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$L1_2$-type ternary titanium aluminides as electron concentration phases

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The structural change from aluminium-rich titanium aluminides ($TiAl_2$ or $TiAl_3$) to $L1_2$ type ternary titanium aluminides is examined in terms of the two alloying variables; these are atomic radius ratio (R_A/R_B) and electron concentration (e/a). Similarity in the stoichiometry of the $L1_2$ alloys (generally $Ti_{25}X_8Al_{66}$ where X = Cr, Mn, Fe, Co, Ni, Pd, Ag or Zn) and the differences in the atomic radii of ternary alloying elements makes it difficult to use R_A/R_B criterion as an alloy variable. It is also found that the structural change in these alloys cannot be explained by the classical definition of e/a because it gives an increase in this ratio rather than a decrease upon the addition of the ternary alloying element to $TiAl_2$ or $TiAl_3$. On the other hand, if a definition given by the Engel–Brewer theory is used, a decrease in e/a is found to occur upon the addition of ternary alloying element to either $TiAl_2$ or $TiAl_3$ with the consequence of achieving $L1_2$-type ternary titanium aluminides at definite e/a values around 2.5.

1. Introduction

The alloying variables atomic radius ratio (R_A/R_B) and electron concentration (valence electrons per atom, e/a) have been shown to change the crystal structure of closed-packed AB_3-type ordered intermetallic compounds [1–4]. Such a change from ordered-hexagonal to ordered-cubic crystal structure by alloying is extremely important in terms of alloy design because it affords a very effective means of improving the ductility of thousands of binary intermetallic compounds that generally do not possess such properties.

Pettifor [5] introduced structure maps where he not only phenomenologically described the presence of AB-, AB_2-, AB_3-type crystal structures by a single coordinate Mendeleev number, but also developed pseudo-binary structure maps that could be very helpful for the design of new ternary and quaternary alloys. However, for genuine alloy design, one needs to know the extent of solubility and type of substitution of the ternary or the quaternary alloying additions as well. Without this information, it is quite difficult to utilize fully the pseudo-binary structure maps of Pettifor.

In recent study [6], we examined the possibility of ternary alloying element substitution (iron or nickel) for titanium in $L1_2$-type $Ti_{26}Fe_8Al_{66}$ and $Ti_{26}Ni_8Al_{66}$ ternary titanium aluminides, rather than for aluminium, the latter substitution being consistently assumed in the literature so far. We stated that ternary alloying element substitution for aluminium or titanium in these alloys would violate the electron concentration criterion, because in both cases such a substitution would lead to an increase in the electron concentration. Hence, we utilized the R_A/R_B criterion and concluded that ternary alloying element substitution for titanium satisfies this latter criterion with the consequence of an agreement for all $L1_2$-type ternary titanium aluminides reported in the literature [7–18]. Such a conclusion also has an important implication with regard to the pseudo-binary structure maps. In this case, because the $L1_2$-type ternary titanium aluminide is $TiAl_2$-based rather than $TiAl_3$-based, the pseudo-binary structure maps should be made for AB_2 systems rather than AB_3 systems as was done by Pettifor [5].

The aim of this study was to develop our views further on the structural transformation in these alloys and examine the problem from an electronic structure point of view. Thus, in this paper we re-examine the second alloy variable, electron concentration, in $L1_2$-type ternary titanium aluminides in terms of both the classical definition and in terms of a definition given in the Engel–Brewer theory. We also summarize studies on the currently known $L1_2$-type ternary titanium aluminides, studies that utilized the alloy variables, as well as Engel–Brewer theory and its mode of calculation of electron concentration in these alloys. Finally, the observed trends in these alloys, with regard to both alloy variables R_A/R_B and e/a are discussed.

