A FRESH PERSPECTIVE ON MEDIUM ENTROPY ALLOYS APPLICATIONS AS COATING AND COATING SUBSTRATE

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Abstract. In order to evolve as a society we need increasingly efficient technologies and implicitly materials with great performance that promote safety and sustainability. The discovery of high entropy alloys was received with much enthusiasm due to the possibility of designing new materials with improved properties, that could be used in applications that require extreme conditions or a very specific combination of properties. As the research in this area is continuously increasing and the results are very promising, this review focuses on the most recent investigations on medium entropy alloys (MEAs) applications, highlighting their properties, but taking into consideration other factors, such as economic and environmental factors. Additionally, considering the high cost associated with MEAs fabrication, MEA coatings are also explored, as they are nowadays regarded as a more convenient procedure to obtain the required properties for various substrate materials.

Keywords: medium entropy alloys, MEA applications, MEA structural material, MEA coating, MEA biomaterial.

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1. Introduction

Around twenty years ago, in 2004 [1,2], a new class of alloys was introduced, marked by an increase in the number of alloying elements. It was hypothesized that when the entropic contribution to the total free energy overcomes the enthalpic value, the formation of intermetallic phases is suppressed. According to thermodynamics, for an alloy to form a solid solution, the Gibbs free energy of the system should be at a minimum value and when the Gibbs free energy approaches zero, this high-entropy effect stabilizes the system [3], thus reducing the number of phases. Based on this idea, high entropy alloys (HEA) were initially defined as alloys formed with at least five principal elements in equiatomic or near-equiatomic proportions that form single-phase solid solutions and the medium entropy alloys (MEA) as their counterparts with lower entropy. However, the

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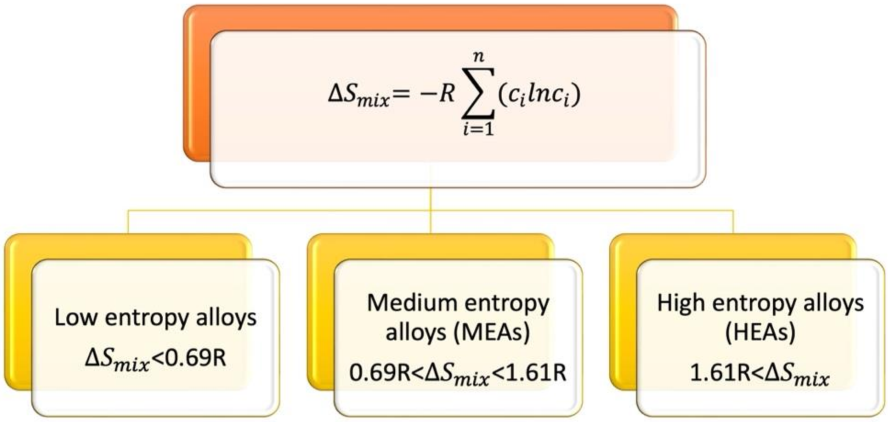
terms have become generic and nowadays many alloys receive this label although they don’t meet those initial requirements. Some other terms were introduced, such as multiple principal element alloys (MPEA) and complex concentrated alloys (CCA), but they are not that popular, mainly because classifying the alloys based on their entropy is simple [4,5]. Based on the entropy of mixing, the categories are presented in figure 1.



R - the gas constant, 8.314 $JK^{-1}mol^{-1}$
n - the number of component elements
c_i - atomic fraction of the corresponding element

Later, the strategy was to introduce a rarer element, with special properties, in a low proportion, typically less than 5%, besides the principal constituents. Due to the random arrangement of elements, the local disorder is leading to outstanding properties such as corrosion, abrasion, and oxidation resistance [5–7]. In addition, due to the variety of elements in such alloys, mechanical and thermal properties, such as high strength/hardness, high toughness, and ultra-high fracture toughness at very high and cryogenic temperatures may manifest [8,9]. Special corrosion properties in bioliquids and superior biocompatibility as a result of well-selected elements in specific ratios have led to the elaboration of bio-HEA and bio-MEA [10–12] representing alloys that are able to function as biomaterials. Initially, a great part of them was based on well-known Ti biomaterials alloys [13–15], but after a while, new HEAs and MEAs were elaborated and tested in vitro and in vivo [16,17].

Since the number of possible alloys seems endless, we need faster, more efficient ways to asses and predict both phase formation and mechanical properties, other than the traditional trial and error method, which is very time-consuming and inefficient. Although high and medium entropy alloys were initially regarded as single-phase solid solutions with equiatomic composition, nowadays, alloys with non-equiatomic compositions, as well as multiphase alloys and intermetallic compounds are being increasingly investigated. These alloys could exhibit superior high-temperature strength and thermal stability [18–21].

