

Martensite and Reverse Transformation Temperatures of TiAu-Based and TiIr-Based Intermetallics

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Abstract

Dependence of transformation temperatures of TiAu- and TiIr-based Intermetallics on Valence Electron Ratio (VER), number of valence electrons (e_v) and average atomic number of the alloys (Z) were investigated. The alloys mostly have medium numbers of valence electrons ($6.5 \leq e_v \leq 7.3$) near 7 with a limited number of TiAu-based alloys belonging to high valence electron group with e_v more than 7.50 and relatively narrow range of average atomic numbers ($Z = 41-53$). The forward and reverse phase transformation temperatures, M_s and A_s of AuTi-based alloys sharply increase with the average atomic number of the alloys. The investigated TiIr alloy compositions have almost similar average atomic numbers (49.5 to 50.2). Clear correlations between transformation temperatures and VER were found. M_s and A_s both decrease from around 1550 °C to as low as 17 °C respectively, with increasing VER from 0.131 to 0.174. The dependence of transformation temperatures on valence electron ratio is discussed based on the variations of elastic properties and atomic bonding due to composition change in these alloys.

Keywords: valence electron, transformation temperature, martensite, shape memory alloy, TiAu, TiIr

Keywords according to the Journal's list: Metals and Alloys, Intermetallics, Phase Transition,

1. Introduction

There is an ongoing demand for high temperature SMAs as novel applications continue to be developed in the areas of designing mechanical and aerospace SMA-actuated structures for better system performance. TiAu and TiIr intermetallic systems are among the high temperature alloys of interest despite their high costs. To adjust the cost or shape memory and mechanical properties of these alloys, alloying elements are added to these systems that alter

their transformation temperatures. Transformation temperature of a shape memory alloy (SMA) is an important characteristic since it is the temperature at which the SMA material recovers from apparent permanent deformation through a reversible martensitic transformation. This shape recovery behaviour is often referred to as shape memory effect and has been adapted in various aerospace, structural and, biomedical applications [1]. Elastic properties of the matrix crystal before martensitic transformation and microstructural features such as precipitates were shown to be important factors affecting the transformation temperatures [2]. To understand the factors that control the transformation temperatures in SMAs system, Zarinejad and Liu. suggested the need to acquire in-depth knowledge of how the atomic bonding strength of the matrix crystal can be influenced by the chemical composition of the alloys. M_s temperature is affected by alloying elements and their influence can be complex. However, how the alloying elements affect the transformation temperature is a subject of importance. To show how different alloying elements, affect the transformation temperature, apart from the number of valence electron per atom (e_v/a), valence electron concentration (c_v) was introduced [3]. It was indicated that some alloying elements increase and some of them decrease the transformation temperatures. The initial work of Zarinejad, and Liu on this subject was on NiTi system in which a trend of variation of M_s with (c_v) was established [3,4]. It was shown why some alloying elements such as Fe, can reduce the transformation temperature and some alloys such as Pt and Au increase the transformation temperature. Zarinejad and Liu attributed the direction of the change to how valence electron concentration changes and in turn how the bonding in the parent phase is affected. By increasing the valence electron concentration (c_v) of the NiTi-based alloys and, the transformation temperatures decrease because of higher elastic properties of the crystal that influence the resistance against shear, responsible for martensitic transformation. [3,5]. The correlations discovered were observed in other shape memory alloys, especially when ($5 \leq$

$e_v/a \leq 7.50$) [6]. However, shape memory systems with very high concentrations of elements with anti-ferromagnetism properties such as Mn in Heusler alloys or alloys with low e_v/a (less than 5) may not entirely follow the trend [5,6]. The influence of some of the extrinsic factors such as microstructural evolution including second phase precipitation and crystallization in NiTi-based alloys were also studied [7,8]. Many works have since used the valence electron parameter (c_v) and the relevant methodology to study alloy systems and design new alloys or reviewed the validity of the trend in different alloy systems. For instance, the correlation was used to propose a strategy for accelerated alloy design [9] and was evaluated in [10]. Furthermore, ZrCu [11,12], ZrCu-based alloys [13,14,15], NiTiHf [16,17,18,19], multiple shape memory effect based on composition change in NiTi [20], Cu-Al-based [21], NiTiNb [22,23,24,25], Ti-Ta-based [26], NiTiPt [27], NiTiSn [28], NiMnGa [29], NiTiV [30], Ni-rich NiTi and NiTiCo [31] and NiCuPdTiZrHf high entropy shape memory alloys [32] are among the alloys or systems studied using valence electron concentration proposed. This understanding was achieved based on the knowledge that prior to martensitic transformation a softening of elastic moduli occurs with lowering the temperature. The experimental results, mainly in Cu-based [33,34,] and NiTi-based SMAs [35,36] suggest that there is a critical value of elastic constant at which transformation takes place, which is not sensitive to alloy compositions,[37] and is only slightly dependant on temperature.[2] Based on this, the elastic moduli of the alloy, which are dependent on both composition and temperature [2,38] are the key parameters influencing the transformation temperatures.[39,40] Since in metallic materials the delocalized valence electrons dominate the strengths of bonds and elastic properties,[41] it is of particular importance to study the electronic parameters of alloys. In the present work, the investigation is extended to the TiAu-based and TiAu-based high temperature SMA family of alloys in detail to reveal in-depth understanding of the dependence of transformation temperatures (M_s , A_s) on the electronic parameters of the alloy.

