Characteristic Mechanical Properties and Phase Stability of L1₂ Intermetallic Compounds

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Synopsis
The present paper deals with the occurrence and magnitude of characteristic mechanical anomalies observed in many L1₂ intermetallic compounds and their relation to the phase stability of the crystal structure against other geometrically close packed (GCP) phases. The dislocation configurations in the crystal structure and resultant plastic behavior are in close relation with anti-phase boundary (APB) and stacking fault (SF) energies in the compounds, while the relative magnitude of these energies on various crystallographic planes actually determines the phase stability of the L1₂ crystal structure. It is shown here, based on our series of investigations carried out over the past decade, that the general tendencies for particular deformation modes to occur can be systematically interpreted in terms of alloy chemistry of the compounds, including variables such as combination of component species, nonstoichiometry and ternary additions in the compounds, all of which affect the stability of the phase.

I. Introduction
A number of L1₂ intermetallic compounds are known to exhibit an anomalous temperature dependence of the yield strength. Actually there are two types of behavior observed in these compounds; 1) the well-known positive temperature dependence of strength as typically observed in Ni₃Al (anomalous behavior), and 2) the substantial increase in strength with decreasing temperature occurring below ambient temperature, which is similar to that normally encountered in bcc metals, for example as is observed in Pt₃Al.

The latter mechanical behavior has become of interest only quite recently, while previous research on the mechanical behavior of L1₂ compounds has mainly been concerned with the positive temperature dependence of the strength, known now for several decades. Most of these efforts have been attempted to elucidate the mechanism which gives rise to the mechanical anomaly. The temperature dependence of the flow stress of single crystalline L1₂ compounds of various crystallographic orientations subjected to tensile or compressive deformation has been examined and mechanisms involving various types of super-dislocations with different APB and SF energies have been proposed to explain the observed plastic behaviors. Among them the Kear–Wilsdorf mechanism¹,² most successfully interprets the anomalous positive temperature dependence of the strength. In this mechanism thermally activated cross slip of screw dislocations from {111} principal glide planes to {100} non-glide planes are assumed to be the cause of the strength increase. It is a fact, however, that the magnitude of the anomalous mechanical behavior is different in different compounds and furthermore, there are many L1₂ compounds that exhibit only the ordinary negative temperature dependence of strength as seen in fcc metals.

The present authors have attempted to provide a comprehensive understanding of the occurrence and the magnitude of such mechanical anomalies in terms of the phase stability of the L1₂ phase relative to other GCP phases. By phase stability we mean the relative tendency for that particular intermetallic phase of specific crystal structure to appear in an alloy system as the composition of the alloy or the combination of the components is varied. It is closely related with the physical and electro-chemical nature of the species constituting the intermetallic phases, and thus is a matter of alloy chemistry. We have carried out systematic investigations of the effect of non-stoichiometry and the effect of ternary substitutions in binary L1₂ compounds, and the analogy we have drawn is, we believe, one of few examples of a successful correlation between characteristic plastic behavior and alloy chemistry.

II. Mechanical Anomalies in L1₂ Intermetallic Compounds
Compressive flow stress-temperature curves showing the temperature dependence of the flow stress of several polycrystalline L1₂ intermetallic compounds of stoichiometric A₃B composition are shown in Figs. 1 and 2. In Fig. 1 the positive temperature dependence of the strength in the intermediate test temperature range is shown for several Ni base compounds and Co₂Ti, while in Fig. 2, the increase in flow stress with decreasing temperature is shown in several Pt-based compounds, some of which also show a slight positive temperature dependence at intermediate temperature. As to the mechanism which gives rise to these mechanical anomalies, the Kear–Wilsdorf mechanism¹,² is widely accepted to explain the positive temperature dependence of strength shown in Fig. 1, while for the behavior shown in Fig. 2, a nonplanar dislocation core structure which makes the dislocations increasingly sessile as the temperature is decreased has been proposed by Pope and his co-workers.³–⁶

