Microstructure and properties of HEA coating

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Abstract. HEA (high entropy alloy) is a new metallic alloy system which received, in the last period, an impressive role in material science field. The nomenclature of HEA is explained by the fact that the entropy suffers a major change at the mixing of the principal constituents in the alloy. This process, the changing of entropy, helps the formation of solid solution instead of chemical compounds. Thanks to their recorded symmetrical crystal structures, resistances to degradation in corrosive/oxidizing environment, high temperature phase stabilities and favourable mechanical properties, HEAs are classified as possible alternatives for high temperature resistant materials. The paper is structured in five point of interest: introduction, obtaining technologies, microstructures, properties of HEA coatings and conclusions.

1. Introduction

Thanks to their original microstructures and reportedly improved mechanical, corrosive, thermal properties, high entropy multi-component alloys are receiving significant interest in the materials engineering field. These materials are not like conventional alloys, HEA have from five to thirteen components in nearly equal proportions [1-4].

HEA are generally developed by casting/melting methods (melting furnace with electric arc or with induction). These materials are obtained by synthesis techniques such as mechanical alloying and rapid solidification processes. Also, was made investigations about HEA coatings which were obtained through various deposition methods such as sputtering and magnetron-laser.

Until now have been conducted extensive research to study multi-components HEA and were developed many systems with different chemical composition which presents outstanding properties like high hardness, improved mechanical strength, heat-resistant, high resistant to corrosion and abrasion, capabilities that gives them a remarkable potential for applications for functional/structural materials. The most important feature of high entropy alloys is their ability to maintain excellent properties in high temperatures fields.

The potential for using HEA in domains with high temperature applications is massive. The understanding of oxidation behaviours and of the successful models development that can predict its behaviour presents a major importance. Besides the conventional structural alloys, regarding the oxidation, HEA are less chemical constrained because these materials can supply higher elements concentrations to develop external protective oxide channels [5].

So far, was made several investigations to observe the oxidation behaviour on different types of HEA [6-10]. The literature about HEA indicate that like more conventional alloys, in many cases this multi-components HEA have a tendency to oxidize selectively and shows many modes for oxide growing. However, in no HEA related works is discussed the attempt to directly correlate the
formation mechanism of active oxides to available models for oxide formation which were derived from model alloys with equiatomic concentrations.

2. Kinetics and alloy preparation
For obtaining multi-components HEA, the processing methods are classified by the initial states of the alloy preparation. So, there are from: the liquid state, the solid state, and the gas state methods and from the electrochemical processes [2, 11÷17]. Figure 1 describes several fabrication processes of HEA.

![Figure 1. HEAs synthesis methods starting from different states.](image)

2.1 Liquid state techniques
The most common liquid processing technique is arc melting. The working temperature of arc melting furnace can be very high (above 3000 °C) and could be customized by electrical power adjustments. So, almost all the elements with high melting point can be mixed at liquid state temperature by these furnaces [2]. But, for elements like Mg, Zn and Al (with low melting point and with tendency of evaporating) this melting method is not reliable. For obtaining HEA the chemical composition has to be controlled with high precision and furnaces with resistance heating or induction heating are more used.

Bridgman solidification is another liquid state technique which is also named the Bridgman–Stockbarger method [18]. By this method are obtained ingots with single crystal microstructure. More than that, the Bridgman–Stockbarger method is suitable for polycrystalline materials which are heated above their melting points and then are slowly cooled where is located a grain crystal.

2.2 Solid state techniques
Solid state processing involves powder metallurgy techniques like mechanical alloying where powder particles are synthesized then are objected to cold welding, to crack operations and at the end are re-welded [19]. It was originally used to produce super alloys with base of nickel and iron strengthened with oxide-dispersion for aerospace industry applications. With this method can be synthesized a series of equilibrium and non-equilibrium alloys starting from combined elements or pre-alloyed
powders. Mechanical alloying is developed in three steps. The mixed alloy elements are ground to fine powders in a ball mill. To compress the powders is applied a process, called hot-isostatic-pressing (HIP). The last stage is heat-treatment which removes the existing internal stresses at cold compaction. By this process was produce, with success, alloys for construction of high-heat turbine blades and for some aerospace parts.

2.3 Gas state techniques
Gas state methods have also been used for obtaining of HEA and can be classified as: ion beam assisted deposition, molecular beam epitaxy, sputtering and pulse laser deposition.

2.4 Electrochemical deposition
HEA coatings can be obtained by electrochemical deposition. The method is reliable also for complex geometry substrates. More than that involves low processing temperatures and minimal energy consumption. For this technique is no need for a complex equipment and costly raw materials. Furthermore, through variation of the deposition parameters, the chemical composition, coating morphology and thickness can be easily controlled [20÷22].

3. Experimental procedures
Spherical FeCoNiCrMn HEA powder (15-53 μm) was used as raw material. In Figure 2 can be clearly observed the dendritic grain structure of the HEA powder. The nominal composition of the HEA powder is provided in Table 1. The HEA coating was deposited on a 10 mm thick A36 steel and the chemical composition was presented also in Table 1, using an in-house CS system.

