Effect of Valence Electron Concentration in High Entropy Shape Memory Alloys/ Review

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Abstract: The shape memory effect is the ability to recover the shape after deformation on heating or stress. High entropy alloys were found by mixing an equiatomic number of complex components; nowadays, a new generation of un equiatomic components are produced. Properties like high strength and slow diffusion are properties of HEAs, and these properties are perfect circumstances for the appearance of the martensitic diffusionless transformation. Combining these two properties of alloy in a new class called high entropy shape memory alloys (HESMAs) opens a door for many new applications in terms of shape recovery and deformation resistance. This paper reviews the combination of (HE and SMA) properties in an alloy, VEC was found for all the different compositions of HESMAs, and the focus is to see how VEC affects this new family of alloys. Configurational entropy of the compositions was all calculated, and the values are mostly greater than 1.5R.

Keywords: VEC, HESMA, High Entropy Alloys (HEAs), Shape Memory Alloy (SMA), Shape Memory Effect (SME)

1. Introduction

In 1932, Arne Olander discovered the effect of shape memory, but the ‘‘shape memory’’ term was first labelled by Vernon in 1941 while working on polymeric dental material. In 1962 the importance of shape memory materials (SMMs) was documented by William Buehler and Frederick Wang when they were working on (NiTi) alloy, and they found the shape memory effect (SME) this alloy (Buehler, Gilfrich, & Wiley, 1963), later this was known as nitinol (NOL). Since this discovery, applications of SMAs have been increasing in numerous commercial fields. SMAs such as Cu-based binary and ternary systems (Cu–Zn, Cu–Al, Cu–Zn–Al, Cu–Al–Ni, Cu–Al–Mn), Ni-Ti, and high-temperature shape memory alloys (HTSMA) are usually used in the automotive, aerospace, and medical fields (Baiz, Canbay, & Ozkul, 2018). Furthermore, intelligent materials attract attention in today’s technological advances (Canbay, Gudeloglu, & Genc, 2015).

In the early 2000s, the entropy principle started to be investigated and then a new kind of alloying was produced. With increasing the number of elements including at least five different materials or more in equiatomic ratios between 5 and 35 percentage of atomic ratios, a new generation of HEA can be

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prepared (Jien Wei, 2006; Koželj et al., 2014; Otto, Yang, Bei, & George, 2013; Tsai & Yeh, 2014; Yeh, 2013; Yeh et al., 2004; Zhang et al., 2014).

Then in 2004, these new alloys were named High entropy alloys (HEAs) by Yeh et al. (Murty, Yeh, Ranganathan, & Bhattacharjee, 2019; Tsai & Yeh, 2014; Yeh et al., 2004; Zhang et al., 2014). Also, the second generation of HEAs is the newest alloys that consist of non-equimolar components (Zhang, 2019b). Besides, HEAs should define based on entropy which states that these alloys have an entropy of configuration higher than 1.5 R (Zhang, 2019a).