A better understanding of microstructural features and deformation mechanisms is crucial to engineering new alloys with suitable properties for future applications that will require better performance and improved resistance in more extreme environments [22–24]. Atomistic methods, such as density functional theory (DFT) and molecular dynamics (MD) are being used to investigate the mechanical properties. The CALPHAD method is used to investigate the phase diagrams and the crystal plasticity finite element method (GPFEM) to predict the microstructural behaviour using experimentally determined mechanical properties [25–28].

Usually, bulk new HEAs and MEAs [29] have higher costs than traditional alloys, containing rare expensive elements, and thus their use on a larger scale could be restricted. Based on their lower costs, HEA and MEA coatings and films have been developed in the last few years for larger industrial applications [30,31]. Such coatings present superior merits compared with traditional coatings, such as high strength and hardness, better wear and corrosion resistance, thermal stability, irradiation resistance, high toughness for special-temperature applications, and so forth. The new advanced technologies seem to be very suitable for the fabrication of such alloys. Therefore, several researchers have worked on the development of coating-based technologies [32–35].

2. MEAs as structural materials

An important aspect of the materials used in structural applications is represented by the resistance of metallic alloys to hydrogen embrittlement. Both high entropy alloys, such as FeNiCoCrMn and medium entropy alloys, such as CoCrV and CoCrNi have a high resistance to embrittlement, but at relatively low hydrogen concentrations. Micro-alloying elements could be an appropriate method to improve their resistance, as shown on the CoCrNi alloy, which was doped with Mo, thus inducing a change in the deformation mechanism by inhibiting the access of hydrogen to the grain boundary [36]. Another MEA with very good resistance to hydrogen embrittlement is the CoNiV alloy, which can also be further improved through micro-alloying with Al [37].

Regarding the corrosion resistance, when the CoCrNi MEA and the CrMnFeCoNi HEA were analyzed comparatively in 0.1 M H_2SO_4 and 0.1 M NaCl, the MEA showed superior corrosion resistance [38]. Due to this behavior, the alloy could be used in ocean engineering structures as it was also shown that it exhibits superior passivity compared with 316L and Inconel 600 [39]. The CoCrNi alloy was also tested under an ultrahigh explosive loading rate to evaluate its suitability as a shaped charge liner, which could be used in many industries, such as oil, mining and construction. Under the extremely high strain rate and large plastic deformation, the grain size was reduced from 16 μm to under 5 μm, thus inducing dynamic recrystallization [40].

Furthermore, these alloys can also be reinforced with particles such as Al_2O_3, SiC and TiC to significantly increase the yield strength, compressive strength and resistance to corrosion [41]. Other methods can also be used to improve the properties of such alloy, such as introducing lattice defects through cold rolling and annealing [42] or introducing nano-scale features through oxide dispersion strengthening [43].

Micro-alloying has also been used to increase the yield strength of FCC structured MEAs and HEAs. The addition of Al in the FeCoNiCrMn alloy led to an increase in yield strength from 200 MPa to 500 MPa. Similarly, using the CALPHAD method, Tian et al. have studied the phase diagrams of VCoNi MEA alloyed with Al and developed several alloys, finding that for the Al_7(VCoNi) alloy the yield strength can reach 1634 MPa, compared to 787 MPa in the VCoNi alloy [44].

An even more impressive enhancement was seen for the NiCoCr MEA in which, after doping with Al and Ti, the yield strength increases from 147 MPa to 792 MPa and the ultimate tensile strength from 447 MPa to 1004 MPa [45].

Another challenge faced by materials in their service life is to resist to microbiologically influenced corrosion. In the same way microorganisms attach to teeth and form a biofilm by producing extracellular polymeric substances [46], they attach to metals causing bio-degradation of the substrate through the metabolites produced. Many materials, such as steels, Cu and Ti alloys are susceptible to this type of corrosion. One study conducted on MEA TiZrNb using *Deulfovibrio desulfuricans* showed that in the absence of an organic carbon source, the microorganisms can use Ti as an electron donor, causing selective dissolution of Ti in the tested MEA [47].

Some technological advancements were hindered by the lack of suitable structural materials that could perform efficiently in specific harsh conditions, but the development of multi principal complex alloys might help in maintaining the fast pace of technological development. One such alloy was developed, namely the MoCrNiCo MEA. This alloy shows ultra-high corrosion resistance in acidic media, which is due to the formation of a medium entropy oxide film with a very low amount of defects [48].