The electronic parameters of nearly all the TiAu- and TiIr-based alloys made or studied to date are examined. Three parameters are paid attention to in the current study: 1) the average atomic number of the alloys; 2) the number of valence electrons, and most importantly; 3) Valence Electron Ratio (VER) of the alloys (Zarinejad had previously, in an original work, defined and called this parameter as c_v , valence electron concentration. However, VER seems to be a more appropriate term for this defined parameter, as the name ratio differentiates it from the valence electron per atom (e/a) which in some literature is referred to valence electron concentration. In the present work, we reveal and explain the dependence of the transformation temperatures of important TiAu and TiIr family of alloys on VER. The correlations found enable an important understanding towards effective alloy design.

2. Materials and Methods

A survey of the literature reveals many TiAu-based and some TiIr-based shape memory alloys (SMAs) with a wide range of martensitic transformation temperatures (17-1500 °C) [42-61]. Different Ti/Au atomic ratios and alloying elements such as Ni, Fe, Co, Cr, Mn, Cu, Rh, Ir, Pt, Ag, Ru, Zr, etc., have been utilized by researchers to alter the transformation temperatures and characteristics of TiAu-based SMAs, whereas in TiIr-based SMA alloys only Pt has been reported as the alloying element. Table 1 presents more than 40 TiAu and TiIr alloy compositions that include nearly all alloy compositions studied so far, together with their forward and reverse transformation temperatures (M_s and A_s) and in ascending order and the thermal hysteresis where available. These data were extracted from the relevant literature as listed in tables or presented in graphs. Most of the data correspond to solution-treated alloys to minimize the effects of precipitates and mechanical work. These possible effects, though possibly existing, were not considered in the present work. The maximum martensite start temperature ($M_s = 617$ °C) for TiAu-based system corresponds to a

binary Au-rich TiAu composition, i.e., Ti₄₇Au₅₃, whereas in the TiIr system, the binary equiatomic TiIr composition has the highest martensite start transformation temperature, with Ti₅₀Ir₅₀ having a M_s of 1550 °C (though this temperature may need further confirmation). The lowest transformation temperatures correspond to alloys with cobalt alloyed minimum Au containing in TiAu-based alloys and alloys with minimum Ir quantity in their compositions in TiIr-based alloys. To study the dependence of the transformation temperatures on the chemistry of alloys the basic electron configurations of the alloys were analyzed in the following section.

3. Theory (elastic properties of crystals and transformation temperatures)

In the martensitic transformation in TiAu- and TiIr-based alloys shear causes shape changes to the austenite parent crystals. The elastic response coefficients are the most fundamental of all the properties of solid crystals and the most important subset of them are the shear and bulk moduli. Bulk modulus is a measure of the resistance of a solid to volume change and shear modulus is a measure of resistance to shape change. Shear moduli have the highest influence on the mechanical properties of the crystals [2,62]. Bonding type (metallic, covalent, ionic, and molecular), and solidity index of a crystal (which is simply the ratio of the shear modulus to the bulk modulus, multiplied by a coefficient of the order of unity), have been used to classify crystals [41]. Therefore, shear and bulk moduli and their ratio in the parent phase (austenite) are of paramount importance for this athermal martensitic phase transformation [62,63]. The chemical factors that affect these parameters in the TiAu- and TiIr-based alloys under study in this work are discussed in the following.

4. Results and Discussion (chemical factors influencing bulk and shear moduli of alloy crystals)

4.1. Average atomic number, non-valence electrons

The average atomic numbers of the alloys were calculated based on the atomic fractions and atomic numbers of the elements comprising the alloys as follows by equation (1):

$$Z = f_{Ti}Z_{Ti} + f_{Pd(Pt)}Z_{Pd(Pt)} + f_T Z_T + f_Q Z_Q \quad (1)$$

where Z is the average weighted atomic number of the alloy, Z_{Ti} , $Z_{Au(Ir)}$, Z_T , and Z_Q etc. are the atomic numbers Ti, Au (or Ir), the ternary, quaternary, quinary elements, and, so on, respectively. The f_x ($x= Ti, Au$ or Ir , the ternary, quaternary, quinary elements, or even quinary element etc.) is the corresponding atomic fraction of each element in the alloy. The average atomic numbers of the alloys under study are tabulated in Table 1. The transformation temperatures M_s , and A_s of TiAu-based alloys increase with Z ($Z=41-53$) of the alloys as plotted in (Fig. 1a). The same increasing trend with Z cannot be observed for TiIr-based alloys due to the limited number of alloys and the similarity of the Z or these alloys ($Z=49.5-50.2$), (Fig. 1b).

