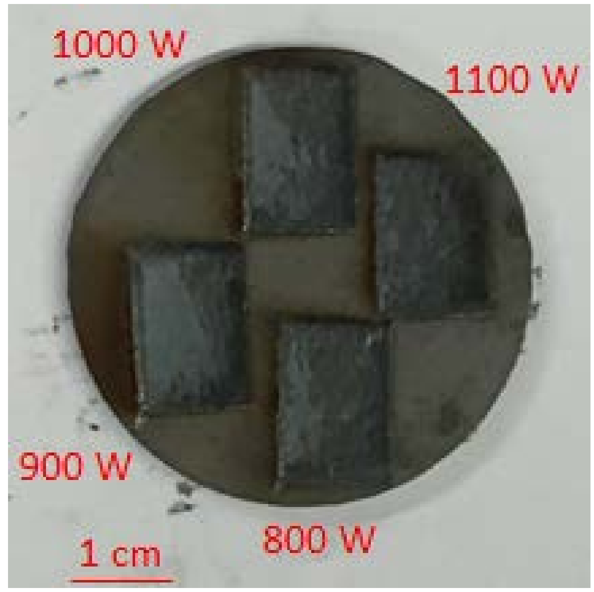


Figure 3. Optical images of H13 steel samples from a die head showing squares where $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA has been laser clad to the surface at eight different power settings ranging from 400 W to 1100 W in increments of 100 W.

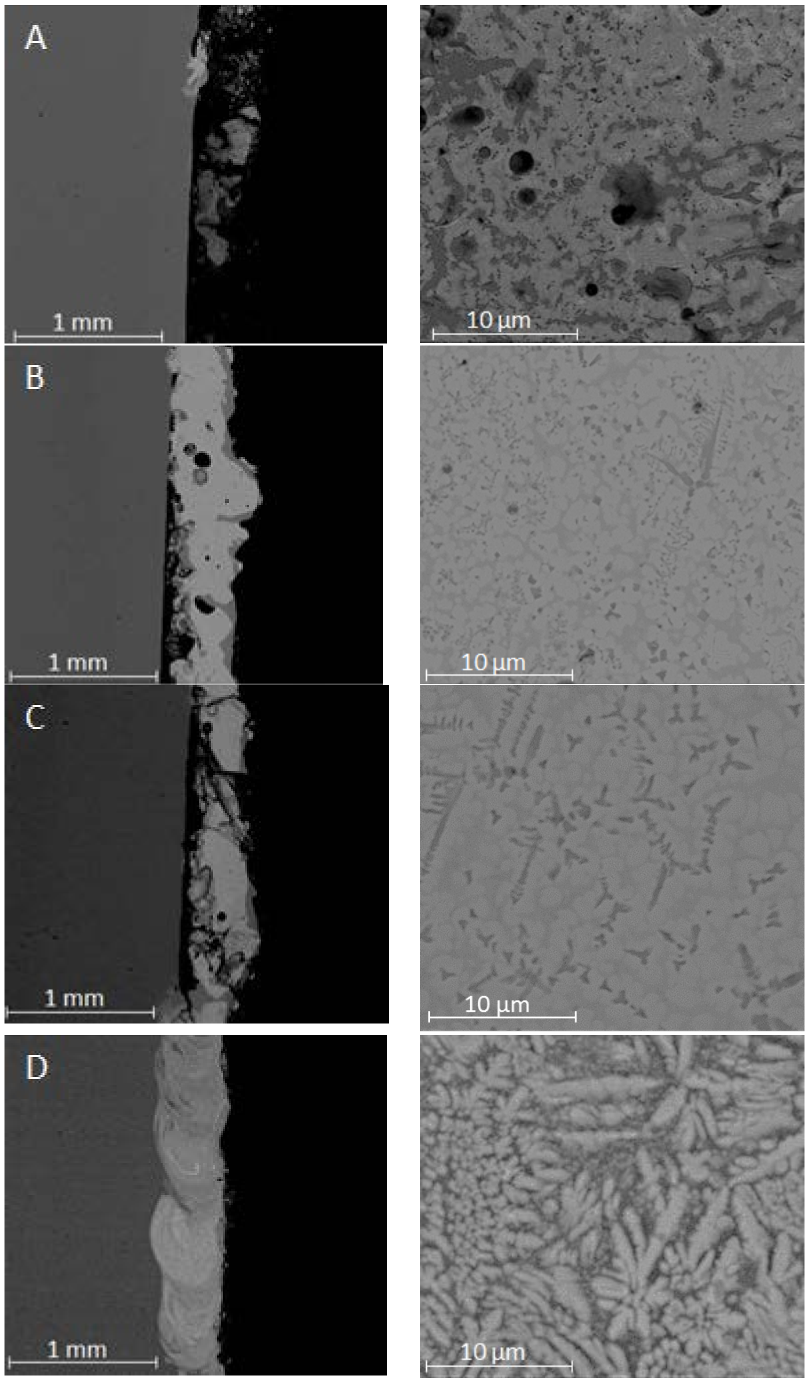
After laser cladding, the samples were sectioned, mounted, and polished in preparation for Vickers hardness testing, SEM, and XRD.