![Figure 2. SEM microstructure of a single FeCoNiCrMn HEA particle.](image)

| Table 1. Nominal composition (wt%) of the FeCoNiCrMn HEA powder and of the A36 steel. |
|-------------------------------------|
| FeCoNiCrMn HEA powder               |
| Fe       | Co | Ni   | Cr   | Mn   |
| Bal.     | 20.96 | 21.01 | 18.86 | 19.08 |
| A36 steel |    |      |      |      |
| Fe       | ≤ 0.5 | ≤ 0.35 | ≤ 0.08 | ≤ 0.4 | ≤ 0.18 | ≤ 0.2 | 0.9-1.6 |
| Si       |      |      |      |      |      |      |
| Cu       |      |      |      |      |      |      |
| Mo       |      |      |      |      |      |      |
| Ni       |      |      |      |      |      |      |
| C        |      |      |      |      |      |      |
| Cr       |      |      |      |      |      |      |
| Mn       |      |      |      |      |      |      |

The CS method was developed in the ‘80s. This technology is used for deposition of coatings in solid state where the raw powder stays in its initial state all during the whole process [23, 24]. In Figure 3 [23] is explained the process.
For Cold spray technique, at temperatures below powder particles melting point, by a supersonic compressed gas jet (typically nitrogen and helium), particles (typically 10-40 µm) are speed up to very high rates. The thin oxide films, which are present on all surfaces of metals and alloys, are interrupted upon the substrate impact, where the particles suffer an extreme and rapid plastic deformation. Between the exposed metal surfaces an intimate conformal contact occurs, fact that allows bonding and rapidly building of deposited material thick layers. With this technique the deposition performance is above 90% for some cases.

In this work, Cold Spray was used to obtain HEA coating on an A36 Steel. Powder of FeCoNiCrMn HEA was used as raw material. For propulsive gas, which enhances the plastic deformation and deposition, was used Helium. Diverse investigation methods were made to characterize the microstructure and phase composition of the HEA coating.

![Figure 3. Schematic of a Cold Spray system and its working principle [23].](image)

4. Results and discussions

4.1 Microstructure and phase composition

The XRD spectra shown in Figure 4 reveals that only a simple FCC structure appear at the obtained HEA coating. The XRD spectra shows diffraction peaks at some values like: 43.68°; 50.70°; 74.62°; 90.32° and 95.86°. The lattice constant was calculated by linear extrapolation method and has the value of 3.596 Å.

Any phase changing and oxidation has been observed at the HEA coating, this fact is explicated by the processing temperature which is low. From all the thermal spray processes, the Cold Spray technique is the only one which uses low temperature at processing.

By EDS analysis the chemical composition of the HEA coating was revealed. As is shown in Figure 5a, all five alloy compounds were uniformly distributed inside the HEA coating. Also, the coating alloy elements have values for an approximated equiatomic concentration. Main elements concentrations can be observed in Table 2.

For the constituents segregation exemplification, over dendrites was made a line scanning, presented in Figure 5b, were Ni and Mn present enhanced in inter-dendrites. This fact can be explained by the difference between melting points. Since melting point of Cr is 1907 °C, for Fe is 1538 °C and for Co 1495 °C while for Mn is 1246 °C and for Ni is 1455 °C, Ni and Mn were enriched in inter-dendrites.
Figure 4. XRD pattern of CrMnFeCoNi coating.

Table 2. EDS of CrMnFeCoNi coating (at%).

|            | Cr  | Mn  | Fe  | Ni  | Co  |
|------------|-----|-----|-----|-----|-----|
| Dendrites  | 20.7| 18.8| 22.1| 16.6| 21.8|
| Interdendrites | 18.4| 24.5| 19.5| 21.0| 16.6|

Figure 5. FeCoNiCrMn coating EDS analysis of: a) distribution of alloy constituents on longitudinal axis; b) linear scan over columnar dendrites.

4.2 Tribological property

The HEA coating was subjected to a sliding test and the result in a wear rate of \((4.76\pm0.22)\times10^{-4}\) mm\(^3\)/N\(\cdot\)m is lower than of the HEA coating obtained by laser cladded and investigated by other authors [25-30]. One reason could be explained by the strengthening effect, while the Cold Spray deposition process is working, which enhances significantly the FeCoNiCrMn coating hardness.

5. Conclusions

FeCoNiCrMn HEA coating without cracks was obtained using Cold Spray deposition with mixed powders and He as a propulsive gas on a substrate of A36 steel. The HEA coating has a minimal porosity and the simple FCC structure is represented by no phase transformation. The FeCoNiCrMn
HEA coating shows a columnar dendrites structure. Also, with the A36 steel substrate forms a proper metallurgical bond. Some constituent segregations appear in the obtained coating between inter-dendrites and dendrites, fact that could be explained by the lower melting point of Ni and Mn which helps the growth of elements in inter-dendrites.

Based on information about laser cladded HEA coatings, the studies about tribological investigations shows that the HEA coating has a lower wear rate.

This results demonstrates that solid-state technology, Cold Spray deposition, is promising for the obtaining of thick, dense and with crack free HEA coating. For in-depth understanding of the HEA coating properties more investigations are highly encouraged.

6. References
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