Directions for High-Temperature Shape Memory Alloys' Improvement: Straight Way to High-Entropy Materials?

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Abstract Nowadays, all thermo-mechanical effects, associated with the martensitic structural phase transitions, are still in the focus of scientists and engineers, especially once these phenomena are taking place at elevated temperatures. The list of the materials, undergoing high-temperature martensitic transformation, is constantly widening. Still, industrial application of these materials, called high-temperature shape memory alloys, is far enough due to the lack of understanding of the peculiarities of the high-temperature martensitic transformation and shape memory effect. The present work attempts to show how the development of the proper directions for high-temperature shape memory alloys' improvement might lead to the creation of essentially new functional materials.

Keywords Martensitic phase transformation · Crystal and electronic structure · Shape memory behaviour · High temperature shape memory alloys · High entropy alloys

Introduction

There is quite a number of reviews and monographs (see [1] or [2] for example) dedicated to the description of shape memory effect (SME) and related phenomena published over the years since the discovery by Buehler, Gilfrich and Wiley [3] of the SME in TiNi intermetallic compound. Generally, they are focused on the two types of shape memory alloys, TiNi- [4] and Cu-based [5], as they have been successfully applied in industry due to the thermoelastic origin of the martensitic transformation (MT), taking place in these materials. Thermoelastic phase equilibrium phenomenon, discovered by Kurdyumov and Khandros in Cu–Al–Ni alloy [6], ensures the structural reversibility during forward↔reverse MT due to the coherency at the austenite/martensite interface. Such coherency results in the rising of the internal stresses during the martensite crystal formation that lead to elastic contribution to the energy balance at MT and, as a result, to reversible appearance–disappearance of “elastic” martensite crystals on cooling–heating through the MT interval, noticed in [6]. Application of the external stresses to alloys, undergoing thermoelastic MT, results in a macroscopic reversibility during shape change at shape memory or superelastic behaviour. Yet, even if the TiNi- or Cu-based shape memory alloys show all signs of thermoelastic behaviour, certain degree of the plastic relaxation (creation and movement of full dislocations) of the internal stresses at austenite/martensite interface might not be avoided. Subsequently, thermal cycling effects (or thermal fatigue) appear [7, 8], as well as the degradation of shape memory effect [9] and mechanical [8], functional or structural [10] fatigue phenomena. Obviously, all these irreversible processes intensify at elevated temperatures, as it might be seen, for example, in the case of Ti₅₀Pd₄₀Ni₁₀ high-

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temperature shape memory alloy [11] because of the irreversible plastic flow in a first place or structural fatigue (ω -phase formation), likewise it can be seen in Ti–Ta during diffusive phase transformation [10]. All of them become the obstacles for successful application of high-temperature shape memory alloys (HTSMAs) [12, 13].

In spite of considerable amount of HTSMA data accumulated over the years, the systematic HTSMA study was not undertaken; all research efforts were split amongst individual HTSMA systems [12, 13]. In the previous work [14], an attempt was made to develop certain physical principles suitable for HTSMA design. The aim of the present paper is to show how the use of such principles leads to the development of the novel class of functional materials—high-entropy shape memory alloys, which were discovered very recently [15].

Experimental

Ti–Zr–Hf–Co–Ni–Cu alloys studied were arc-melted from iodide Ti, Zr and Hf and electrolytic Co, Ni and Cu in a pregettered argon atmosphere and poured into a water-cooled copper mould. The weight of the ingots was typically 15–25 g. MT temperatures were detected with the help of Netzsch 404 F1 differential scanning calorimeter using a heating–cooling rate of 10 K/min. Shape memory behaviour was studied in three-point bending under the static load in 77–1100 K temperature range. Hardness and elastic modulus at room temperature were measured using instrumented indentation test for hardness (ISO 14577-1:2002(E)) with the help of “Micron-Gamma” device equipped with Berkovich indenter.