* This article was presented to the 1984 Materials Research Society Fall Meeting, 1984, by the financial support of the Hyuga Fund of ISIJ. Permission has been granted to reproduce this article published in High-temperature Ordered Intermetallic Alloys, ed. by C. C. Koch, C. T. Liu and N. S. Stoloff, copyright 1985 Materials Research Society, Pittsburgh, Pennsylvania, for Transactions ISIJ by Materials Research Society. Manuscript received on March 29, 1985; accepted in the final form on May 10, 1985. © 1983 ISIJ
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According to the Kear–Wilsdorf mechanism the drag stress increases with increasing temperature due to the formation of sessile segments on the mobile screw dislocations by thermally activated cross slip from \{111\} to \{100\} planes, because in the L\textsubscript{1}\textsubscript{2} crystal structure the normal slip plane and the lowest APB energy plane are not identical. Flinn\textsuperscript{9} has shown that the \{100\} APB energy is the lowest in the L\textsubscript{1}\textsubscript{2} crystal structure. The difference between the \{111\} and the \{100\} APB energy is assumed to be the driving force for the cross slip in the Kear–Wilsdorf mechanism. But if the situation is so simple, the magnitude of the positive temperature dependence of strength would be greater for compounds with higher \{111\} APB energy. It has been shown, however, that a high \{111\} APB energy is not necessarily responsible for a more pronounced anomalous mechanical behavior because some of the Daltonide- or Berthollide-type compounds,\textsuperscript{8} in which the ordered structure is stable up to the melting point, show no such anomalous mechanical behavior.\textsuperscript{9,10}

The discussion hereafter mainly considers the relation between the positive temperature dependence of strength in L\textsubscript{1}\textsubscript{2} compounds and the phase stability of the crystal structure relative to other GCP phases. Thermally activated cross slip must occur in close relation to the anisotropy in APB energy and the resulting configurations of dissociated super-dislocations must be determined essentially by the relative magnitude of APB and SF energies.\textsuperscript{11,13} The stability of the L\textsubscript{1}\textsubscript{2} crystal structure relative to other GCP phases is also controlled by these same energies, and they also control the ordered structure and stacking sequence. In a later section, we also discuss the strong negative temperature dependence of strength shown in Fig. 2 in terms of the phase stability of L\textsubscript{1}\textsubscript{2} phase against the D\textsubscript{0}\textsubscript{3} (U\textsubscript{3}Si type) phase.

III. Phase Stability of the L\textsubscript{1}\textsubscript{2} Structure against Other GCP Phases

As stated above, the SF and APB energies on \{111\} planes are thought to be important factors determining the slip mode and strength of an L\textsubscript{1}\textsubscript{2} compound. These factors obviously affect the phase stability of the L\textsubscript{1}\textsubscript{2} compound with respect to the ordered hcp phase (D\textsubscript{0}\textsubscript{19}) and to the disordered fcc phase (Al). Regarding thermally activated cross slip in L\textsubscript{1}\textsubscript{2} compounds, the value of the APB energy on \{100\} planes is important, which is closely related to the phase stability of the L\textsubscript{1}\textsubscript{2} phase against the D\textsubscript{0}\textsubscript{22}, D\textsubscript{0}\textsubscript{23} or a long period superlattice phase. These structures are composed of unit-cells of the L\textsubscript{1}\textsubscript{2} structure but have regularly spaced antiphase boundaries on \{100\} planes spaced at a definite multiple of the unit-cell length. A family of ordered close-packed structures is known to form by various types of layers of composition A\textsubscript{3}B in various stacking sequences.\textsuperscript{16} Several notation systems have been proposed to describe the crystal structures of GCP phases.\textsuperscript{16,17} In the following discussion, we shall use the symbols T and R to indicate triangular and rectangular ordering of the atomic layers on close packed planes, as seen in the L\textsubscript{1}\textsubscript{2} and D\textsubscript{0}\textsubscript{32} structure, respectively, and the symbols c and h to denote cubic and hexagonal stacking sequences. The relative phase stabilities as influenced...
by the factors discussed above, of different GCP phases are shown schematically in Fig. 3.