2. Summary

2.1. $L1_2$-type ternary titanium aluminides

Because of their low density and good oxidation properties, aluminium-rich titanium aluminides are considered as potential candidate materials for intermediate temperature applications (700–900 °C). However, they are brittle at ambient temperatures because of their complex crystal structures that, in turn, limit

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TABLE I Currently known $L1_2$-type ternary titanium aluminides

Alloy (Ti–X–Al)	Reference	Atomic radius of X (nm)[a]
$Ti_{25}Ag_8Al_{67}$	[19]	0.144
$Ti_{25}Co_8Al_{67}$	[18]	0.125
$Ti_{25}Cr_8Al_{67}$	[15, 17]	0.128
Ti_2CuAl_5	[8–10, 13]	0.128
$Ti_8Fe_3Al_{22}$	[10, 11, 13]	0.128
$Ti_{25}Mn_8Al_{67}$	[14, 15]	0.118
$Ti_{25}Ni_8Al_{67}$	[8, 10, 12, 13]	0.125
$Ti_{25}Pd_8Al_{67}$	[16]	0.137
$Ti_{25}Zn_9Al_{66}$	[7]	0.137

[a] Goldschmidt atomic radii of the ternary alloying element are taken from Reference 20.

bulk deformation behaviour for these alloys. A possible means of overcoming this brittleness is macroalloying, which changes the crystal structure to an ordered fcc ($L1_2$) form which could afford the necessary number of slip systems.

Since the pioneering work of Raman and Schubert [7, 8] in the 1960s, several $L1_2$-type ternary titanium aluminides have been reported in the literature. A list is given in Table I.

Some common features of these alloys with regard to composition can be noted as follows.

1. The amount of aluminium and titanium in these alloys is around 67 and 25 at %, respectively.
2. All the ternary alloying elements belong to the fourth and fifth periods of the Periodic Table with a composition of around 8 at %, except for copper, which is around 12.5 at %.
3. All the ternary alloying elements have smaller Goldschmidt atomic radii than either aluminium (0.143 nm) or titanium (0.147 nm). The only exception being silver which has a slightly higher atomic radius than aluminium.

2.2. Alloy variables; R_A/R_B and e/a

In predicting the solid solubility limits for pure metals, Hume-Rothery *et al.* [21] proposed that atomic size, electrochemical and valence effects are the primary factors. Although these factors are assumed to be the major variables that determine the stability of an alloy [22], there have been numerous reports in the literature on attempts that use one of these variables and examine the problem within only this domain and ignore the contribution of other factors. A recent example of such an approach can be seen in studies that attempt to explain ambient temperature brittleness of $L1_2$-type AB_3 ordered intermetallics in terms of only the differences in valence [23], electronegativity [24], or size [25].

Similar approaches were utilized in the 1960s to explain the structural change from ordered-cubic to ordered-hexagonal structures in AB_3-type ordered intermetallic compounds. The structural changes in rare-earth trialuminides were related to the atomic size ratio, R_A/R_B, by van Vucht and Buschow [3]. In this study, it was shown experimentally that, as the R_A/R_B ratio increased, one obtained an ordered-hexagonal structure. In another study by Sinha [1, 2], on transition metal AB_3 type intermetallic compounds, a similar type of structural change is related to an increase in electron concentration (e/a) or valence.

These two alloy variables, i.e. R_A/R_B and e/a, were utilized by Liu in the early 1970s and this led to the development of a series of $L1_2$-type ternary and quaternary $(Fe, Co, Ni)_3V$ intermetallic compounds with very good mechanical properties [26, 27]. To our knowledge, this is the first successful attempt, published in the literature, that genuinely uses both alloy variables to achieve desired properties through structural change introduced by macroalloying.

2.3. Engel–Brewer theory and a "new definition" of electron concentration

The theory is based on the idea by Engel [28–33] that correlates crystal structure of a pure metal or an alloy to only the outer-shell (s + p) electrons. Such a correlation excludes the direct effect of d-electrons in transition metals and f-shell electrons in rare-earth metals to the crystal structure. The stability range of each structure, in terms of electron concentration, is given as 1–1.75 for bcc, 1.8–2.2 for hcp, and 2.25–3 for fcc crystal structures [28–32]. In the early 1960s, Brewer [34, 35] utilized the data on the "electronic states of gaseous atomic elements" and gave not only very strong experimental evidence and an explanation for the validity of Engel correlations, but also a high degree of predictability of crystal structures; better than any other theory available at that time [33, 36]. The theory was further developed by Brewer [34, 35] to predict phases present in unknown binary systems.

