BONDING ENERGIES AND LONG-RANGE ORDER IN THE TRIALUMINIDES

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CONF-901105--92

DE91 007709

ABSTRACT

The degree of long-range order in the trialuminides is determined by X-ray powder diffraction techniques. Long-range order exists to their melting points. For the binary trialuminides Al_3Ti , $\text{Al}_{73}\text{Ti}_{27}$, and Al_3Sc , the degree of long-range order is nearly perfect and is a measure of the lack of mixing of the aluminum atoms onto the sublattice occupied by either Ti or Sc. A calculation of the bond energy between neighboring pairs of atoms from the ordering (melting) temperature is made following the Bragg-Williams mean field theory approach. These bond energies compare favorably with more sophisticated calculations. Bond energies are found to be larger than the energy difference between the crystal structure forms DO_{22} , Li_2 , and DO_{23} , and therefore, more relevant to understanding the mechanical and chemical behavior of the trialuminides. Ordering or melting temperatures of these intermetallics reflect the strong Al-metal near-neighbor pair potentials and may provide insights to their brittle properties.

INTRODUCTION

Trialuminides have received much attention as a possible structural material because of their low density and their good oxidation resistance [1]. However, their extreme brittleness continues to block their usage for structural purposes. Efforts to improve their ductility include alloying, rapid quenching, and powder metallurgy. Though alloys of Al_3Ti with Cr and Mn have shown limited ductility in tension of $\sim 0.5\%$ strain [2], plastic strains in excess of 2% where practical usage is possible are still elusive.

This engineering interest in trialuminides has generated a host of theoretical papers aimed at understanding their phase stability, element substitutions and cleavage behavior [for example, see refs. 3-6]. Calculations have been made of the energy difference between the various crystal structures of fully ordered stoichiometric compositions. Such calculations improve our insight to the important parameters affecting alloy behavior. So far, no obvious answers have been provided which lead to ductile trialuminides. We propose that the ordering temperature as reflected in the melting point of these trialuminides in the Bragg-Williams pairwise approximation [7], as extended by Cowley [8] gives reasonable values for the energies of interaction between neighboring pairs of atoms. We make comparisons with more accurate calculations to justify this use of ordering/melting temperature data that are readily available. Since the melting temperatures are actual experimental observations, then if they reflect the pair potentials they could provide useful insight to the mechanical behavior of these compounds. Comparisons with the more sophisticated calculations show that these pair potentials derived from the melting temperatures which are readily available do indeed reflect phase stability. Our purpose is to provide arguments why this could be and to show trends predicted by theory which are related to the melting points of the trialuminides. Existing physical information such as ordering and melting temperatures may prove useful for alloy development efforts to ductilize these intermetallics.

EXPERIMENTAL PROCEDURE

Sample Preparation

Alloys having the compositions, Al_3Ti , $\text{Al}_{73}\text{Ti}_{27}$, and Al_3Sc were fabricated. The composition $\text{Al}_{73}\text{Ti}_{27}$ was chosen to obtain a single phase on slow cooling to room temperature. Rapid cooling of the composition Al_3Ti does result in a single-phase structure at room

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temperature. To maximize chemical homogeneity in the alloys, we arc melted high-purity (99.9%) elemental starting materials in water-cooled copper molds four or more times. The nominal composition of these alloys after melting was the same as the starting composition because of the small weight lost in melting ($\leq 0.1\%$). These buttons were then homogenized for two days at $\sim 1200^\circ\text{C}$. Powders (-325 mesh) were produced by hand grinding in an agate mortar and pestle. Powders were annealed in evacuated and sealed quartz capsules for ~ 48 h at 800°C and furnace cooled. For rapid quenching of the Al_3Ti alloy, thin slices were electro-discharge machined and then ground to remove possible contamination from the machining. These slices were then used to make ~ 250 μm thick rapidly solidified splats in an arc-hammer device [9].