Results and Discussion

First of all, let us consider the directions for HTSMA improvement based upon the physical principles developed in [14]. In general, materials possessing high melting temperatures (T_{melt}) and relatively high MT temperatures (above $0.3 T_{\text{melt}}$) are quite promising for SME at elevated temperatures. These materials are intermetallic compounds that undergo MT from B2 austenite into low symmetry martensitic phase, and for them the processes of the plastic relaxation of arising internal stresses are suppressed. Especially attractive are those intermetallics that possess the symmetry of high-temperature austenitic phase lower than cubic, like in the case of Ni_3Ta intermetallic compound [16] with high-temperature phase structure belonging to tetragonal syngony. In this case, the basic planes for martensite do not coincide with easy gliding planes for dislocations in austenite, which prevents irreversible plastic

deformation. Amongst the group of materials with high-temperature shape memory, alloy systems with inexpensive constituents like (Cu, Ni, Co)–(Ti, Zr) and Ni_3Ta in its homogeneity range attract special attention. For them, the temperature interval of high-temperature shape recovery is in 400–900 K temperature range.

It should be fairly noted that the absolute values of shape recovery temperatures are less important than the ratio of the starting temperature of the reverse MT (A_s) to melting temperature as plastic flow and diffusive processes, including thermal, mechanical, functional and structural fatigue, mentioned in the introduction, intensify above $A_s/T_{\text{melt}} \approx 0.5$. It can be seen, when one considers candidates among intermetallics for the so-called ultra-high-temperature shape recovery. Analysis of phase diagrams with AB binary compounds (A–Ti, Zr, Hf, Nb, Ta; B–Co, Ni, Cu, Ru, Rh, Pd, Ir, Pt, Au) has shown that in some of these intermetallics MT at relatively high temperatures was already detected or might be deduced from the information available [17–26]. A_s , T_{melt} , A_s/T_{melt} ratio and shape recovery ratio (K_{SME}) for these intermetallics are shown in Table 1.

It is visible (Table 1) that A_s temperature might be chosen from 800 to 1860 K and for most studied intermetallics [18–26] MT was reported as quite reversible and even thermoelastic similar to TiNi and CuAlNi. While TiNi and CuAlNi exhibit complete shape recovery, the candidates for ultra-high-temperature shape recovery performed poorly except for two intermetallics: ZrRh and HfIr (Table 1, bold). The reason is that for ZrRh, $A_s/T_{\text{melt}} = 0.39$, while for HfIr it is even smaller—0.36, which is almost the same as for CuAlNi industrial shape memory alloy. A_s/T_{melt} ratio is well below 0.5 for TiNi, CuAlNi, ZrRh and HfIr, indicating that diffusive and plastic processes are frozen well enough. That is why HfIr shows the complete recovery of about 1 % of accumulated strain in the 1000–1300 K temperature range [24]. On the other hand, for HfNi ($A_s = 1400$ K), where temperature-induced MT shows all signs of thermoelasticity, the shape recovery does not happen at all because $A_s/T_{\text{melt}} = 0.78$, indicating that diffusive and plastic flow processes already lead to complete loss of coherency on the austenite/martensite interface through internal stress relaxation. The same is very true for HfPd ($K_{\text{SME}} = 5.8$ %) [21] and TiPt ($K_{\text{SME}} = 7.5$ %) [26] intermetallics. It can be also seen that in general the decrease of A_s/T_{melt} leads to the increase in shape recovery although if this ratio is above 0.4 the shape recovery is incomplete.

According to [12–14], existing HTSMA drawbacks are poor mechanical properties that lead to unacceptable machinability, insufficient recoverable deformations and the fact that these recoverable deformations are accompanied by irreversible plastic ones. To overcome

Table 1 A_s , T_{melt} , A_s/T_{melt} ratio and shape recovery ratio ($K_{\text{SME}} = \varepsilon_R/\varepsilon_M \times 100\%$, where ε_M is the accumulated strain and ε_R is the recovered strain) of intermetallic candidates for ultra-high-temperature shape recovery and TiNi and CuAlNi classic shape memory alloys given for comparison

Intermetallic	A_s (K)	T_{melt} (K)	A_s/T_{melt}	K_{SME} (%)	Reference
TiAu	800	1770	0.45	55–78	[17, 18, 21]
ZrAu	840	1848	0.45	–	[17]
ZrRh	840	2180	0.39	100	[19]
TiPd	850	1670	0.51	60	[17, 20]
HfPd	930	1880	0.49	5.8	[17, 21]
Zr ₅₀ Cu ₂₅ Ni ₂₅	960	1370	0.70	90	[17, 22]
Zr ₅₀ Co ₂₅ Ni ₂₅	970	1510	0.64	90	[17, 23]
HfIr	970	2700	0.36	100	[17, 24]
ZrPd	1040	1870	0.56	–	[17]
HfAu	1070	1690	0.63	–	[17]
NbRu	1150	2215	0.52	50	[17, 25]
ZrIr	1150	2320	0.49	75	[19]
TiIr	1300	2400	0.54	–	[17]
TiPt	1320	2130	0.62	7.5	[17, 26]
TaRu	1370	2320	0.59	50	[17, 25]
Ti ₅₀ Pt ₂₅ Ir ₂₅	1400	2270	0.62	45	[17, 26]
HfNi	1400	1795	0.78	0	[19]
TiRh	1550	2210	0.70	–	[17]
ZrPt	1860	2270	0.82	–	[17]
TiNi	350	1580	0.22	100	[4, 17]
CuAlNi	470	1320	0.35	100	[5, 17]