In transition metals and intermetallics it is known that when the average atomic number is halfway through in the transition metals rows of the periodic table of elements, i.e., either $Z = 25-26$, or $Z = 43-44$, and so on., the martensitic transformation temperature can be reduced. This is because the elastic properties of the parent crystal hit maxima at or near these atomic numbers [62] and martensitic transformation should start at a lower temperature. This effect may be seen in alloys with the atomic numbers of around 41 to 44 that are among the alloys with the lowest transformation temperatures. (Table. 1). As shown the existing TiIr alloys can have higher transformation temperatures than TiAu alloys, though the trend of change of M_s and A_s temperatures with atomic number is similar. These temperatures increase with increasing Au or Ir in the alloys. In other words, the transformation temperatures of the

alloys increase with increasing the total number of electron (average atomic number) of the alloy. Non-valence electrons do not contribute to bonding and together with the protons comprise the ion kernel in the metallic bonding of the transition metal alloys. Increasing non-valence electrons or size of the kernels at constant (or nearly constant) valence electron numbers lead to weaker elastic bonding [62,63]. This, in turn, means the resistance to shape and volume change of the crystal will be lower (at least in some of the crystallographic directions) and therefore the phase change from austenite to martensite may occur at higher temperatures. The presence of Au ($Z = 79$) and Ir ($Z = 77$) in the alloys causes the total number of non-valence electrons to extensively increase. Based on this it is expected that in TiAu based alloys show higher maximum transformation temperatures than TiIr-based alloys. However, this is not the case (Table 1). The reason is related to the difference in the number of valence electrons which is 11 for Au and 9 for Ir. Therefore, non-valence electrons are not influencing alone, and the number of valence electrons is of high importance as discussed in the following section. The number of valence electrons has a significant effect on the transformation temperature of shape memory alloys in general including in TiAu and TiIr based alloys under study in the current work. Although this effect is less pronounced in these systems but it exists. The wide range of e_v/a in the x-axis of Fig 2 has been chosen to show where these alloys belong when it comes to the number of electrons. The author (Zarinejad) has categorized the TiAu and TiIr based alloys into three categories depicted by the areas shown in the plots based on their e_v/a [6]. Therefore, the graphs were plotted to show that most of the alloys belong to the medium electron category. Additional plots with a narrower e_v/a range are embedded on the main plots to show the influence of e_v/a on the transformation temperatures in these two alloy systems more clearly as can be seen in Fig. 2 a and b.

4.2. Number of valence electrons, d–d Orbital Overlapping Occupancies

The number of valence electrons is usually considered as the number of d and s electrons for an atom of transition metals. The valence electrons per atom of TiAu-based and TiIr-based alloys can be calculated based on the atomic fractions of the elements in the alloy by equation (2):

$$e_v = f_{Ti}e_v^{Ti} + f_{Au(Ir)}e_v^{Au(Ir)} + f_T e_v^T + f_Q e_v^Q + \dots \quad (2)$$

where similarly f_{Ti} , $f_{Au(Ir)}$, f_T and f_Q represent the atomic fractions of Ti, Au (or Ir), the ternary quaternary elements etc., in the alloy and, e_v^{Ti} , $e_v^{Au(Ir)}$, e_v^T and e_v^Q are the corresponding numbers of valence electrons of elements Ti, Au(Ir), ternary and quaternary elements, respectively. A similar but more detailed explanation of the calculation of e_v can be found in [3,5,6] Alloys with M_s and A_s temperatures from as high as 1500°C down to 17 °C were included in this investigation. In the categorization of the shape memory alloys (SMAs) concerning their number of valence electrons, a wide range was previously observed ($4 \leq e_v \leq 12$) by Zarinejad and Liu [6]. The alloys were divided into low ($e_v < 5$), medium ($5 \leq e_v \leq 7.50$) and high ($e_v > 7.50$) valence electron groups. On this basis, apart from Au-rich binary AuTi alloys of $Ti_{49}Au_{51}$ ($e_v = 7.57$) and $Ti_{47}Au_{53}$ ($e_v = 7.71$) that can be categorized as high valence electron alloys, all other TiAu-based, and TiIr-based alloys belong to the medium valence electron group with their e_v (6.50-7.50) in a range surrounding 7 (Table 1). A considerable number of non-magnetic SMAs happen to belong to the medium range [6]. Majority of the highest M_s in shape memory alloy systems are usually observed in the medium electron group ($5 \leq e_v \leq 7.50$) [6]. In both alloy systems, wide variations of M_s and A_s temperatures of the alloys in the narrow range of the number of valence electron are observed (Fig 2). Also, in both systems when the average number of valence electrons (e_v) closely approaches 7, lowest transformations temperatures the corresponding alloy systems are seen. (Fig. 2a,b). Higher e_v than 7 in TiAu system and lower e_v than 7 in TiIr system

increase the transformation temperatures. This can be attributed to the degree of d-d overlapping orbital occupancy when e_v is 7 or close to it as opposed to when it is higher or lower than 7. In the former, when d-d overlapped orbital of the transition alloy is half filled in these two alloy systems the alloys is like a metal of atomic number in the middle of the row of the transition metal with enhanced elastic properties of the crystal and therefore lower transformation temperatures are observed (Fig 2). In this condition, e_v is not the controlling factor of transformation temperature as it was shown in previous work in TiNi-based alloys [4-6]. Whereas, when e_v is not 7 or close to it the degree of d-d orbital occupancy is reduced and as a result, the elastic properties of the metal crystals are changed (usually lowered). This leads to weaker atomic bonds at least in some shear directions and martensitic transformation could take place at higher temperatures (Fig 2). Hence, the transformation temperature among other factors could also be dependent on the degree of d-d overlapping occupancy in these alloys. The wide range of transformation temperatures that is observed, in TiAu- and TiIr-based alloy systems, is observed even though the number of valence electrons, that contribute to the bonding strengths, are close to each other. This indicates that although the number of e_v is a factor in bonding, its effect must be studied along with other influencing factors such as the average atomic number (Z). With the increasing number of non-valence electrons because of increasing the average atomic number of the alloys at an almost constant bonding power (valence electrons), the interatomic bonding that keeps the ion kernels in the metallic bonds together is affected by the size and density of the kernels [6,41,62]. Higher numbers of non-valence electrons and protons in this condition reduce the bonding effects of the valence electrons and therefore reduce the elastic moduli at least in some shear directions.