X-Ray Diffraction Measurements

X-ray diffraction patterns were measured with either β -filtered CuK_α radiation or 10 keV X rays obtained from the Oak Ridge National Laboratory beam line at the National Synchrotron Light Source, Brookhaven National Laboratory. The long-range order parameters are not often determined from measurements of the intensity ratios of the superlattice reflections to the fundamental reflections of the same order to lessen any effects from preferred orientation. We did a least squares fit to the integrated intensities of about the first ten Bragg reflections including both superlattice and fundamental type reflections. Site occupations, thermal parameters, and scale factors were varied to arrive at the best fit.

RESULTS AND DISCUSSION

From Cowley [8], the long-range order parameter, S , is related to the ordering temperature, T_c , divided by the temperature, T , by the expression

$$\frac{T_c}{T} = \frac{3}{16S^2} \ln \left\{ \frac{(1/3 + S^2)(3 + S^2)}{(1 - S^2)} \right\} \quad (1)$$

for the L1_2 structure. The long-range order parameter is defined as $S = r_\alpha - \omega_\beta$, where r_α is the fraction of α -sublattice sites occupied by the right atom and ω_β is the fraction of β -sublattice sites occupied by the wrong atom. This theoretical curve is shown in Fig. 1 by the dashed line and assumes long-range pairwise interactions. At the critical temperature, T_c , the long-range order drops rapidly to zero. On this theoretical curve are plotted the observed long-range order parameters for Al_3Ti splat cooled, and $\text{Al}_{73}\text{Ti}_{27}$ and Al_3Sc . Al_3Sc has the L1_2 structure, but Al_3Ti splat-cooled and $\text{Al}_{73}\text{Ti}_{27}$ have the DO_{22} structure. Because these structures have the same nearest-neighbor bonds, we plot them on the curve for the L1_2 structure and discuss their similarities in a later section. The observed S is not a test of the theoretical prediction as no attempt was made to fix the equilibrium temperature, T . Instead, we plot the observed S 's on the theoretical curve to illustrate that these compositions are nearly fully ordered. As two were furnace cooled from 800°C , we do not know the equilibrium temperature. Splat cooling of Al_3Ti resulted in a reduction of ordering which is still far from complete disorder. The large amount of order retained in the splat cooled Al_3Ti supports the phase diagram information for ordering to the melting temperature for the trialuminides. Even with this reduction in long-range order to $S = 0.78 \pm 0.04$, this alloy was still brittle [9]. Much more rapid cooling is required to approach the disorder that may be necessary to achieve some ductility in Al_3Ti . The near perfect long range order achieved for Al_3Sc and the off-composition $\text{Al}_{73}\text{Ti}_{27}$ gives us confidence that indeed the trialuminides are ordered to temperatures near or at their melting points as shown by published phase diagrams [10]. We will use this melting temperature to obtain insight to pair potentials for comparison with more elaborate calculations.

We present an argument that the L1_2 structure does not differ greatly from the DO_{22} and DO_{23} structure in terms of near-neighbor coordination (bonding). Shown in Fig. 2 are the unit cells for the L1_2 , DO_{22} , and DO_{23} structures. From this information we calculate the number and

Fig. 1. Long-range order parameter, S , plotted against the equilibrium temperature, T , divided by the ordering temperature, T_c . ---- is the Cowley theory for the L1_2 structure and symbols with error bars denote our experimental values.

Fig. 2. The atom positions for Al and the element M used to form the most prevalent crystal structures of the trialuminides (with permission, ref. 4).

kinds of first-, second-, and third-neighbor bonds. Presented in Table I are the kinds of bonds (Al-M representing a pair bond between an Al atom and M atom) and their number. We note that the first-neighbor pairs remain unchanged while the second- and third-neighbor pairs increasing differ as we progress from the $L1_2$ to the DO_{23} to the DO_{22} structures. In general the near-neighbor coordinations are not greatly different as the basic $L1_2$ structure is maintained but with a variation in the density of the antiphase boundaries along the c axis. The DO_{22} structure has a (100) antiphase boundary between every $L1_2$ unit; whereas, the DO_{23} structure has one every second $L1_2$ unit. This accounts for the result in Table I which shows that for the first three neighboring shells the number and kind of bonds for DO_{23} are more nearly like those of the $L1_2$ structure than are the DO_{22} bonds.