One of the primary difficulties in NiTi-based shape memory alloys is their limitation in high-temperature applications. Researchers have been trying to overcome this issue by adding alloying elements or even applying the concept of HEAs to improve the temperature of transformation (Chang, Lin, & Tsai, 2019). High entropy shape memory alloys originated from NiTi binary SMAs (Firstov, Timoshevski, et al., 2015). HESMAs enable research into SMAs and high entropy or complicated alloys to be connected. The latter currently attracts considerable scientific attention (Yeh et al., 2004). From a fundamental perspective, HESMAs are particularly interesting. Researchers can explore how martensitic transformations are affected by chemical complexity. The dependency of transformation behavior and memory forming properties on alloy chemistry and microstructure for NiTi SMAs are now relatively well understood (David Piorunek, Frenzel, Jöns, Somsen, & Eggeler, 2020). Numerous investigations have shown that Zr, Nb and Hf are more soluble with and similar to Ti electron configuration in the NiTi-based. At the same time, Co and Cu are more soluble with and identical to Ni electron configuration in the NiTi-based (Ma, Karaman, & Noebe, 2010). In 2015, the first work, which was deals with both High entropy alloys (HEAs) and Shapes memory alloys SMAs together were done by Firstov et al. (Firstov, Kosorukova, Koval, & Odnosum, 2015) that termed High entropy Shape memory alloys (HESMAs). They improved martensitic transformations in $Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{25}Cu_{25}$ alloy with DSC, XRD and shaped memory behavior test to show the shape memory effect (SME). Thus, this gives a chance to benefit several new and unique properties to these new HEAs with SMEs. Firstov et al. then suggested that HESMA solve plastic deformation in high-temperature Shape memory alloy HTSMA (Firstov, Kosorukova, Koval, & Verhovlyuk, 2015). Furthermore, to better understand performance properties and potential HESMA, an alloy $(TiZrHf)_{50}Ni_{25}Co_{10}Cu_{15}$ homogenized HESMA was developed by Chen et al. (Chen & Chen, 2019). They indicate that $(TiZrHf)_{50}Ni_{25}Co_{10}Cu_{15}$ HESMA displays shape memory compatibility similar to traditional $Ni_{1/2}Ti_{1/2}$ alloys but can handle the higher bending stress of 650 MPa, resulting in a higher working performance density.

VEC have a significant role in phase formations. For example, an alloy ductility improved by high VEC, which forms the FCC phase, while alloy's strength improved with low VEC, leading to BCC phase (Chen et al., 2018). The electron's concentration fundamentally has two definitions: the average number of itinerant electrons per atom (e/a) and valence electron concentration (VEC) which is the total number of electrons including d-electrons in the valence band (Mizutani, 2012). Here, VEC differs from e/a, the average number of moving electrons per atom in which VEC counts the total electrons, including the d-electrons housed in the value band (Massalski, 2010). This study focused on VEC role in determining phases and how martensitic transformations occur in HESMAs. It gives an overview of the VEC effect on phase stabilities in HESMAs, for that, it reviews the most works are done in that area in the last six years, which started with $Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{25}Cu_{25}$ alloy were done by Firstov et al. (Firstov, Kosorukova, Koval, & Odnosum, 2015). Moreover, in this article HESMA studies were listed, VEC and ΔS have been calculated.

2. VEC in HESMA

Electrons play a significant role inside materials in conducting energy. During the phase transition, the martensitic phase of alloys by heating/cooling (changing in vibrational entropy) is first-order and diffusionless. The entropy change ΔS of the average periodic lattice formation closely depends on the electron concentration (e/a) (Wang & Ma, 2004). SMAs endure martensitic transformation, and they obey the Hume Rothery Rules, which states that the behavior of alloys can be controlled through the average number of valence electrons, the atomic size factors, and electronegativity. However, the electron means free path reduced by impurities in impure solid materials at high temperature because of the collisions that contribute conduction electrons too small and negligible to the entropy of SMAs, affecting several physical properties of the alloy. In a study by E. Obrador et al. in 1997, a Cu-Al-Mn SMA at a particular e/a rate of 1.46 value showed the transformation from 18R to 2H martensitic phase. This value is very close to the eutectoid point's e/a rate and agrees to the composition for which the BCC phase is stable at a high-temperature range, and dependence on this particular e/a value in martensitic transformation gives shape memory effect to alloy (Canbay, Aziz, Özkul, & Dere, 2020). In general, the 1.45-1.49 e/a value is the range that SME can be seen (Furuya, 1996).

Phase stabilities research is critical for the novel design HEAs. In the last decade, significant efforts have been made in this field (Yang, Lu, Xing, Zhang, & Zhong, 2020). Some scientific criteria's have been used, such as mixing entropy ΔS_{mix} (Chen et al., 2018; Yeh et al., 2004; Zhang et al., 2014), the enthalpy of mixing ΔH_{mix} (Takeuchi & Inoue, 2005), melting points Tm and differences in atomic size ∂ (Yang & Zhang, 2012), the ratio of ΔS_{mix} to ΔH_{mix}, which is symbolled as Ω (Yang & Zhang, 2012) and the valence electron concentration (VEC) (Chen et al., 2018; Guo, Lu, & Liu, 2011; Sheng & Liu, 2011). Mizutani stressed that instead of e/a, the VEC parameter should be employed to consider the d-electron contribution in realistic electronic structure computations (Mizutani, 2012).