Vickers hardness testing was performed using a Shimadzu micro hardness tester, SEM was performed using a FEI quanta 200 ESEM instrument. XRD was performed using a Rigaku Ultima III X-ray diffractometer operated at 40 kV and 44 mA with a CuKα radiation source. XRD patterns were recorded from 20° to 90°, respectively, at a scanning rate of 1°/min.

SEM was performed on the HEA-coated samples for each power setting to observe the mixing and adhesion of the metallic HEA coating to the H13 steel sample. SEM also revealed the microstructure and phases present of the HEA-coated samples for each power setting. XRD was performed on selected samples to identify the number of phases present in the HEA coating and compared with the XRD pattern of the H13 base metal. Vickers hardness testing was then performed on the HEA-coated samples for each power setting using a load of 9.807 N with a dwell time of 10 seconds. For each power setting, five hardness measurements were collected to determine an average hardness value.

Results & Discussion

The SEM images in Figure 4 show a general overview of the interfacial region between the H13 base metal and the CrMoTaWZr HEA coating. The general trend is that the cohesion of the two materials increased with increasing power of the laser .



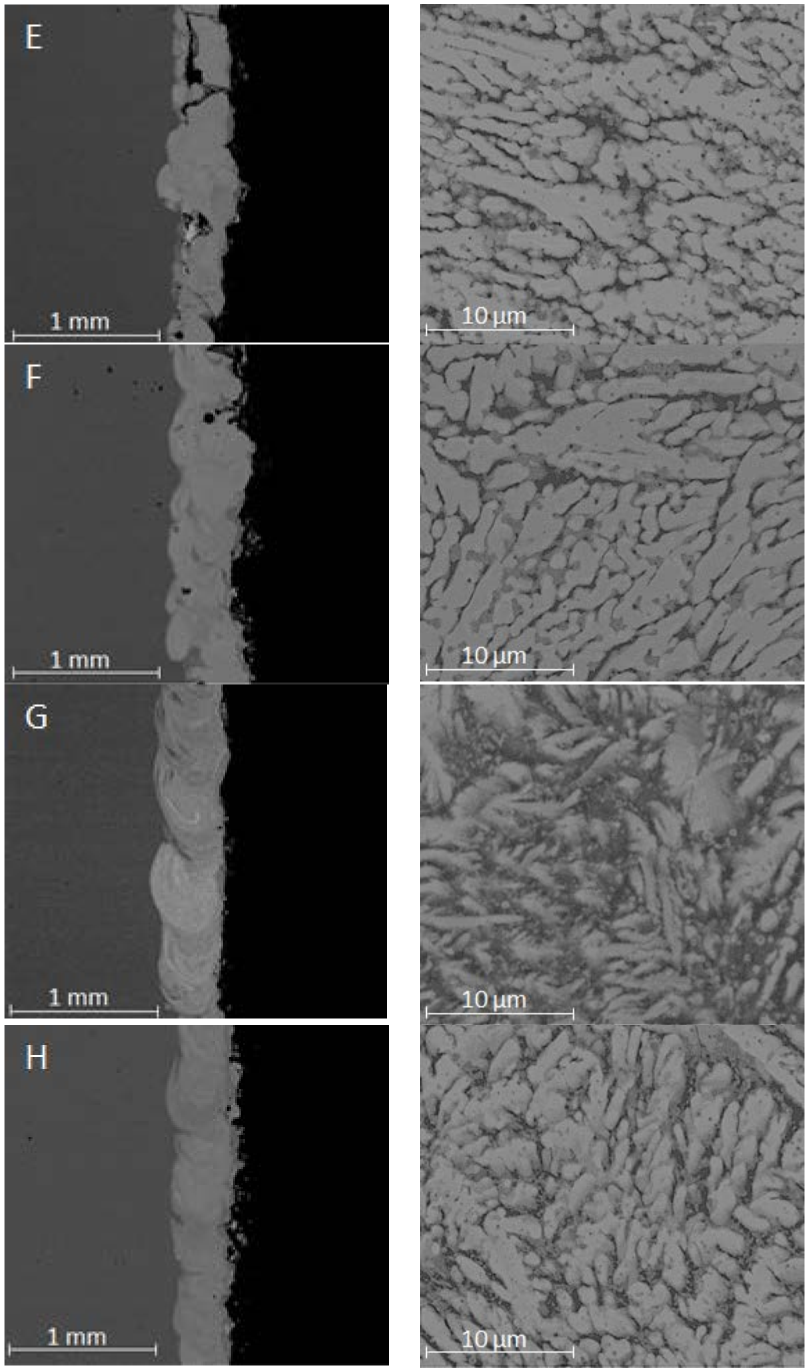


Figure 4. SEM images of the cross-section (first column) and close-up (second column) of a laser clad CrMoTaWZr HEA on a H13 die head sample corresponding to eight different power settings: A (400 W), B (500 W), C (600W), D (700 W), E (800 W), F (900 W), G (1000 W) and H (1100 W).

Very poor adhesion is observed in Figures 4a-c and e, which corresponds to the cladding powers of 400 W, 500 W, 600 W, and 800 W, respectively. The microstructure for Figure 4a is inhomogeneous, exhibits porosity, and shows at least three distinct phases. The microstructure for

Figure 4b-c shows less porosity and has at least three phases present with darker phase dendrites. The microstructure for Figures 4d-h exhibits a lighter phase dendritic structure with a two-phase inter-dendritic structure. The optimal power cladding from SEM imaging appears to be 1100 W, as the adhesion of the HEA to the H13 looks the most homogenous with the inter-dendritic structure appearing mostly single-phase.