these difficulties, one might use the path of HTSMA production via amorphous state [27] to obtain chemically homogeneous material or/and increase martensitic deformation through structure refinement [28]. The accumulation of the irreversible plastic deformation during SME, which becomes easier in HTSMA due to the coincidence of the easy gliding planes for dislocations in austenite and basic planes of martensite, can be avoided with the help of complication of MT crystallography through the symmetry decrease of the austenitic phase [16], solid solution hardening, ageing [29], creation of natural shape memory composites [23] and also by suppression of the diffusion processes of relaxation of internal stresses, which can be ensured through the increase of HTSMA melting temperatures and minimization of A_s/T_{melt} ratio [14]. It should be also noted that mutual use of the directions for HTSMA improvement is rather difficult, although such an attempt was made already for ZrCu-based HTSMA through Ni, Co and Ti alloying additions [30, 31]. This five-component HTSMA was the best among ZrCu-based family although the saturation of the positive influence on shape memory characteristics was noticed.

On the other hand, once the race for HTSMA kept going for the last 15 years, almost at the same time, Yeh and co-authors produced an impressive breakthrough in structural materials' design by proposing entirely new concept of high-entropy alloys (HEAs) [32]. This concept involves the creation of the multi-element metallic materials close to

equimolar composition (without the principal element) with the entropy of mixing higher comparing to the existing materials and ensuring in such way high phase stability [33, 34]. HEAs can be obtained as solid solutions, bulk metallic glasses and even intermetallic compounds, some of them being reported to possess B2 type of structure [35] to which the structure of the NiTi shape memory alloy austenite belongs. It was shown already that HEAs possess unusually high hardness due to the non-obvious solid solution hardening [36] and diffusion in these materials is sluggish [37]. These HEA properties were those that existing HTSMA needed for improvement, including multi-component ZrCu-based HTSMA [30, 31].

Very recently, following HEA concept mentioned above, it was found that one $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Ni}_{25}\text{Cu}_{25}$ HEA of TiZrHfCoNiCu intermetallic family undergoes B2 $\leftrightarrow$ B19' martensitic transformation (MT), which is accompanied by shape memory effect with attractive parameters [15], including MT and shape memory temperatures above 400 K that indeed make it HTSMA a good candidate. Below, further studies of MT and SME in TiZrHfCoNiCu high-entropy intermetallic family will be presented.

As it was clear from the results of [15], Co in equiatomic TiZrHfCoNiCu intermetallic completely stabilized high-temperature austenite B2 phase. So, MT ought to be found somewhere between $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Ni}_{25}\text{Cu}_{25}$ and $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{16.667}\text{Ni}_{16.667}\text{Cu}_{16.667}$

compositions. To do that, $(\text{TiZrHf})_{50}(\text{CoNiCu})_{50}$ alloys were prepared, containing different amounts of Co, Ni and Cu (Ti, Zr and Hf in equal amounts—16.667 at.%). It should be also noted that all HEAs were studied in the as-cast state. Dendritic segregation was found in all of them by scanning electron microscopy. Broad description of this study will be published elsewhere. Here we will use its results for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Ni}_{25}\text{Cu}_{25}$ intermetallic, where compositions for dendrites and interdendritic space were determined and arc-melted as a separate $\text{Ti}_{14.53}\text{Zr}_{14.26}\text{Hf}_{21.17}\text{Ni}_{30.15}\text{Cu}_{19.89}$ and $\text{Ti}_{18.15}\text{Zr}_{18.75}\text{Hf}_{14.33}\text{Ni}_{21.64}\text{Cu}_{27.13}$ alloys. The results of DSC and SME measurements for all these alloys underwent MT are shown in Table 2.