Guo et al. (2011) proposed BCC and FCC structured solid solutions of HEAs using the VEC. Based on the Hume–Rothery rule (Mizutani, 2010), VEC becomes a key parameter lacking atomic size. This important variable influences the crystallinity of a solid-solution phase (Guo et al., 2011; Ye, Wang, Lu, Liu, & Yang, 2016). If the atomic valence between elements is similar, the component's solid solubility is more significant, and the reliable solution in the alloy is nearly constant (Zhang, 2019a). While the VEC varies or reaches a specific limit, the connection between the elements is disordered, so the solid solution's stability is reduced (Zhang, 2019a). For HEAs, the VEC is defined as in equation 1 below (Guo et al., 2011):

$$VEC = \sum_{i=1}^{n} c_i \, (VEC)_i \qquad [1]$$

$(VEC)_i$ is VEC for each element and the percentage of atoms is c_i (Chen et al., 2018; Guo et al., 2011). Regarding Guo et al. (Guo et al., 2011), VEC determines the phase stabilities, BCC or FCC solid solutions in HEAs. So, for example, wherever the value of VEC reaches eight or more (VEC ≥ 8), then the single FCC phase would detect. Still, when this number went down to range 6.87 ≤ VEC ≤ 8, thus both FCC and BCC phases were co-existed and also in low values for VEC (VEC < 6.87), the single BCC phase could notice (Chen et al., 2018; Guo et al., 2011; Yang, Zhang, & Liaw, 2012).

Although, this critical rule faces some limitations that barriers applications for predictions in HEA phases (Yang et al., 2020). Additionally, the VEC may describe which solid solution structure in HEAs is suitable to produce and could not be used as a particular tool to form phases in HEAs (Zhang, 2019a). Recently, Zhong et al. (Yang et al., 2020) used the high-temperature CALPHAD (HT-CALPHAD)

method in the system containing Al, Co, Cr, Fe, Ni, reviewed the experimental VEC rule. Furthermore, their investigations gave that above 90 per cent of compositions are detected to have BCC phase in the range of 5.7 ≤ VEC ≤ 7.2, and the showed %100 FCC phase where VEC is equal or greater than 8.4 (Yang et al., 2020).

Most recently, after the concept mentioned above of HEA, Ti16.667Zr16.667Hf16.667Ni25 Cu25 HEA from the intermetal family TiZrHfCoNiCu was shown to undergo B2-B19' martensitic transformation, combined with a memory forming effect with attracting Characteristics (Firstov, Kosorukova, Koval, & Odnosum, 2015). Therefore, even though the HESMAs doesn't focus on base elements as same as HEAs, as these kinds of alloys gave a limitless opportunity to make new alloys with different compositions, but researchers in HESMAs should take a look at the boundary which they face since HESMA comes from NiTi SMAs to get SME property. Furthermore, when NiTi-based SMAs become a source of HESMAs, it can be obtained SME when we substitute a part of Ti with some elements named A-group (Nb, Ta, Hf, Zr) and Ni with some other elements known as B-group (Co, Cu, Ru, Rh, Pd, Pt, Au, Ir) (Firstov, Koval, et al., 2015). Since the SME NiTi alloys were determined where the phase structure is B2 type, where these elements increased and went to HEA, we are trying to remake these phases to get SME in these new alloy HESMAs. To detect these phases and examine that, researchers use a significant parameter which is VEC. For instance, in Firstov's work (Firstov, Kosorukova, Koval, & Odnosum, 2015), the NiTi were located in B2 with the value of VEC equal to 7. The HEA compositions have to be around it to make the B2 phase and determine SME. It should also be pointed out that intermetallic TiZrHfCoNiCu that undergoes martensitic transformations are available in a very small VEC range 7–7.2, with stable B2 of this intermetallic Group in a larger variety of VECs 6.75–7.25 (Firstov, Kosorukova, Koval, & Verhovlyuk, 2015).