Now, let us analyse electron concentration as a variable in terms of the "classical definition" and the "new definition" within the context of the Engel–Brewer theory. With regard to the first definition, electron concentration is defined as the number of electrons per atom present in the outermost shell (s + p for non-transition elements and s + d for transition elements) of an element or an intermetallic compound [3]. Hence, an $L1_2$-type intermetallic compound like Ni_3Al has an electron concentration of 8.25 [37]; this is the average sum for each element, where $(e/a)_{Ni} = 10$ and $(e/a)_{Al} = 3$. Similarly, DO_{22}-type Ni_3V has an electron concentration of 8.75, where $(e/a)_{Ni} = 10$ and $(e/a)_V = 5$.

On the other hand, the Engel–Brewer theory takes into consideration only the (s + p) electrons as the structure-determining variable, where d-shell electrons have an indirect effect [38]. According to the theory, the electronic state of an element in an alloy is not independent of the other elements present in the system. An element is assumed to establish its "valence" depending on the particular environment. Hence, the interaction between a non-transition element and another non-transition element is different from the interaction between a non-transition element and a transition element. This is basically the result of the distinction between (sp)–(sp) outer-shell interactions in the first case and (sp)–(dsp) outer-shell interactions in the second case. Now let us examine

TABLE II Electron concentration of the $L1_2$-type ternary titanium aluminides in terms of "classical definition" $(e/a)_c$ and Engel–Brewer theory $(e/a)_{E-B}$

Alloy (Ti–X–Al)	Electronic configuration of X, ground state	$(e/a)_c$	Electronic configuration of X, metallic state	$(e/a)_{E-B}$	Electronic configuration of X in ternary alloy
$Ti_{25}Cr_8Al_{67}$	. . . d^4s^2	3.49	. . . d^5s	2.51	. . . d^6s^0
$Ti_{25}Mn_8Al_{67}$	. . . d^5s^2	3.57	. . . d^6s	2.51	. . . d^7s^0
$Ti_8Fe_3Al_{22}$	. . . d^6s^2	3.85	. . . d^7s	2.49	. . . d^8s^0
$Ti_{25}Co_8Al_{67}$	. . . d^7s^2	3.73	. . . d^7sp	2.51	. . . d^9s^0
$Ti_{25}Ni_9Al_{66}$	. . . d^8s^2	3.88	. . . d^7sp^2	2.48	. . . $d^{10}s^0$
$Ti_{25}Pd_8Al_{67}$	. . . d^8s^2	3.81	. . . d^7sp^2	2.51	. . . $d^{10}s^0$
Ti_2CuAl_5	. . . $d^{10}s$	4.25	. . . d^8sp^2	2.50	. . . $d^{10}s$
$Ti_{25}Ag_8Al_{67}$	. . . $d^{10}s$	3.89	. . . d^8sp^2	2.51	. . . $d^{10}s$
$Ti_{25}Zn_9Al_{66}$	. . . $d^{10}s^2$	4.06	. . . $d^{10}sp$	2.66	. . . $d^{10}sp$
$TiAl_3$		3.25		2.75	
$TiAl_2$		3.33		2.67	

electron concentrations of Ni_3Al and Ni_3V within the context of this theory.

The Engel–Brewer theory gives the electronic configuration of the two f c c metals, nickel and aluminium, as, $1s^22s^22p^63s^23p^63d^74s4p^2$ for nickel, and $1s^22s^22p^63s3p^2$ for aluminium. The average sum of the (sp) electrons in Ni_3Al leads to a value of $(e/a)_{Ni_3Al} = 3$. In other words, in Ni_3Al, there is an interaction between nickel and aluminium atoms. Such an interaction moves (sp) electrons of nickel to the d-shells and leaves the s-shell vacant for the aluminium s-shell electrons. This leads some of the nickel atoms (25 at %) to the . . . $3d^{10}4s^04p^0$ electronic state. Hence, the rest of the nickel atoms (50 at %) are going to be in the normal state . . . $3d^74s4p^2$ and 25 at % aluminium atoms will remain in the same electronic configuration . . . $3s3p^2$. This gives an average electron concentration of $(e/a)_{Ni_3Al} = 2.25$. A similar analysis of electron concentration within the context of Engel–Brewer theory can also be given for Ni_3V. Bcc vanadium metal has the electronic structure of $1s^22s^22p^63s^23p^63d^44s$. In Ni_3V, because both nickel and vanadium have d-shell electrons, the interaction of nickel with vanadium will not lead to a considerable change in the (sp) shell electrons for both elements. If we assume a very small effect due to this interaction, then for Ni_3V, e/a will be 2.5. It should be remembered that the main difference between Ni_3Al and Ni_3V is that nickel is interacting with a non-transition element, aluminium, in the first case and nickel interacting with a transition element, vanadium, in the second case.