In attempt to understand the relative phase stability of various types of $A_3B$ compounds, two factors have been taken into consideration: 1) the electron concentration criterion\textsuperscript{18–21} and 2) the atomic size difference criterion.\textsuperscript{22–24} Sinha\textsuperscript{18–19} has noted that an increase in hexagonality of the $A_3B$ structure is associated with an increase in electron atom ratio ($e/a$), defined as the average number of electrons outside the filled shells per atom, whereas, van Vucht pointed out that an increase in hexagonality is associated with an increase in atomic radius ratio of the components, $R_B/R_A$.\textsuperscript{23,24} These criteria predict that the crystal structure tends to shift not only in the direction of $c\rightarrow h$ stacking but also in the direction of $T\rightarrow R$ layering by an increase in either factor. It should be noted that the crystal structure of a particular phase can be expressed by such notations as $cT$ for $L1_2$, $chT$ for $D0_{24}$, $cR$ for $D0_{22}$ and $cTR$ for $D0_{23}$.

Table 1 summarizes crystal structures of $A_3B$ GCP phases of transition metals compiled from the literature for sixty possible $A$–$B$ combinations, where $A$ is a transition metal of Group 8B or 8C and $B$ is a transition metal of Group 4, 5, 6 or 7. This table first appeared in Ref.\textsuperscript{9} but is updated here. Although it is rather busy, the table shows the variation in $e/a$ ratio in the top row and the deviation of the atomic radius ratio from unity for each $B$ element (see the numbers below the $B$ elements), both of which are determined by the combination of $A$ and $B$ elements in the $A_3B$ compounds. The use of Table 1 is based on the pre-
mise that structural transitions occur in the sequence cT→ hT→ cR→ hR. When the compounds of 8C metals and the compounds of 8B metals are superimposed, as is done in the table, apparent conflicts with the electron concentration criterion can be seen, as has been pointed out by many workers.18-21 However, it is observed that the size criterion holds within a group of compounds of a given minority component (B) with the majority component (A) of the same group in the periodic table. Numerals in the second row from the top indicate (R_B−R_A)/R_A, where Goldschmidt’s atomic radius for a co-ordination number 12 is employed for the radius of the components. For instance, the hexagonality increases on changing A from Ir to Rh and to Co in an A_3B compound in which B is Nb or Ta. On the other hand, the size effect is not so great in compounds of a given majority component with a minority component of the same group.

For instance, the chT structure prevails in Pt_3Ti, Pd_3Ti and Ni_3Ti. It is to be noted that although the hT structure seems to be absent in a series of compounds of 8C metals, the occurrence of chR or hT structures has been confirmed in ternary compounds by many workers.19-21,23-28 Some of these results on ternary compounds are indicated by diagonal lines on the diagram, showing pseudo-binary alloys. Along some of these lines transitions from chchT to chhT to hT sequences are seen. Also in this table the L1_2 compounds (cT) which exhibit a positive temperature dependence of strength are marked so that the position of those compounds can be seen relative to other GCP phases. It now becomes evident that L1_2 compounds exhibiting the anomalous mechanical behavior are mostly on the boundary of L1_2 phase stability. Compounds showing a normal mechanical behavior are isolated in stable regions of the diagram surrounded by other structures, due to unknown incidental effects. For example, the L1_2 compounds of iridium with Ti group and V group metals are very stable and do not show any anomalous behavior. It is interesting to note that a strong positive or negative temperature dependence of the strength appears most frequently in compounds based on platinum and in those with titanium. Those L1_2(cT) compounds which show the anomalous positive temperature dependence of strength are near regions on the diagram where the D0_{22}(cR) phase forms. In these regions a large difference in APB energy on the {111} and {100} planes is expected and thereby provides a large driving force for the Kear–Wilsdorf mechanism. We would like to add that the stability condition for the T and R layers has been given in terms of the ratio of first-neighbor (V_1) and second-neighbor (V_2) bond energies.29-31 where if V_2/V_1 is positive the structure L1_2 (T layer) is preferred while if it is negative, the D0_{22} (R layer) is preferred.