4.3. Valence Electron Ratio (VER) and Transformation Temperatures

The average ratio of valence electrons (VER) of an alloy can be defined as the ratio of the number of valence electrons to the total number of electrons of the alloy, $VER = (e_v/e_t)$, which can be simply calculated as follows (equation (3)):

$$VER = \frac{e_v}{e_t} = \frac{f_{Ti}e_v^{Ti} + f_{Au(Ir)}e_v^{Au(Ir)} + f_T e_v^T + f_Q e_v^Q}{f_{Ti}Z_{Ti} + f_{Au(Ir)}Z_{Au(Ir)} + f_T Z_T + f_Q Z_Q} \quad (3)$$

where Z_{Ti} , $Z_{Au(Ir)}$, Z_T , Z_Q etc., represent the atomic numbers of Ti, Au(Ir), the ternary and quaternary elements, etc., respectively. Similarly, f_{Ti} , $f_{Au(Ir)}$, f_T , f_Q represent their corresponding atomic fractions in the alloy. Depending on the alloying elements, atomic fractions of elements comprising an alloy, different VER values have resulted. These values for the alloys examined are tabulated in Table 1. The variations of M_s and A_s temperatures versus valence electron ratio (VER) are plotted in Figure 3. In both cases, the main trend is observed with increasing the electron ratio. M_s and A_s both, decrease consistently from temperatures as high as 1550 °C with VER values as low as 0.131 down to temperatures as low as 17°C with VER values of as high as 0.174. The general trends of variation of M_s and A_s with VER are similar (Fig 3a, b).

The influence of atomic number (the total number of electrons) and e_v , the number of valence electrons of the alloys, on the transformation temperatures were discussed in previous sections. The combination of these two parameters, i.e., valence electron ratio (VER) as a more influential factor controlling the elastic properties of the crystals is discussed here. The relationship between valence electron ratio, elastic properties, and transformation temperatures of the alloys was discussed in earlier works [3,6]. It was shown that in metallic bonding the valence electrons act like ‘glue’, bonding non-valence electrons and nuclei units together [62]; whereas non-valence electrons contribute to the total atomic volume of the alloy. Increasing VER could mean thickening of the ‘glue’ bonding the ionic

kernels together. An established empirical relationship between the valence electron density and bulk modulus of metallic materials and intermetallic compounds is known. Higher VER usually results in higher bulk and therefore higher shear moduli [62,63]. Increasing VER of the TiAu- and TiIr-based alloys, therefore, is expected to result in higher elastic and shear moduli. The change of VER by replacing alloying elements for Ti and Au (Ir) is accompanied by a change in the elastic constants as the interatomic bonding is affected. A key factor controlling the bonding is the VER of the alloy. Before the martensitic transformation, the elastic moduli decrease during cooling and reach a critical value in a phenomenon known as the pre-cursor effect [2]. If the elastic moduli of B2 austenite of these alloys are enhanced because of higher VER, the cooling should continue to lower temperatures before a critical elastic constant is reached because of pre-martensitic softening of bulk and/or shear moduli, hence M_s is decreased. This is the case in nearly all alloying elements added in the present alloys that result in the transformation temperatures to reduce from that the highest M_s alloy to the lowest (Table 1). On the contrary, if the alloy has lower elastic bulk and shear moduli in the austenite phase, the critical elastic constant can be reached at higher temperatures and M_s is increased. Any alloying elements that increase the VER of the alloy, decrease the transformation temperatures. Ni, Cu, Fe, Co, Mn, Ag, etc. are examples of alloying elements in TiAu system that increase VER and lower the transformation temperatures. In case the addition of the alloying elements results in a reduction of VER, the transformation temperatures are elevated. In the tested alloys only further addition of Au, to TiAu system reduces the VER of the alloy and elevates the transformation temperatures. Similarly, further increase of Ir in TiIr-based alloys results in the decrease of VER of the alloys and leads to higher transformation temperatures (Table 1, Fig 3). M_s is determined, based on the elastic moduli of austenite and A_s follows its variation based on the thermoelastic nature and degree of reversibility of transformation for each specific shape memory alloy (SMA). These explain