With the fast-paced development of technology in the aerospace industry and gas transporting, better-performing alloys at cryogenic temperatures are also needed. The traditional CoCrFeMnNi high entropy alloy showed an impressive high-yielding strength of 1692 MPa at 77 K. However, due to the increased cost of Co, Co-free alloys, such as $Fe_{50}Mn_{20}Cr_{20}Ni_{10}$ MEA were also investigated, showing a yield strength of 605 MPa at 77 K [49].

Lightweight materials are also very desired in the field of aerospace and in the automobile industry to improve energy efficiency and multiple MEAs and HEAs, such as AlMgLi, TiVZrNb, TiVCrAl, AlBeFeSiTi and AlNbTiV were found to have densities between 2.2 g/cm^3 and 6.5 g/cm^3 and promising mechanical properties [50,51]. Another lightweight alloy, Al-Ti-Cr-Mn-V, with great compression strength (1940 MPa) and ductility (30%), was developed by Liao et al., who identified a dual phase comprised of BCC and FCC with approx.. 4,5 g/cm^3. Other MEAs, based on vanadium, could be used in advanced energy applications, such as hydrogen storage [52]. It is to mention the investigation on $V_{47}Fe_{11}Ti_{30}Cr_{10}RE_2$ (RE = La, Ce, Y, Sc), which shows a significantly faster hydrogen uptake compared to other vanadium-based alloys [53].

3. Coatings with MEA

MEA coatings with good metallurgical bonding are also an option to increase the performance of structural material, while also being more cost-efficient. For example, a coating of CoNiTi on a Ti substrate has increased the hardness from 114 HV to 571 HV [54] and on an Mg substrate the deposition of $TiB/Ti_{50}Zr_{25}Al_{15}Cu_{10}$ refined with LaB_6 has reduced the wear rate by 77%, while increasing the resistance to corrosion and the micro-hardness from 62 HV to 679 HV [7].

As researchers observed that single-phase BCC complex concentrated alloys tend to have high strength, but low plasticity and single-phase FCC complex concentrated alloys possess great plasticity, but have low strength, the development of eutectic MEAs and HEAs has started to get momentum [55–57].

A similar approach had Meghal et al., who combined AlCoCrFeNi BCC/B2 as a hard phase and CoCrFeNi FCC to create a coating on 316 L substrate. The coating thus created exhibited superior wear resistance even at elevated temperatures and higher hardness that the individual phases [31].

Other materials that could benefit from MEAs coating are the materials used in nuclear reactors, such as the zirconium alloys used as cladding material. Xin et al have created on N36 Zr alloy substrate a coating of AlNbTiZr. It was shown that the addition of Al initially decreased the hardness and the elasticity, but both increased after increasing the Al content. Additionally, the corrosion resistance was significantly improved [58]. Furthermore, the alloy might have better irradiation resistance [59]. The properties of other MEA coatings are presented in Table 1 in comparison to those of the uncoated substrate. It is worth mentioning that choosing an appropriate surface treatment prior to the coating deposition could improve the film adhesion and thus the properties of the coated material [17,60].

Table 1. MEAs coatings

Coating	Substrate	Preparation method	Substrate properties	Coated substrate properties	Ref.
$Cu_{55}Al_{20}Ni_{12}Ti_8Si_5$	AISI 1020 steel	High-velocity oxygen-fuel	I_{corr} - 48.4 μA·cm^{-2} (3.5% NaCl) Microhardness – 188 HV	I_{corr} - 6.5 μA·cm^{-2} (3.5% NaCl) Microhardness – 470 HV	[61]
NbTaTiZr	Zr sheet	Pulsed laser cladding	Wear rate – 4.6 x 10^{-4} mm^3·N^{-1}·m^{-1} Microhardness – 196 HV	Wear rate – 2.8 x 10^{-5} mm^3·N^{-1}·m^{-1} Microhardness – 430 HV	[62]
CrNiTi	Ti sheet	Pulsed laser cladding	Wear rate – 5.8 x 10^{-4} mm^3·N^{-1}·m^{-1} Microhardness – 119 HV	Wear rate – 4.6 x 10^{-5} mm^3·N^{-1}·m^{-1} Microhardness – 940 HV	[63]
CoCrNiTi	Ti sheet	Pulsed laser cladding	Wear rate – 5.4 x 10^{-4} mm^3·N^{-1}·m^{-1} Microhardness – 114 HV	Wear rate – 1.7 x 10^{-5} mm^3·N^{-1}·m^{-1} Microhardness – 762 HV	[64]
CrFeNiTi	Ti sheet	Pulsed laser cladding	Wear rate – 5.4 x 10^{-4} mm^3·N^{-1}·m^{-1} Microhardness – 114 HV	Wear rate – 2.8 x 10^{-5} mm^3·N^{-1}·m^{-1} Microhardness – 820 HV	[64]
CrCoNi/Ti	AISI M2 steel	DC magnetron sputtering	-	Residual stress – 1101.4 MPa Hardness – 9.2 GPa Elastic modulus – 230 GPa	[65]
CrCoNi	A36 steel plate	Pulsed laser cladding	I_{corr} - 1.14 μA·cm^{-2} (3.5% NaCl) I_{corr} - 1803.7 μA·cm^{-2} (0.5M H_2SO_4)	I_{corr} – 0.99 μA·cm^{-2} (3.5% NaCl) I_{corr} - 12.9 μA·cm^{-2} (0.5M H_2SO_4)	[66]