It is visible (Table 2) that M_s temperature varies in the wide temperature range from 260 to 675 K. Co additions indeed strongly suppress MT. The strongest is the effect of Ni substitution by Co, as the rate of M_s decrease is -25 K/at.% of Co. The effect of Cu substitution is much less pronounced (rate of M_s decrease is -7 K/at.% of Co), while mutual substitution of Ni and Cu by Co is almost the same for Ni substitution only—rate of M_s decrease is -24 K/at.% of Co. As for dendrite and interdendritic $\text{Ti}_{14.53}\text{Zr}_{14.26}\text{Hf}_{21.17}\text{Ni}_{30.15}\text{Cu}_{19.89}$ and $\text{Ti}_{18.15}\text{Zr}_{18.75}\text{Hf}_{14.33}\text{Ni}_{21.64}\text{Cu}_{27.13}$ compositions, it is clear that in the first (dendritic) composition an increase in Hf and Ni content is observed, which resulted in the highest M_s amongst considered alloys. The second (interdendritic) composition is characterised by the increase in Ti, Zr and Cu content, while M_s is still just above 400 K (Table 2). These effects are definitely related to interatomic interaction specific for HEA in question and will need further structural experimental and modelling studies.

Still, the most attractive amongst all HEAs in question is $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$, as it exhibits high values of MT heats (implying that most of the material is taking part in MT), narrow MT hysteresis (Fig. 1) and the highest value of martensitic strain in HTSMA temperature range (Table 2) that was recovered completely (Fig. 2).

Fig. 1 DSC measurements of the complete MT cycle for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ high-entropy intermetallic

DSC measurements of the complete MT cycle for this high-entropy intermetallic (Fig. 1) show also that not only the hysteresis is narrow ($\Delta T = 55$ K) but the temperature intervals of MT are also narrow (50–60 K), comparing with wide $\Delta T = 92$ K and MT intervals for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Ni}_{25}\text{Cu}_{25}$ ([38], Table 2). This kind of behaviour during MT in $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ is quite close to thermoelastic one. It is indirectly confirmed during SME measurements in three-point bending shown in Fig. 2.

After heating over 800 K, the plate-like specimen was loaded in three-point bending. The load induced 500 MPa in surface layers in the upper and bottom sides of the specimen. Load–unload at this temperature confirmed that no plastic flow occurred. Then, the specimen was cooled under the static load and already at 700 K the strain additional to elastic one started to occur. Further cooling registered more intensive bending below 420 K, which corresponds to M_s of the stress-free MT measured in DSC (Fig. 1; Table 2). Accumulation of the martensitic strain of

Table 2 Composition of TiZrHfCoNiCu high-entropy intermetallics, their MT temperatures (M_s , M_f , A_s , A_f) and heats (Q^{M-A} —released upon forward MT on cooling; Q^{A-M} —absorbed upon reverse MT on heating)

Ti at. %	Zr	Hf	Co	Ni	Cu	M_s K	M_f	A_s	A_f	ΔT	Q^{M-A} J/g	Q^{A-M}	Ed	ε_R %
14.53	14.26	21.17	–	30.15	19.89	675	482	659	911	206	20.08	22.42	2.34	0.6
16.67	16.67	16.67	–	25	25	500	385	458	611	92	3.47	5.248	1.78	0.4
16.67	16.67	16.67	5	25	20	454	405	462	532	68	10.3	11.28	0.98	1.16
16.67	16.67	16.67	10	25	15	430	373	423	488	55	11.11	12.89	1.78	1.63
18.15	18.75	14.33	–	21.64	27.13	414	339	354	520	60	9.75	11.19	1.44	0.55
16.67	16.67	16.67	5	20	25	376	259	319	451	68	8.678	9.797	1.12	1.19
16.67	16.67	16.67	10	20	20	263	200	240	317	47	6.623	7.152	0.53	1.84

$$\Delta T = (A_s + (A_f - A_s)/2) - (M_f + (M_s - M_f)/2)$$

MT thermal hysteresis, ΔT energy lost in a complete MT cycle $Ed = Q^{A-M} - Q^{M-A}$, according to [38], and strain recovered in three-point bending experiments (ε_R) are also shown

Fig. 2 SME measurements of the complete MT cycle for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ high-entropy intermetallic in three-point bending. Arrows indicate cooling and subsequent heating as well as application or removal of external load ($\pm P$) that resulted in the stress of 500 MPa