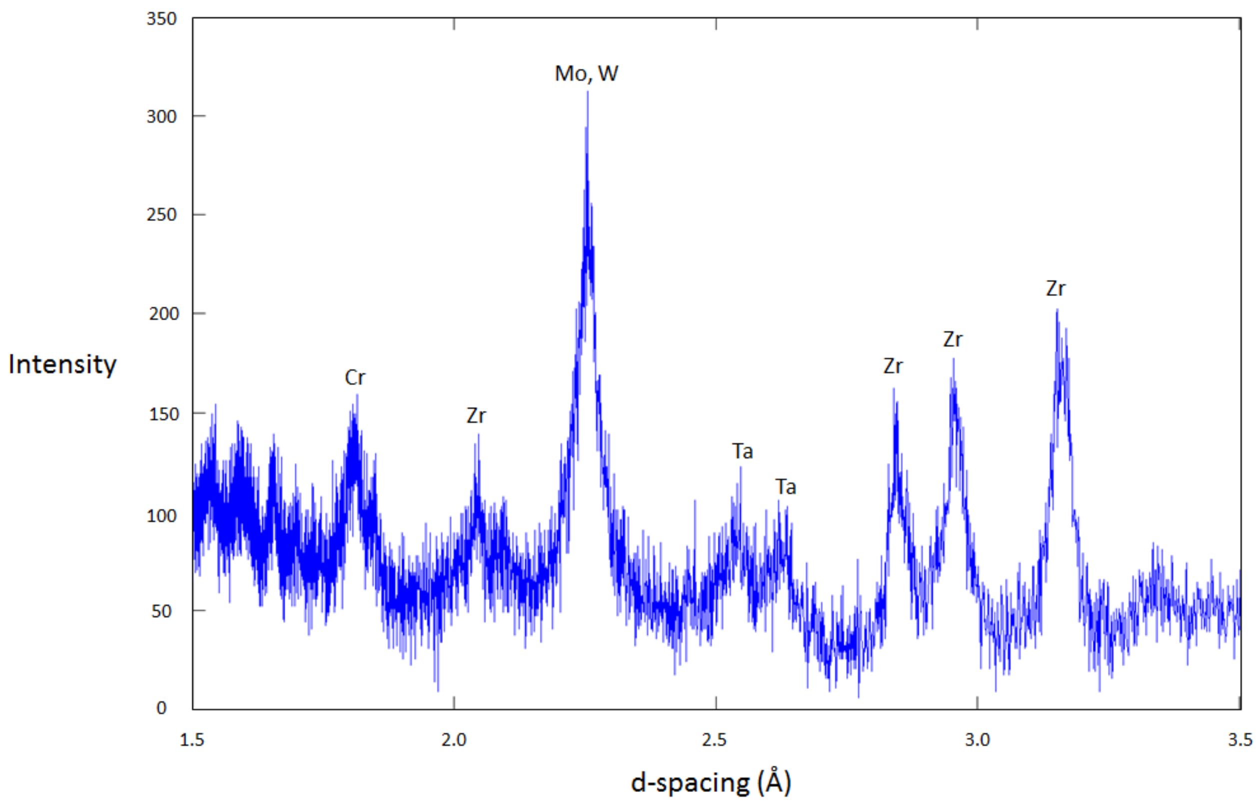


Figure 5. XRD plot of intensity versus d-spacing of the 1100 W clad CrMoTaWZr HEA on a H13 die head sample.

Figure 5 shows the XRD pattern for the 1100 W HEA cladded onto the H13 die head sample. The HEA appears to be two phase with a HCP phase and two BCC phases Comparing the diffraction peaks with a powder diffraction file (PDF) it appears that the Mo, W, and Zr peaks have all increased in d-spacing from their single component states, Cr has decreased its d-spacing from that of its single component state, and Ta is approximately the same as its single component state. The most likely cause of the peak shifting in the elements is due to the lattice distortion effect inherent in the atomic size mismatch of the corresponding substitutional elements, while the lack of peak shifting in Ta may indicate the formation of nano precipitates.

Sample	H13	400 W	500 W	600 W	700 W	800 W	900 W	1000 W	1100 W
Hardness (HV)	458.0 ± 52.4	529.4 ± 53.6	665.4 ± 58.6	755.8 ± 92.4	714.4 ± 67.2	722.4 ± 61.9	661.4 ± 58.1	414.0 ± 51.8	534.8± 38.5

Table 1. Average Vickers hardness values for the H13 steel and cladded regions of a CrMoTaWZr HEA on a H13 die head sample at eight different laser settings. Hardness values are an average value from 5 random spots within the cladded region with at least a minimum distance of 1.5 mm.

Based on the microstructure and hardness, the 1100 W clad CrMoTaWZr HEA on a H13 die head sample was selected for further hardness testing at elevated temperatures. Hot hardness was performed to assess the stability of the material at 5 elevated temperatures as shown in Table 2. The temperature ranged from 100 °C to 300 °C with a step size of 50 °C and a hold time of 30 minutes at each temperature was performed before testing to ensure equilibrium conditions.

Temperature (°C)	100	150	200	250	300
Hardness (HV)	630.4 ± 11.1	622.4 ± 18.7	583.4 ± 16.5	578.4 ± 13.4	571.6 ± 8.9

Table 2. Hardness of the 1100 W clad CrMoTaWZr HEA on a H13 die head sample at elevated temperatures (100, 150, 200, 250, and 300 °C) taken consecutively. Hardness values are an average value from 5 random spots within the cladded region with at least a minimum distance of 1.5 mm.