According to the maximum amount of the elements to be mixed in an equivalent atomic ratio; Yeh et al. suggested in early works a concept $\Delta S_{conf} \geq \ln\ (5R)\ = 1.6\ R$ to set up HEA (Ye et al., 2016). Based on Boltzmann's hypothesis that deals with the relationship between the complexion and system's entropy, from equation 2 and the configurational entropy can compute for each mole (Yeh, 2013):

$$\Delta S_{conf} = -k \ln w = -R\left(\frac{1}{n} \ln \frac{1}{n} + \frac{1}{n} \ln \frac{1}{n} + \cdots \frac{1}{n} \ln \frac{1}{n}\right) \quad [2]$$

$$\Delta S_{conf} = -R \sum_{i=1}^{n} X_i \ln X_i \quad [3]$$

If R= 8.314 J/K mol as a gas constant, and n is the number of elements (Murty et al., 2019; Yeh, 2013) where w is the number of possibilities to mix or exchange available energy amongst the particles in the system and k is Boltzmann constant.

Table 1: Various components of HESMAs, Configurative entropy of components, different phases, and VEC

Sample no.	Alloy Elements (at%)	ΔS_{conf} /R	Phases	VEC	References
1	$Cr_{20}Mn_{20}Fe_{20}Co_{40}$	1.33	FCC↔HCP	7.8	(Lee et al., 2019)
2	$Cr_{20}Mn_{20}Fe_{20}Co_{35}Ni_{5}$	1.48		7.85	
3	$Cr_{20}Mn_{20}Fe_{20}Co_{30}N_{10}$	1.56		7.9	
4	$Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$	1.61		8	
5	$Cr_{30}Mn_{10}Fe_{20}Co_{40}$	1.28		7.7	
6	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{16.667}Ni_{16.667}Cu_{16.667}$	1.79	B2↔B19`	7	(Firstov, Kosorukova, Koval, & Odnosum, 2015)
7	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{25}Ni_{25}$	1.59		6.75	
8	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{25}Cu_{25}$	1.59		7.25	
9	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{25}Cu_{25}$	1.59		7	
10	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{25}Cu_{25}$	1.59	B2↔B19`	7.25	(Chang et al., 2019; David Piorunek et al., 2020)
11	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Pd_{16.667}Ni_{16.667}Cu_{16.667}$	1.79		7.17	
12	$Ti_{14.53}Zr_{14.26}Hf_{21.17}Ni_{30.15}Cu_{19.89}$	1.57	B2↔B19`	7.2	(Firstov, Kosorukova, Koval, & Odnosum, 2015; Firstov, Kosorukova, Koval, & Verhovlyuk, 2015; Lee, Chen, & Chen, 2019)
13	$Ti_{18.15}Zr_{18.75}Hf_{14.33}Ni_{21.64}Cu_{27.13}$	1.59		7.2	
14	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{10}Ni_{25}Cu_{15}$	1.77		7.05	
15	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{10}Ni_{20}Cu_{20}$	1.78		7.1	
16	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{5}Ni_{20}Cu_{25}$	1.72		7.2	
17	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Co_{5}Ni_{25}Cu_{20}$	1.72		7.15	
18	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{50}$	1.25	B2↔B19`	7	(Chang et al., 2019)
19	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{45}Cu_{5}$	1.41		7.05	
20	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{35}Cu_{15}$	1.56		7.15	
21	$Ti_{16}Zr_{15}Hf_{19}Ni_{26.3}Cu_{22.3}$	1.58	B2↔B19`	7.08	(Peltier et al., 2020)
22	$Ti_{17.2}Zr_{13.7}Hf_{20}Ni_{26.6}Cu_{22.5}$	1.58		7.17	
23	$Ti_{17.3}Zr_{13.4}Hf_{20}Ni_{26.6}Cu_{22.7}$	1.58		7.19	
24	$Ti_{32.3}Zr_{19.5}Hf_{16.5}Ni_{19.5}Cu_{12.2}$	1.55		6.02	
25	$Ti_{32.2}Zr_{19.4}Hf_{17}Ni_{19.5}Cu_{11.9}$	1.56		6	
26	$Ti_{31.8}Zr_{18.9}Hf_{17.6}Ni_{19.6}Cu_{12.1}$	1.56		6.02	
27	$Ti_{9.2}Zr_{14}Hf_{20}Ni_{24}Cu_{32.8}$	1.52		7.74	
28	$Ti_{9.2}Zr_{13.6}Hf_{20}Ni_{24.1}Cu_{33}$	1.52		7.75	
29	$Ti_{9.5}Zr_{13.4}Hf_{19.8}Ni_{24.2}Cu_{33.1}$	1.52		7.77	
30	$Ti_{16.333}Zr_{16.333}Hf_{16.333}Ni_{17}Cu_{17}Pd_{17}$	1.79	B2↔B19`	7.23	(Piorunek et al., 2021)
31	$Ti_{16.667}Zr_{16.667}Hf_{16.667}Ni_{16.667}Cu_{16.667}Pd_{16.667}$	1.79		7.17	