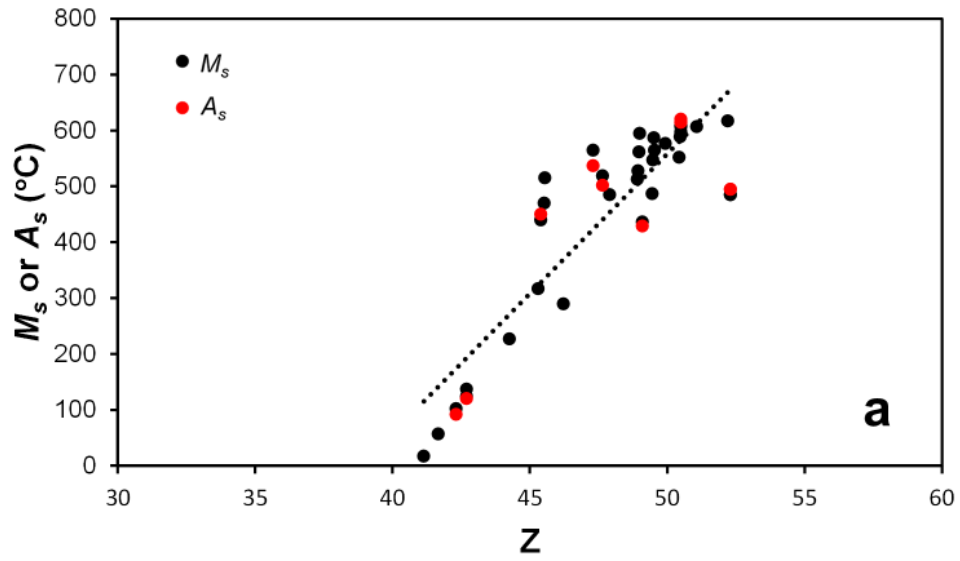
why some of the TiAu- and TiIr-based SMA compositions have higher and some others have lower transformation temperatures. Moreover, in austenite to martensite transformation in these alloys where shear is responsible for phase change from cubic to orthorhombic, the change of VER in austenite may affect the shear moduli of the crystals in different directions (C_{44} and C^* as two main shear constants of the austenite B2 cubic crystal) differently and therefore the Zener's anisotropy factor $A = C_{44}/C^*$ will be affected by VER [62,63]. The anisotropy factor in turn facilitates shear and the martensite start temperature to be changed.

The revealed trends are general and indicative of a major and clear underlying influence of VER on the transformation temperatures. This correlation provides an overall criterion for the design of the alloys with the desired service temperature. However, comparisons at small differences in temperature or compositions with reference to this overall trend are not recommended (Fig 3). Details of the microstructural features and deformation regime of the alloy need to be known for comparisons in small differences between the alloys. However, VER proves to be the most influential factor dominating the transformation temperatures.

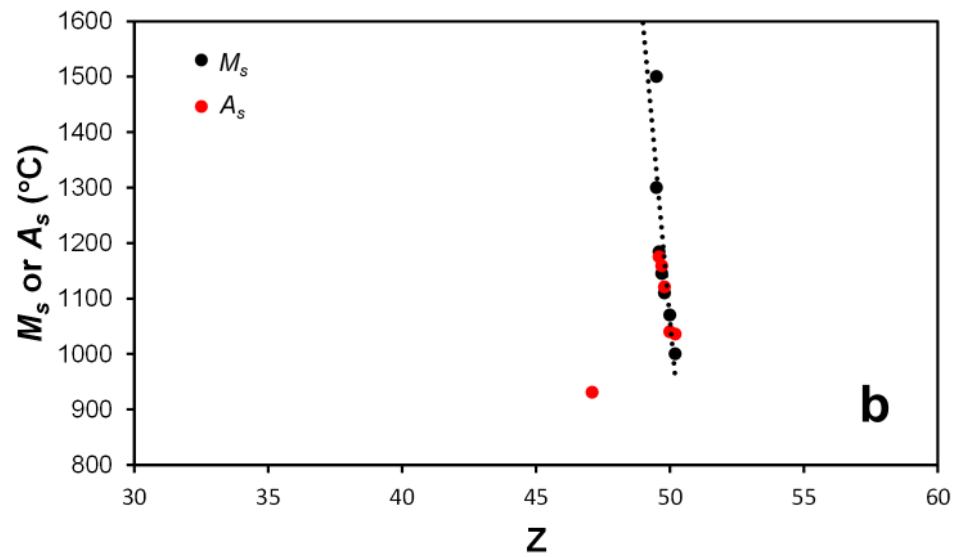
The investigation is based on the theory of electronic basis of the mechanical property of materials (in this case elastic properties of crystal in phase transformation) and successfully links the transformation temperature of these alloys to their fundamental subatomic (electron) parameters. To do this, VER was used to show how the alloying elements influence the martensitic and reverse transformation temperatures in shape memory alloys. This approach is rather unique. It correlates a characteristic of the alloys (Transformation temperature) to a fundamental electron parameter by linking this electron parameter (VER) to metallic bonding and elastic properties of the crystal. This finding is based on an established solid-state physics knowledge of the electronic basis of the strength of materials by using empirical results from the literature.

4. Conclusions

The main correlations shown in this work confirm clear dependence of the transformation temperatures of TiAu-bases and TiIr-based alloys on the most dominant factor, i.e., valence electron ratio (VER), of these transition metal shape memory alloys. Alloying elements and in general, alloy chemistry influences the number and ratio of valence electrons of TiAu-based and TiIr-based shape memory alloys and, changes the transformation temperatures through their effects on elastic properties of the crystals. M_s and A_s both significantly decrease with increasing VER from 0.131 to 0.174. This gives rise to transformation temperatures from 1550 °C to 17°C in these alloy systems. VER is a major parameter of importance that can be utilized to take concrete steps toward successful alloy design with the desired service temperatures.