1.6 % on cooling under 500 MPa finished just above 300 K, which also corresponds with the DSC data (Fig. 1; Table 2) well enough. After cooling to liquid nitrogen temperature, the specimen was unloaded and heated up to 600 K. At temperatures about 200 K, shape recovery already started but the most intensive shape recovery process began at around 300 K and was finished just above 500 K. Complete shape recovery has been taking place not only for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ intermetallic shown in Fig. 2 but for all HEAs in Table 2. Only recovered strain accumulated at 500 MPa varies (Table 2). The reason for this is related to crystal structure parameter changes in austenitic B2 and martensitic B19' phases, which are described in [39]. Here we shall use only relative volume change during forward MT calculated from volume per atom values for martensite and austenite, which are calculated in their own turn from lattice parameters, taking into account the number of atoms in the unit cell. So, Fig. 3 represents relative volume change during forward MT, recovered strain and MT hysteresis depending upon M_s temperature for all HEAs from Table 2.

It can be seen (Fig. 3) that for most of the HEAs the volume change is quite significant and has a positive sign (martensite has bigger specific volume comparing to austenite). Yet, in the case of the most attractive in a sense of HTSMA parameters $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ intermetallic, the volume change undergoes a minimum at M_s dependence ($M_s = 430$ K). Moreover, it changes sign from positive to negative and its absolute value is the smallest one. It means that MT in $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ intermetallic shows all signs

Fig. 3 Forward MT relative volume change ($\Delta V/V$), recovered strain ε_R and MT hysteresis depending upon M_s for HEAs studied in the present work (Table 2)

of thermoelastic behaviour similar to TiNi, which has negative sign for the volume change also, and contrary to HTSMAs that exhibit positive sign of the volume change [14]. That is the reason why MT hysteresis that represents the degree of irreversible processes shows minimum that coincides with the minimum in volume change. It is no surprise that recovered strain exhibits maximum that coincides with the minima mentioned above (Fig. 3). As for the fact that despite quite high external stresses (500 MPa) applied at elevated temperatures, there is complete shape recovery for all HEAs in question, one should take into account their mechanical properties. It was expected to see significant solution hardening mentioned above [36], although this hardening was observed for solid solutions only. In our case, we are dealing with high-entropy intermetallics, which could behave differently. In the present work, hardness (H_{Meyer}) was measured simultaneously with elastic modulus by means of instrumented indentation test for hardness (ISO 14577-1:2002(E)) with the help of “Micron-Gamma” device equipped with Berkovich indenter. The results depending upon M_s for all HEAs in question are shown in Fig. 4.

It should be noted that absolute hardness values are higher for HEAs, comparing with TiNi, which we measured also and obtained $H_{\text{Meyer}} = 6$ GPa for it. In general, hardness increases from 9 to 12 GPa with M_s increase. So, solution hardening takes place indeed and that is the reason for complete shape recovery for all HEAs studied in the present work. Still, hardness produces a minimum together with elastic modulus (Fig. 4) that corresponds to the minima in volume change and hysteresis (Fig. 3), and hardness becomes close in value to TiNi for $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ high-entropy intermetallic. In the case of TiNi, during the hardness measurements, the formation of stress-induced martensite and reorientation of existing one take place under the indenter due to high mobility of the

Fig. 4 Elastic modulus and hardness (H_{Meyer}) dependences upon M_s for HEAs studied in the present work (Table 2)

austenite/martensite and martensite/martensite interfaces. Most probably, the same takes place in $\text{Ti}_{16.667}\text{Zr}_{16.667}\text{Hf}_{16.667}\text{Co}_{10}\text{Ni}_{25}\text{Cu}_{15}$ and a strong drop in hardness is observed as a result. The reason for such high interface mobility and general lattice softening (minimum in elastic modulus in Fig. 4) is definitely related to crystal structure peculiarities of the austenite and martensite, including substructural ones, which would need additional extensive studies.

Finally, let us consider relative position of the studied high-entropy shape memory alloys (Table 2) among binary intermetallic compounds like classic shape memory alloy TiNi [4, 17], HTSMA ZrCu [17, 40], B33 stable ZrNi [17] and equimolar TiZrHfNiCu, TiZrHfCoCu [41] amorphous HEAs, using parameters to characterise the collective behaviour of the constituent elements in the multi-component HEA: the atomic size difference (δ), the mixing enthalpy (ΔH_{mix}), the mixing entropy (ΔS_{mix}) and the valence electron concentration (VEC) according to [35] together with Ω parameter ($\Omega = \frac{T_{\text{melt}}\Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}$) proposed in [42]. The results of such consideration are shown in Figs. 5 and 6.