32	$Ti_{17.5}Zr_{17.5}Hf_{17.5}Ni_{15.833}Cu_{15.833}Pd_{15.833}$	1.79		7	
33	$Ti_{18.33}Zr_{18.33}Hf_{18.33}Ni_{15}Cu_{15}Pd_{15}$	1.79		6.85	
34	$Ti_{20}Zr_{20}Hf_{20}Ni_{13.33}Cu_{13.33}Pd_{13.33}$	1.77		6.53	
35	$Ti_{21.667}Zr_{21.667}Hf_{21.667}Ni_{11.667}Cu_{11.667}Pd_{11.667}$	1.75		6.22	

3. Discussion

Here we listed all the compositions of HESMAs from the studies. We see that elements like (Ti, Zr, and Hf) are the most used elements; they are on the same column of elements in the periodic table. Each has four electrons in its outer shell of electron configurations. Along with the mentioned elements, (Cu, Ni, Co, and Pd) are the most used elements to produce HESMAs. In order to observe SME in alloys, it is essential to use elements that will enhance the existence of metastable phases of austenite B2 and martensite B19`. VEC and entropy of configuration are calculated to see if the values fall in the standard range stated in the literature. In general, the computed value of entropy is above the revealed value by literature (1.5R) except in two compositions (1 and 18), where R is the gas constant. Where two sorts of elements, A=(Ti, Zr, Hf) and B=(Co, Ni, Cu), are kept, the A50B50 stoichiometry is (VEC=6.75-7.25) (Firstov, Kosorukova, Koval, & Odnosum, 2015). From the table (Table 1), we see that the values of VEC are between 6 to 8 electrons per atom in general. In a study by (Peltier et al., 2020) by increasing the atomic percentage of Ti and because the valence electron number in Ti is four, the samples (24, 25, and 26) VEC value's decreased to around six. The same case is valid for samples (33, 34, and 35) where the percentage of each of (Ti, Zr, and Hf) increased compared to the other elements.

4. Conclusion

In this study, we reviewed HESMAs in general. We found that combining the two significant behaviors SME and HE alloys in a new class of alloys giving a limitless applications opportunity. HESMAs have combinations of specifications (resistance to deformations, corrosion resistance, and shape memory recovery); besides, most of the produced samples are high entropy-high temperature shape memory alloys. (B2↔B19`) is the most seen mixture of phases in HESMAs; this is one of the indicators of SME in studies. Equiatomic percentages of mostly more than four alloys clear the complex composition of HE alloys, which is mostly investigated in the studies. The VEC was calculated for all the samples, and it was found that they mostly rely between 6.8 and 8. The configuration entropy of the samples was also calculated, and as the standards of HE, the values are all around 1.5R and above. Here are the important key points of HESMAs considered for future studies in this field.

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