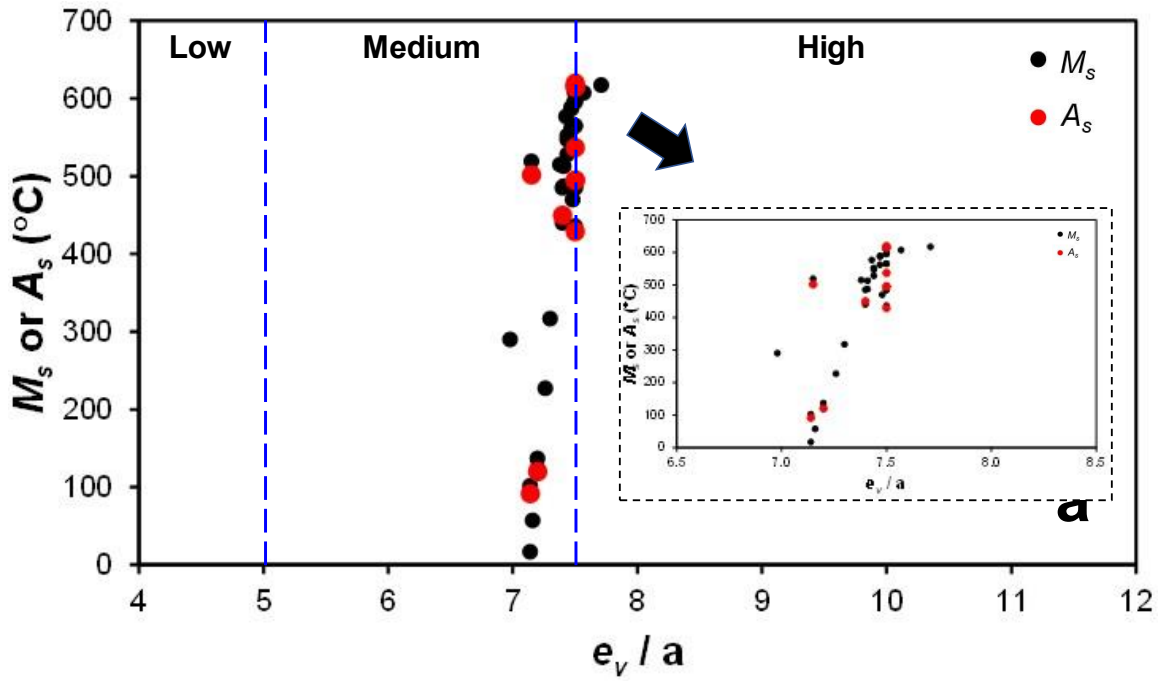


(a)

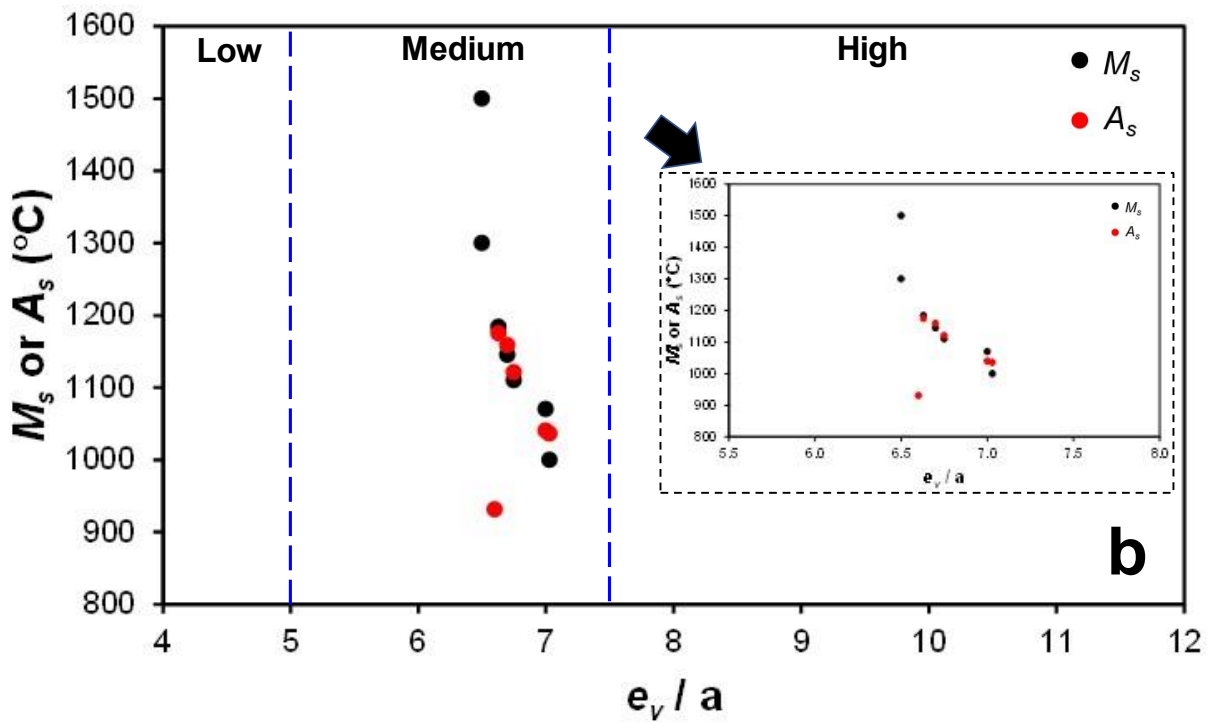


(b)

Figure 1. Transformation Temperatures vs. Z : Variations of Martensite start (M_s) and Austenite start (A_s) temperatures with average atomic number (Z) of (a) TiAu-based alloys (b) TiIr-based alloys.