IV. Phase Stability and the Positive Temperature Dependence of Strength

In order to describe the magnitude of the positive temperature dependence of strength in L1_2 compounds, a method to determine the activation constant for the thermally activated process is first briefly reviewed. The flow stress–temperature curve as shown in Fig. 1 should be divided into two temperature-dependent components. One is the ordinary negative temperature dependence of strength arising from the modulus change with temperature and the other is the positive temperature dependence of strength caused by thermally activated cross slip. Then the flow stress can be written in the form,

\[ \sigma = \sigma_0(1−BT)+A \exp \left( \frac{-U}{RT} \right) \]

where, \( \sigma_0 \): the flow stress at 0 K
\( U \): the activation constant
\( R \): the gas constant
\( T \): temperature
\( A, B \): constants.

A bottom temperature \( T_s \) is defined by the condition \( d\sigma/dT=0 \). These are schematically depicted in Fig. 4. The activation energy, \( U \), can be deduced by an Arrhenius plot of the flow stress after subtracting the term \( \sigma_0(1−BT) \). The smaller is the activation constant, the more extensive is the positive temperature dependence of the strength. In cases where the temperature range from the bottom to the peak in flow stress is too narrow to estimate \( U \), the bottom temperature \( T_s \) is a good index to evaluate the activation constant. It has been shown that \( T_s \) gradually shifts to higher temperatures at a constant stress level as the activation constant increases.10

Figure 5 summarizes the relationship between the activation constant and the deviation from unity in atomic radius ratio, \((R_{A}−R_{B})/R_{A}\), incorporating data for binary nickel-based and platinum-based A_3B alloys having the L1_2 crystal structure and for pseudo-binary (ternary) L1_2 compounds.10,33 In the case of pseudo-binary alloys, for example Pt_3(In, Ga), the weighted mean of atomic radius of B-subgroup elements, \( R_{B} \), is derived from the lattice spacing of the alloys, assuming that atomic radius of platinum, \( R_{A} \), is regarded as

\[ \sigma = \sigma_H + \sigma_B \]

\[ \sigma_H = A \exp(-U/RT) \]

\[ \sigma_B = \sigma_0(1−BT) \]

**Fig. 4.** A schematic representation of flow stress-temperature curve showing anomalous positive temperature dependence of strength.
that of pure fcc metal. In the figure, the reciprocal activation constant is used so as to make the value $U=\infty$ visible. An infinite value of the activation constant means that the $L_12$ alloy has the ordinary, negative temperature dependence of strength, while a zero activation constant means that the $D_022$ crystal structure is the stable phase. It is successfully shown here that there is a general trend in the relationship between the activation constant, the atomic radius ratio, and the electron concentration. The values of the activation constants of the alloys containing elements of the same B-subgroup pass smoothly through a minimum at about $(R_B-R_A)/R_A=0.05$. Both curves are quite similar in nature and the increase in the activation constant with increase in radius ratio after the minimum is very drastic. Noting that a small activation constant implies instability relative to the $D_022$ structure, 4B-subgroup elements make the $L_12$ phase less stable with respect to the $D_022$ phase than do 3B-subgroup elements.