Besides this difference in interaction, the number of d-shell electrons in the transition element is also considered important in determining the crystal structure of the particular intermediate phase or intermetallic compound indirectly. This point can further be clarified by the analysis of equiatomic NiAl and TiAl intermetallic compounds within the context of the Engel–Brewer theory [39, 40]. Nickel in the metallic state has an electronic configuration of . . . $3d^7sp^2$. As described above, when nickel interacts with aluminium, the (sp) electrons will move to the d-shell. Then, in NiAl, we have 50 at % Ni atoms in the . . . $d^{10}s^0p^0$ electronic configuration and 50 at % Al atoms in the . . . $3s3p^2$ state. This leads to a value of $(e/a)_{E-B} = 1.5$ for NiAl. According to Engel's correlation, the upper limit of e/a for b c c metals or alloys is 1.5 and this places the ordered b c c NiAl to have a B2-type crystal structure in this category. Titanium in the metallic state, has an electronic configuration of . . . d^2sp at room temperature. When it interacts with aluminium, its electronic configuration does not change much because of the small number of d-shell electrons (i.e. less than 5) it possesses. Hence, for TiAl, which has an ordered f c c $L1_0$-type crystal structure, $(e/a)_{E-B}$ is equal to 2.5. This value is again consistent with the Engel correlation given for f c c metals or alloys.

As shown in the above analysis, the classical definition of electron concentration and the definition in terms of the Engel–Brewer theory lead to different values of electron concentration. In the next section, we will examine the electron concentration of $L1_2$-type ternary titanium aluminides within the context of classical definition and the definition given in the Engel–Brewer theory. As indicated, the latter introduces an "interactive term" to its computation of electron concentration of alloys.

2.4. Electron concentration of $L1_2$-type ternary titanium aluminides

The electron concentration of $L1_2$-type ternary titanium aluminides, in terms of these two definitions, is given in Table II. In calculating the e/a values for ternary titanium aluminides a similar procedure to that as described in Section 2.3 was utilized. In order to make e/a calculations clearer, the electronic configurations of the ternary alloying element in the ground state, metallic state, and in the ternary alloy are also given in Table II. Different from the binary case, we assumed that the only interaction in the system is that of the ternary alloying element and aluminium. Such an assumption excludes the interaction between aluminium–titanium, and titanium–ternary alloying element. Because the d-shell electrons of titanium are not high (i.e. less than 5), the assumption can be regarded as a fairly good approximation, especially in cases where the ternary alloying element is another transition element. Zinc is the only non-transition ternary alloying element in these alloys and it leads to an electron concentration of 2.66; different from the other $L1_2$-type ternary titanium aluminides. In calculating this value we did not consider any interaction term because the d-shell electrons of zinc are complete (see Table II). Hence, this difference in electron concentration can be attributed to the different type of interaction mechanism between Zn–Ti and Zn–Al, and our assumption only involves transition metal–aluminium interaction.

As shown in Table II, the addition of a ternary alloying element to $TiAl_3$ or $TiAl_2$ leads to an increase in $(e/a)_c$ and this violates the electron concentration criterion developed for transition metal intermetallic compounds [3, 4] to explain the structural transformation in these alloys. On the other hand, addition of a ternary alloying element to $TiAl_2$ or $TiAl_3$ leads to a decrease in $(e/a)_{E-B}$. Hence, it is possible to obtain a reduction in electron concentration if we only consider outer-shell (sp) electrons as structure-determining electronic configuration, and assume an interaction between the ternary alloying element and aluminium.