The hardness of the 1100 W clad CrMoTaWZr HEA decreases slightly from 100 °C to 150 °C and then drops off more sharply when the temperature was increased to 200 °C and stayed fairly constant up to 300 °C.

The SEM images in Figure 6 show a general overview of the interfacial region between the H13 base metal and the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA coating. The cohesion appears to be more favorable than in the CrMoTaWZr HEA coating; however some cracking is still observed. The microstructure for the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.}$ HEA is hard to observe due to the small cladding layer, which ranges from about 10-25 µm.

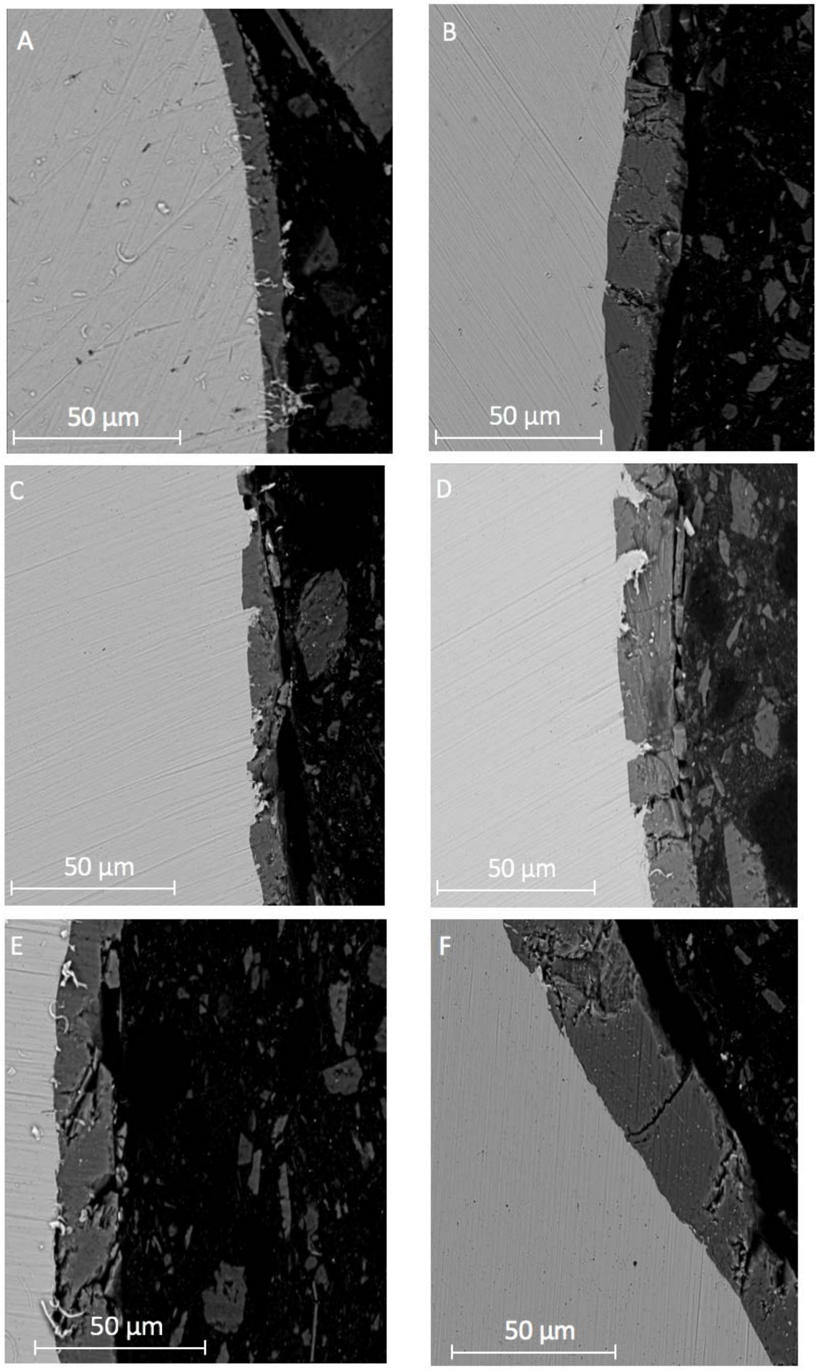


Figure 6. SEM images of the cross-section (first column) and close-up (second column) of a laser clad $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.}$ HEA on a H13 die head sample corresponding to eight different power settings: A (500 W), B (600 W), C (700W), D (800 W), E (900 W) and F (1000 W)

Very poor adhesion is observed in Figures 6e, which corresponds to the cladding powers of 900W. Cracking and porosity is observed in figures 6a-c,e, and f, which leads to an undesirable interface and could ultimately lead to early failure.

Sample	H13	400 W	500 W	600 W	700 W	800 W	900 W	1000 W	1100 W
Hardness (HV)	458.0 ± 52.4	641.0 ± 15.0	549.4 ± 21.5	623.2 ± 9.6	541.2 ± 15.9	817.4 ± 23.9	707.2 ± 12.7	726.2 ± 16.6	635.2 ± 17.3

Table 3. Average Vickers hardness values for the H13 steel and cladded regions of an $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA on a H13 die head sample at eight different laser settings. Hardness values are an average value from 5 random spots within the cladded region with at least a minimum distance of 1.5 mm.

Based on these results, the 800 W setting for the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA was selected for the cladding onto a H13 die head. On the first attempt, the H13 die head was coated only once with the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA, which proved to be too thin for testing at Queen City Forge Company, as the coating was ground off in preparation for testing. Therefore, after polishing off all remnants of the previous coating, the die head was recoated by applying the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA four times to the H13 die head with a polishing step after each layer. Based on the observed thicknesses of the samples in SEM, it was estimated that the final thickness of the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA on the H13 die head was approximately 100 μm after polishing. The $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA clad H13 die head is currently at Queen City Forging Company and will undergo testing in the future.