V. Positive Temperature Dependence of Strength in Ternary $L_12$ Compounds

It has already been shown, in Fig. 5, that ternary additions to $L_12$ compounds can remarkably alter the degree of its positive temperature dependence of strength. For example, it can be seen that only a 0.1 at\% addition of Ti to Pt$_3$In results in a dramatic increase in activation constant resulting in a sudden loss of the mechanical anomaly. In this case Ti additions to the compound would not change the $e/a$ ratio but the atomic radius of Ti is larger than that of In. The present authors have shown elsewhere that Ni$_3$Ge and Fe$_3$Ge, both of which are $L_12$ but only Ni$_3$Ge shows the positive temperature dependence of strength, form continuous (Ni, Fe)$_3$Ge solid solutions and that the pseudo-binary compound loses the mechanical anomaly at about 30 at\% Ge.

Since the findings by Pope, Cu$_3$Au has been recognized as one of the $L_12$ compounds to exhibit the positive temperature dependence of strength although it is weak compared with that of Ni$_3$Al. This is reasonable to us in view of the presence of a long period superlattice structure nearby the $L_12$ phase in the Cu–Au system, implying a relatively low phase stability of the $L_12$ phase. It is well known that the morphology of anti-phase domain (APD) in Cu$_3$Au is maze-like with a strong preference for (100) planes, instead of swirl-like, as is often observed in compounds which do not show the mechanical anomaly. This fact tells us that the (100) APB energy is very low in Cu$_3$Au. We have carried out an investigation of the effect of Ni additions to the compound on the magnitude of the positive temperature dependence of strength. Ni additions are expected to decrease the $e/a$ ratio of the compound if the valence of Ni is taken to be zero and are therefore expected to enhance the phase stability of the $L_12$ structure. A comparison of the flow stress-temperature curves, normalized by the flow stress at 4 K and Young’s modulus, is shown in Fig. 6 between Cu$_3$Au and Cu$_3$Au–5 at\% Ni. It is obvious that the magnitude of the positive temperature dependence of strength, being clearly judged by an increase in $T_\alpha$, is reduced by the Ni addition and concurrently it was shown that the morphology of APD’s is swirl-like in a Cu$_3$Au–5 at\% Ni alloy.

Considerations of the effect of ternary additions on the positive temperature dependence of strength is especially important in Ni$_3$Al, which is one of the major...
microstructural constituents in Ni-base superalloys. From such a point of view, the present authors have systematically investigated the effect of ternary additions of B-subgroup elements as well as transition metal elements on the substitution behavior, solubility limit, lattice parameter, and mechanical properties of the compound. Upon additions of B-subgroup elements, for each of which the valence is strictly defined, the magnitude of the mechanical anomaly can be interpreted in terms of the phase stability concept as affected by electron concentration and the atomic size ratio in the compounds. For additions of transition metal elements, the atomic size criterion has generally been found to be most useful to interpret the relative magnitude of the mechanical anomaly. In this case the apparent valence of each element could be assigned by an analytical method in light of knowledge of the effect of B-subgroup elements additions.

VI. Effect of Deviation from Stoichiometry on the Positive Temperature Dependence of Strength

Many L1$_2$ compounds are Kurnakov or Berthollide compounds that exist over a range of compositions on either side of stoichiometry. Figure 7 shows that the positive temperature dependence of strength is considerably enhanced by increasing the Al content beyond stoichiometry. This has been shown previously. Also as is shown in Fig. 8 the activation constant for the thermally activated cross slip process decreases as the amount of minority element increases and is discontinuous at the stoichiometric composition, not only in Ni$_3$Al but also in Ni$_3$Ga.45,48)