4. MEAs as biomaterials

The development of HEAs and MEAs has also gained interest in the world of biomaterials. Although not an extreme environment, the alloys used as biomaterials need a specific set of properties, such as high strength, superior corrosion resistance and Young's modulus close to that of the human bone to avoid "stress shielding" [67]. One such alloy, based on the traditional TiZr alloy which has outstanding biocompatibility [68,69] is the $Ti_{45}Zr_{37}Nb_{16}Fe_1Mo_1$, having a tensile strength over 700 MPa and Young's modulus below 63 GPa [70]. The $Zr_{50}Ti_{35}Nb_{15}$ MEA also shows a promising combination of mechanical properties, having an Young's modulus of 62 GPa, an yield strength of 657 MPa and great corrosion resistance [71].

Other Ti-based MEAs such as TiVMo, TiZrMo, TiZrNbTa TiZrNbMo and TiVZrMo were also recently investigated [72–74]. Compared to the traditional and highly researched Ti-6Al-4V alloy, the newly developed $Ti_{40}Zr_{20}Hf_{10}Nb_{20}Ta_{10}$ shows similar strength and ductility. However, compared with cp-Ti in terms of biocompatibility, it shows a significantly better response in the interaction with human gingival fibroblasts [75].

The TiZrHfNbTa and its three sub-variants, TiZrNbTa, TiZrHfTa and TiZrHfNb are of particular interest due to their combination of yield stress and compression ductility, but also biocompatibility, making them great candidates for multiple applications [76,77].

These alloys can also prove strong and ductile, such as the $Ti_{45}Nb_{25}Zr_{25}Ta_5$, which has a tensile strength of over 900 MPa, but a tensile strain to fracture greater than 15% [78]. The ternary Ti-Nb-Zr MEA was also evaluated for its potential medical applications, showing a good combination of mechanical properties, having an elastic modulus of 72 GPa and a yield strength of up to 1060 MPa, while also displaying corrosion resistance [79]. It was found that depending on the elemental composition and if heat treatments are applied, the yield strength can vary from 694 MPa to 831 MPa and the Young's modulus from 74 GPa to 104 GPa. It was observed that these alloys also exhibit superior resistance to corrosion in PBS compared with Ti-6Al-V and cp-Ti. Moreover, cell adhesion also proved comparable to that of cp-Ti, thus recommending these alloys as biomaterials [80].

Other possible future bio-MEAs are those composed of TiZrNbTa, having outstanding mechanical properties, namely an ultra-high bending strength of 1102 MPa and an ultra-low Young's modulus of 49 GPa. Furthermore, they display superior resistance to corrosion probably due to the rich oxide layer [81].

5. Conclusions

MEAs seem to be more sustainable materials that could be elaborated via greener technologies. One of the biggest challenges that mankind is facing right now is reducing the use of fossil fuels and thus the level of CO_2 emission and finding alternatives with zero-carbon energy sources. A highly researched idea is the use of hydrogen, due to its high caloric value and environmental friendliness and therefore of storage materials, where, as was mentioned above, MEAs have a place.

More environmentally friendly alternatives to conventional applications are also desired. One such example is the use of magnetic refrigeration as compared to vapor compression refrigeration. For this, materials with high magnetic entropy change and outstanding magnetic refrigerant capacity are needed. Additionally, the possibility of microalloying HEAs and MEAs with small amounts of rare elements is a great strategy in designing materials with specific properties

However, we can conclude that MEAs are part of the materials of the future and the future has to be a sustainable one.

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