Such a result has two important implications. The first one is the validity of the electron concentration criterion, as defined within the context of the Engel–Brewer theory, in explaining the structural transformation in $L1_2$-type ternary titanium aluminides. The second one is the occurrence of these $L1_2$-type ternary aluminides at nearly the same electron concentration which is around 2.5. Both of these may help us to design new ternary and quaternary alloys with the desired properties.

3. Discussion

In our initial work [6], we examined the $L1_2$-type ternary titanium aluminides in terms of the classical definition of electron concentration $(e/a)_c$ and atomic radius ratio criteria $R_A R_B$ and proposed that in these alloys the ternary alloying element substitutes for titanium rather than for aluminium, in contrast to assumptions made in the literature so far. The conclusions of that study [6] are essentially based on the difficulties associated with using $(e/a)_c$ to explain the structural transformation observed in these alloys. Hence, we emphasized the importance of geometrical considerations and explained the transformations in these alloys in terms of atomic radius ratio criterion. However, it appears that two critical points are associated with the use of this approach.

The first one is related to the occurrence of these alloys within the same composition limits although the atomic radius of the ternary alloying elements utilized differ considerably (Table I). Especially in the case of the ternary alloying element silver, with a similar atomic radius to aluminium and titanium, an easy explanation of the structural transformation is not allowed and its similar stoichiometry of $Ti_{25}Ag_8Al_{67}$ to the other ternary alloys that have smaller atomic radius than either titanium or aluminium makes this explanation more difficult still.

The second critical point is more general, and can be related to the use of a single alloy variable (R_A/R_B or $(e/a)_c$) in explaining the phase stability of these geometrically closed packed ternary alloys. As discussed earlier, both of these variables have been utilized successfully in the past to explain the observed trends in AB_3-type intermetallic compounds. However, in both approaches [1–4], the specified alloy variable had been taken as an independent alloy variable. That is, only elemental state properties were considered without any interaction term that emanates from the presence of the element in an alloy. In other words, could we assume the atomic radius of an element A (or B) to be the same in an AB_3-type intermetallic compound as it was in the elemental state? Similarly, how reasonable is it to calculate the electron concentration of an AB_3-type intermetallic compound by simply taking the average sum of the electron concentration of A and B elements? Obviously an alternative thinking is required here.

As indicated earlier, the definition of electron concentration given in the Engel–Brewer theory $(e/a)_{E-B}$ does involve an interaction term. Electron concentration in this case is not an independent variable and is determined by the electronic configuration of the elements in the alloy. Hence, due to this interaction term, $(e/a)_{E-B}$ may give a more complete description of the electron configuration assumed by the alloy and thus of the observed trends.

The analysis given for $L1_2$-type ternary titanium aluminides in the previous section showed that the structural transformation in these alloys can be explained by an electron concentration criterion (with a decrease in e/a in the transformation from DO_{22} to $L1_2$) if it is defined in terms of the Engel–Brewer theory. As shown in Table II, the addition of ternary alloying elements to $TiAl_2$ (or $TiAl_3$) leads to an increase in $(e/a)_c$ and this violates the observed structures (the transformation should then be towards rectangular packing.) On the other hand, ternary alloying element addition to $TiAl_2$ (or $TiAl_3$) leads to a decrease in $(e/a)_{E-B}$ with the consequence of more cubic structures, as have been reported in the literature so far. If the latter case is correct, as it seems to be, then these alloys can be regarded as electron concentration phases that occur at definite values of $(e/a)_{E-B} = 2.5$.

Another important point in the transformations observed in these alloys is the type of substitution and hence the nature of transformation. So far it has been uniformly assumed in the literature that, in these alloys, the ternary alloying element substitutes for aluminium and the transformation takes place from $TiAl_3 to L1_2$. In our previous work [6], based on the validity of the atomic radius ratio criterion, we questioned the validity of this assumption and stated that the ternary alloying element substitutes for titanium and the transformation occurs form $TiAl_2$ to $L1_2$. Because the addition of a ternary alloying element to $TiAl_2$ or to $TiAl_3$ reduces the electron concentration (see Table II) in both cases, let us examine this point again in terms of the $(e/a)_{E-B}$ criterion that we aim to develop in the present study.