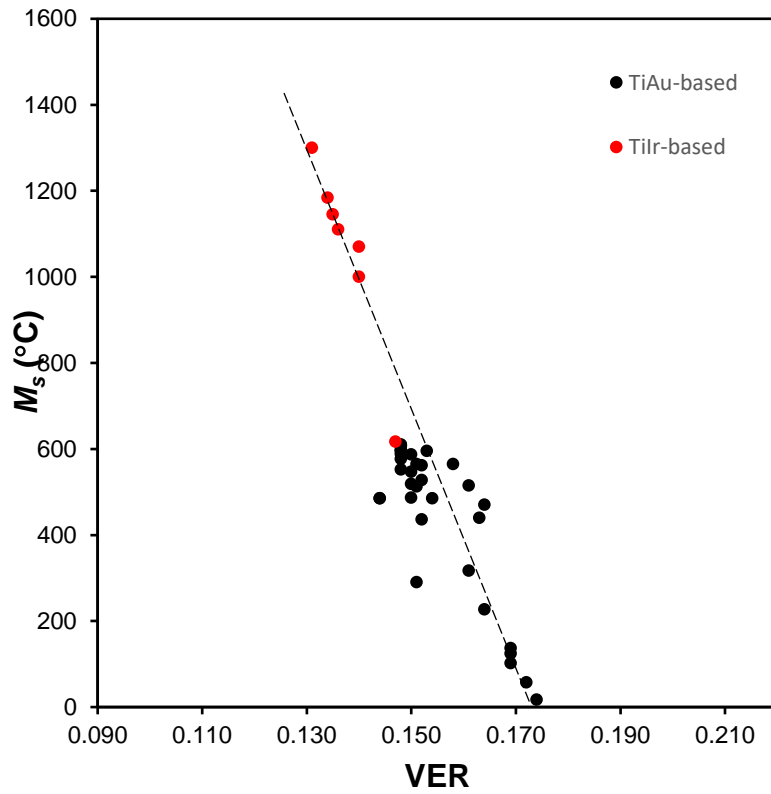


(a)

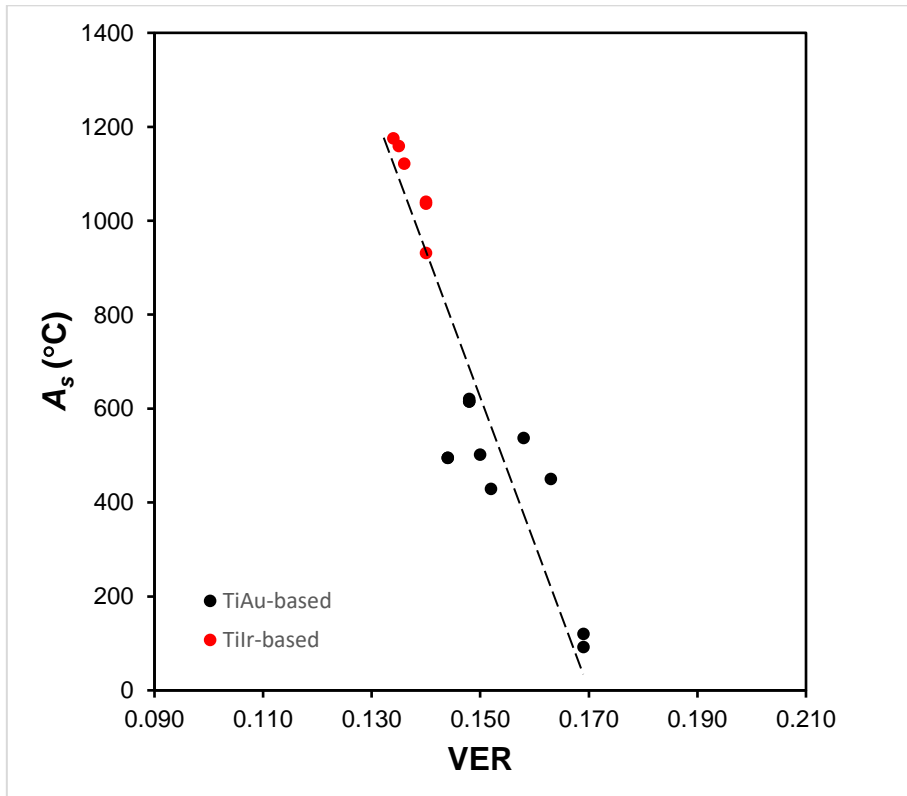


(b)

Figure 2. Transformation Temperatures vs e_v/a : Variations of M_s and A_s with the number of valence electrons (e_v) of (a) TiAu-based and (b) TiIr-based alloys. The smaller plots show the same data in more focus, i.e with narrower e_v range.



(a)



(b)

Figure 3. Transformation Temperatures vs. VER: Dependence of M_s and A_s on the Valence Electron Ratio (VER) of the TiAu-based and TiIr-based alloys: (a) Martensite start (M_s); and (b) Austenite start (A_s) temperatures.