According to our theory of the relation between the stability of the L1$_2$ phase against other GCP phases and the magnitude of the positive temperature dependence of strength, Fig. 8 implies that an increase in the minority element should reduce the stability of the L1$_2$ phase. Unfortunately, we can not find any evidence for this in the case of the results shown in Fig. 8, however, there are several cases where an increase in the minority element does give rise to a shift from the L1$_2$ to a long period superlattice structure and in which the period, M, of the structure is decreased with further increase in the minority element. Such instances can be found in the Cu–Au, Cu–Pt and Cu–Pd systems and there are more extreme cases, as in the Pt–Sb system, where the L1$_2$ (cT) structure appears at Pt$_4$Sb and the compound Pt$_4$Sb has the D0$_{29}$ (cTTR) long period superlattice structure. Sato and Toth have termed such an effect caused by an increase in the minority element (B) in A$_3$B compounds a "concentration effect". It has also been reported that an increase in minority element often results in a change from the L1$_2$ structure to hexagonal stacking (h) to yield the D0$_{29}$ (cT) structure, as is observed in the Pt–Ti, Pt–Zr, Pd–Ti and Rh–Nb systems. In view of such evidence, it appears that an increase in the minority element can provide the same effect as increasing the e/a ratio, and thereby reduce the stability of L1$_2$ phases against such GCP phases as the D0$_{29}$ and D0$_{19}$.

It should be noted that L1$_2$ compounds such as Ni$_3$Si and Ni$_3$Ge, which also exhibit a strong positive temperature dependence of strength, exist only in nonstoichiometric compositions on the Ni-rich side of stoichiometry. The relation between compositional stability range and the magnitude of the positive temperature dependence of strength has been discussed elsewhere in terms of the shape of the free energy curve of the phase in the vicinity of stoichiometry and the bond strength as affected by the valence of the minority component from B-subgroup.
VII. The Low Temperature Mechanical Behavior and Phase Stability

As has been mentioned at the beginning of this paper, there is an other type of mechanical behavior observed in L1_2 compounds that has drawn considerable interest quite recently. A substantial increase in flow stress with decreasing temperature, generally below ambient temperature, is most often observed in Pt-based compounds. Such mechanical behavior is common in bcc metals and alloys but is unusual in L1_2 compounds based on the fcc structure. There have been a series of work by Pope and his co-workers in which atomistic studies on dislocation core structures in L1_2 ordered alloys and associated Peierls stresses are performed. Recently, results by Pope et al. have conducted compression tests on single crystalline Pt3Al and found some supporting evidence for the deformation modes predicted by them. It is proposed that the strength increase at low temperatures is caused by a sessile configuration of the dislocation core structure due to SISF (superlattice intrinsic stacking fault)-type dislocation dissociation on the {111} plane. The other type of dissociation possible on the {111} plane is the APB-type which is glissile and thus does not cause a strength increase at low temperatures.

Now that the behavior is found to occur in association with a particular dislocation configuration determined by the SF and APB energies in the crystal structure, it might be possible again to discuss the occurrence and the magnitude of the behavior in terms of the phase stability of L1_2 structure against other GCP phases with various SF and APB energies. A series of investigations is now underway by the present authors on various Pt-based compounds on the effect of composition on the magnitude of the mechanical behavior. Preliminary results indicate that such compounds as Pt3Al and Pt3Ga exhibiting the low temperature strength increase exist at the stability boundary between L1_2 and the U3Si-type D0_2 phase. Currently, attempts are being made to correlate the relative phase stability of the two phases in various systems with e/a ratio as well as atomic radius ratio aiming at analytically deducing the relative magnitude of SF and APB energies in the phases. It is then hoped to be able to provide a comprehensive interpretation of the low temperature mechanical behavior of L1_2 compounds which can be coupled with the work on dislocation core structure.

VIII. Concluding Remarks

We have discussed the occurrence of particular plastic deformation modes in L1_2 intermetallic compounds in terms of the phase stability of L1_2 relative to other GCP phases. Such factors as SF and APB energies, which control the configuration of dissociated dislocations in the ordered structure, are actually determined by phase stability as affected by the composition of the compounds and are thus determined by alloy chemistry. The phase stability is essentially governed by the physical and electrochemical nature of the species constituting the phase, and therefore to understand and further to predict the magnitude of the mechanical anomalies approaches are desired in which electronic theory and solid state physics are fully utilized.

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