In calculating the $(e/a)_{E-B}$ values we assumed that in $L1_2$-type ternary aluminides, the ternary alloying element X (X = Cr, Mn, Fe, Co, . . .) only interacts with aluminium and because of this interaction the elements Cr, Mn, Fe, Co, Ni, Pd take zero valence configuration and a valence of one is assumed for elements copper and silver. In the fcc unit cell of an $L1_2$-type AB_3 intermetallic compound there are two distinct lattice sites. The first type of site is the cube corners ⟨0, 0, 0⟩ and is occupied by A atoms. The second type of site is the cube faces ⟨0, 1/2, 1/2⟩ and is occupied by B atoms. Hence, in an $L1_2$-type crystal structure A atoms have 12 B atoms as nearest neighbours, whereas B atoms have 4 A atoms and 8 B atoms as nearest neighbours. Now if we assume that the ternary alloying element in these alloys occupy cube corners, than it will have more aluminium atoms as nearest neighbours than if it occupies the cube faces. Hence, it is energetically more favourable for the ternary alloying element to occupy the cube corner sites so that the interaction with aluminium leads to the valence states given above and reduction in electron concentration. If this is the case, then the ternary alloying element in these alloys substitutes for titanium and the transformation is occurring from $TiAl_2$ to ternary $L1_2$.

Several remarks can be made with regard to the *e/a* or valence values of the ternary alloying elements in these alloys. The first one is about the similarity of the valences of the ternary alloying elements Fe, Co, Ni, Pd, Cu and Zn with the values given by Barrett and Massalski [41], where they defined the valence as "the number of electrons in excess of the last complete shell". However, differing from their values that are given for metals in the elemental state, the values given in Table II were calculated due to the interaction of the ternary alloying element with aluminium.

The second remark on the valence values of the ternary alloying elements in these alloys is the zero valence of all the elements to the left of copper in the first transition series of the Periodic Table. All these ternary alloying elements (Cr, Mn, Fe, Co, and Ni) have more than 5 d-shell electrons in their metallic state (see Table II). As discussed previously, according to the Engel–Brewer theory, the number of d-shell electrons is important in determining the valence state of an element in an alloy. According to the Engel–Brewer theory, if an element has less than 5 d-shell electrons, it may promote electrons from the d-shell to its sp-shell upon its interaction with other elements. Hence, we expect the elements scandium and vanadium, which belong to the first transition series, to have different valence states from zero in titanium aluminides because they have less than 5 d-shell electrons (1 d-shell electron for scandium and 4 d-shell electrons for vanadium, according to the Engel–Brewer theory). In other words, the addition of scandium or vanadium to aluminium-rich titanium aluminides will increase the electron concentration of these alloys because of the promotion of electrons from d-shell to sp-shells. This may explain the absence of $L1_2$-type ternary titanium aluminides of scandium and vanadium, although they belong to the first transition series like the other ternary alloying elements (Cr, Mn, . . .) which form these types of alloy.

4. Conclusion

In this study we examined the possibility of using the electron concentration definition given in the Engel–Brewer theory, $(e/a)_{E-B}$ to explain the observed trends in $L1_2$-type ternary titanium aluminides. Our analysis showed that these ternary alloys (with the exception of $Ti_{25}Ag_8Al_{67}$ and $Ti_{25}Zn_9Al_{66}$) occur at nearly the same $(e/a)_{E-B}$ of 2.5. It is also found that, due to energetic considerations, the ternary alloying element should substitute for titanium rather than for aluminium and the transformation possibly occurs from $TiAl_2$ to ternary $L1_2$ rather than from $TiAl_3$ to ternary $L1_2$-type titanium aluminide. The main conclusion of this study is the notion that $L1_2$-type ternary titanium aluminides can be regarded as electron concentration phases if the definition of electron concentration given in the Engel–Brewer theory is used.

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