Figure 5 shows mixing entropy (ΔS_{mix}) depending upon valence electron concentration (VEC). It can be seen that mixing entropy of TiZrHfCoNiCu intermetallics is indeed in the high entropy range between 13.196 and $14.897 \text{ Jmol}^{-1} \text{ K}^{-1}$; these values are much higher, comparing with binary intermetallic compounds shown in Fig. 5. TiZrHfCoNiCu intermetallics with a stable B2 structure (data taken from [15, 39]) have $\Delta S_{\text{mix}} = 13.211 \text{ Jmol}^{-1} \text{ K}^{-1}$, which is slightly smaller than the value for amorphous HEA— $13.381 \text{ Jmol}^{-1} \text{ K}^{-1}$, while most of the TiZrHfCoNiCu intermetallics that undergo $\text{B2} \leftrightarrow \text{B19'}$ MT have significantly higher ΔS_{mix} in the range of 14.252 – $14.897 \text{ Jmol}^{-1} \text{ K}^{-1}$. Obviously, a rise in the mixing entropy might stabilize the forming phases only to diffusion transformations, while diffusionless structural instability is quite possible. It should be also noted that TiZrHfCoNiCu intermetallics undergoing MT

Fig. 5 Mixing entropy (ΔS_{mix}) dependence upon valence electron concentration (VEC) for TiZrHfCoNiCu high-entropy intermetallics and some amorphous HEAs and binary intermetallic compounds

Fig. 6 Ω parameter ($\Omega = \frac{T_{\text{melt}}\Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}$) dependence upon atomic size difference (δ) for TiZrHfCoNiCu high-entropy intermetallics and some amorphous HEAs and binary intermetallic compounds

exist in the very narrow VEC window—7–7.2 electron per atom, while stable B2 phase of this intermetallic family exists in much wider VEC range 6.75 – 7.25 electron per atom.

In Fig. 6, the Ω parameter ($\Omega = \frac{T_{\text{melt}}\Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}$) dependence upon atomic size difference (δ) can be seen. It is clear that Ω is below 1, which, according to [42], means that intermetallics or bulk metallic glasses ought to form. It was proved for TiZrHfCoNiCu equiatomic alloy in [15], where (100) superstructural reflection, characteristic for B2 type of ordering, was detected. On the other hand, atomic size difference for intermetallic compounds of TiZrHfCoNiCu family is higher than for amorphous HEA, confirming definite tendency towards sluggish diffusion.

HEAs studied in the present investigation have shown resistance to plastic deformation and diffusion processes

superior to existing HTSMA due to their intrinsic multi-component design. So, the directions for HTSMA improvement indeed lead us successfully to the qualitatively novel functional materials—high-entropy shape memory alloys.

Conclusions

- It can be concluded that existing HTSMAs based upon certain chemical elements still show significant drawbacks mostly related to plastic deformation that accompanies accumulation of the martensitic one and to diffusive processes, taking place in these materials.
- Directions for HTSMA improvement are related mostly to suppression of the plastic deformation through strengthening by substructure refinement, solid solution hardening and prevention of the diffusion processes of internal stresses relaxation and structural fatigue.
- Mutual application of these directions lead to the creation of the novel functional materials, high-entropy shape memory alloys; for them, all those directions are implemented by their multi-component design.
- Martensitic transformation in high-entropy shape memory alloys takes place at elevated temperatures and is accompanied by shape memory behaviour with complete shape recovery (1–2 % of the recovered strain), which favourably distinguishes these novel shape memory materials from the existing high-temperature shape memory alloys.
- There is definite need in extensive experimental (X-ray, TEM, SEM, etc.) and modelling and of the crystal and electronic structure of such materials in order to develop certain models for prediction MT temperatures, mechanical and functional properties' further enhancement, etc.
- On top of the understanding of the physical origin of the phase stability, interatomic interaction and chemical bond in these materials, it is necessary to continue experimental studies of the alloying changes within existing compositions of high-entropy shape memory alloys and additional alloying as well.
- As these materials were studied only in the as-cast conditions, it is necessary to explore the influence of various thermal/mechanical treatments on structural and phase transformations in them.

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