Table 1. Martensite start temperature (M_s), Austenite start temperature (A_s), temperature hysteresis, number of valence electrons per atom (e_v/a), Valence Electron, Ratio (VER) and average atomic number (Z) of TiAu-based and TiIr-based shape memory alloys. The references show the sources of transformation temperatures and hysteresis data.

Alloy	M_s [°C]	A_s [°C]	Hysteresis [°C]	e_v	VER	Z	Reference
Ti ₅₀ Au ₃₂ Co ₁₈	17	-	-	7.14	0.174	41.14	[42,43]
Ti ₅₀ Au ₃₃ Co ₁₇	57	-	-	7.16	0.172	41.66	[42,43]
Ti ₅₀ Au ₃₄ Co ₁₅ Nb ₁	102	92	53	7.14	0.169	42.32	[42,44]
Ti ₅₀ Au ₃₅ Co ₁₅	124	120	37	7.20	0.169	42.70	[42,44]
Ti ₅₀ Au ₃₅ Co ₁₅	137	-	-	7.20	0.169	42.70	[42,43]
Ti ₅₀ Au ₃₈ Co ₁₂	227	-	-	7.26	0.164	44.26	[42,43]
Ti ₅₀ Au ₄₀ Co ₁₀	317	-	-	7.30	0.161	45.30	[42,43]
Ti ₄₀ Au ₄₀ Ag ₁₀ Zr ₁₀	436	429	49	7.50	0.152	49.10	[45]
Ti ₅₀ Au ₄₀ Ni ₁₀	440	450	-	7.40	0.163	45.40	[46]
Ti _{48.73} Au _{40.09} Ni _{11.18} Co _{0.059}	470	-	-	7.48	0.164	45.52	[47]
Ti ₄₀ Au ₅₀ Zr ₁₀	485	495	43	7.50	0.144	52.30	[48,49]
Ti ₄₀ Au ₅₀ Zr ₁₀	485	495	43	7.50	0.144	52.30	[45,48]
Ti ₅₀ Au ₄₅ Co ₅	485	-	-	7.40	0.154	47.90	[42,43]
Ti ₅₀ Au ₄₇ Ru ₃	487	-	-	7.41	0.150	49.45	[50]
Ti ₅₀ Au ₄₇ Fe ₃	513	-	-	7.41	0.151	48.91	[50]
Ti _{50.53} Au _{40.44} Ni _{9.03} Co _{0.086}	515	-	-	7.38	0.161	45.55	[51]
Ti ₅₅ Au ₄₅	519	502	42	7.15	0.150	47.65	[52]
Ti ₅₀ Au ₄₇ Co ₃	528	-	-	7.44	0.152	48.94	[50]
Ti ₅₀ Au ₄₇ Rh ₃	547	-	-	7.44	0.150	49.48	[50]
Ti ₅₀ Au ₄₇ Ir ₃	552	-	-	7.44	0.148	50.44	[50]
Ti ₅₀ Au ₄₇ Ni ₃	562	-	-	7.47	0.152	48.97	[50]
Ti ₅₀ Au ₄₇ Ag ₃	565	-	-	7.50	0.151	49.54	[50]
Ti ₅₀ Au ₄₀ Ag ₁₀	565	537	64	7.50	0.158	47.30	[45]
Ti ₅₁ Au ₄₉	577	-	-	7.43	0.148	49.93	[42,53]
Ti ₅₀ Au ₄₇ Pd ₃	587	-	-	7.47	0.150	49.51	[50]
Ti ₅₀ Au ₄₇ Pt ₃	589	-	-	7.47	0.148	50.47	[50]
Ti ₅₀ Au ₄₇ Cu ₃	595	-	-	7.50	0.153	49.00	[50]
Ti ₅₀ Au ₅₀	597	615	38	7.50	0.148	50.50	[45,54]
Ti ₅₀ Au ₅₀	597	615	-	7.50	0.148	50.50	[55]
Ti ₅₀ Au ₅₀	607	-	-	7.50	0.148	50.50	[42,43]
Ti ₄₉ Au ₅₁	607	-	-	7.57	0.148	51.07	[42,53]
Ti ₅₀ Au ₅₀	609	-	-	7.50	0.148	50.50	[50]
Ti ₅₀ Au ₅₀	610	620	-	7.50	0.148	50.50	[46]
Ti ₄₇ Au ₅₃	617	-	-	7.71	0.147	52.21	[42,53]
Ti ₅₅ Pt ₃₅ Ir ₁₀	-	931	-	6.60	0.140	47.10	[56,57]
Ti ₅₀ Ir _{12.5} Pt _{37.5}	1000	1036	25.1	7.03	0.140	50.2	[57-58]
Ti ₅₀ Ir ₅ Pt ₄₅	1070	1040	65	7.00	0.140	50.0	[57,59]
Ti ₅₀ Ir ₂₅ Pt ₂₅	1110	1121	80	6.75	0.136	49.80	[57,58]
Ti ₅₀ Ir ₃₀ Pt ₂₀	1145	1159	44	6.70	0.135	49.70	[57,58]
Ti ₅₀ Ir _{37.5} Pt _{12.5}	1184	1175	34	6.63	0.134	49.60	[57,58]
Ti ₅₀ Ir ₅₀	1300	-	-	6.50	0.131	49.50	[60]
Ti ₅₀ Ir ₅₀	1550	-	-	6.50	0.131	49.50	[61]

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Declaration of competing interest

The authors declare no competing financial interests.