Conclusions

A CrMoTaWZr and an $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA coating was laser clad at eight different power settings onto a H13 tool steel and analyzed using SEM and XRD to evaluate the microstructure and the number of phases present in the HEA coating of each power setting, respectively. Vickers hardness measurements were taken at room temperature for each laser cladding condition and at elevated temperature for the laser cladded CrMoTaWZr HEA coating at 1100 W to evaluate the HEA's hardness as compared to the base metal. The hardness and microstructure were then evaluated together to observe which wattage of the laser was ideal for both high hardness as well as a homogenously mixed region between the base metal and the HEA coating. It was determined that the 700 W laser setting was the ideal candidate for the CrMoTaWZr HEA based on this experiment due to its homogenous microstructure and relatively high hardness when compared against other wattages and the base metal. For the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA, it was determined that 800 W was the ideal candidate based on its hardness and SEM results. SEM and XRD were performed to assess the microstructure and number of phases of the material. SEM and XRD revealed that the CrMoTaWZr HEA cladding at each setting exhibits at least two phases and that the higher wattage The CrMoTaWZr HEA cladding exhibits a dendritic structure with a one- or two-phase inter-dendritic structure, and XRD also indicates that there may be some

Ta nano-precipitates that form. SEM showed that the $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA cladding at each setting exhibits better cohesion that CrMoTaWZr HEA but there is still some porosity and cracking.

For testing at the Queen City Forging Company, the H13 steel die head was clad with a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA at the 800 W power setting. The first attempt resulted in a $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA layer that proved to be too thin for testing at the Queen City Forging Company, so it was subsequently returned to UNT, where the layer was completely removed from the surface. The $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA coating was reapplied four more times, and subsequently polished after each layer, to increase the thickness of the cladding to about 100 μm after the final polish. The $Al_{3.3}Co_{24.2}Cr_{16.1}Fe_{16.1}Ni_{24.2}Ti_{16.1}$ HEA clad H13 steel die head is currently at the Queen City Forging Company awaiting testing.

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