Table I. The number and kinds of pair bonds for the first three shells of an Al_3M trialuminide in the structures of $L1_2$, DO_{23} , and DO_{22}

Neighbor Distances		$L1_2$ Structure	DO_{23} Structure	DO_{22} Structure
1st	M atom	12 Al-M	12 Al-M	12 Al-M
	<110> Al atom	4 Al-M + 8 Al-Al	4 Al-M + 8 Al-Al	4 Al-M + 8 Al-Al
2nd	M atom	6 M-M	5 M-M + 1 Al-M	4 M-M + 2 Al-M
	<200> Al atom	6 Al-Al	5 $\frac{2}{3}$ Al-Al + $\frac{1}{3}$ Al-M	4 Al-Al + 2 Al-M
3rd	M atom	24 Al-M	20 Al-M + 4 M-M	16 Al-M + 8 M-M
	<210> Al atom	24 Al-M	17 $\frac{1}{3}$ Al-Al + 6 $\frac{2}{3}$ Al-M	24 Al-Al

Because of the similarity between the near-neighbor coordinations of the three structures, we will use the Cowley relationship between T_c , the melting temperature in this case to get a value of the ordering energy. This energy, V_1 , represents the pair bonding energy difference between a pair of like atoms replaced by two unlike atoms assuming first neighbors interactions only. This relationship derived for the $L1_2$ structure [8] is

$$V_1 = 0.67 kT_c, \quad (2)$$

where k is the Boltzmann constant, 0.862×10^{-4} eV/K. Since trialuminides are ordered to their melting temperatures (-900 to 1600°C), it is difficult to know what the ordering temperature would have been if melting had not interceded. We will use the melting temperature for T_c with the understanding that T_c may have been even higher. It seems reasonable that this strong Al-M bonding is a major contributor to the melting temperature since without this bonding Al melts at 660°C . Shown in Table II is this pairwise potential calculated from the melting temperatures obtained from ref. 10. The pairwise potential of 0.093 eV for Al_3Ti compares favorably with the value for V_1 of 0.10 eV calculated from the generalized perturbation method [5]. Even though melting occurs before disordering, the use of the melting temperature gave a reasonable value for the pairwise potential. We now compare these pairwise potentials with the trends calculated for phase stability.

Table II. First-neighbor pairwise energy potential for various trialuminides calculated from the melting temperatures

Trialuminide	Transition metal group	Structure	Melting temperature, T °C	Pairwise potential, V_1 eV
Al_3Sc	III	L1_2	1320	0.091
Al_3Ti		DO_{22}	1350	0.093
Al_3V		DO_{22}	1362	0.094
Al_3Y	IV	L1_2	980	0.072
Al_3Zr		DO_{23}	1580	0.106
Al_3Nb		DO_{22}	1605	0.108
Al_3La	V	DO_{19}	1170	0.083
Al_3Hf		DO_{22}	1540	0.104

Since the L1_2 , DO_{23} , and DO_{22} structures are similar with similar near-neighbor bonding, we assumed that their energy differences would be small compared with the bonding energy of the Al-M nearest-neighbor pairs. We would expect that the energy difference between DO_{23} - L1_2 would be smaller than for DO_{22} - L1_2 since the former has more nearly the same near-neighbor coordination as L1_2 . The energy difference between the DO_{22} and L1_2 ordered structure has been calculated by Nicholson et al.[5] to be ~ 0.048 eV/atom for Al_3Ti . Carlsson and Meschter [4] using the augmented-spherical-wave (ASW) method obtained a value of ~ 0.1 eV/atom. Typically, their values for Al with Group III, IV, and V transition metals were between 0.02 and 0.2 eV/atom for the energy difference between DO_{22} - L1_2 and about half those values for the energy difference between DO_{23} - L1_2 . As they point out, this smaller energy difference is to be expected because of the closer match in near-neighbor bonding. However, most of their energy differences between DO_{22} - L1_2 are not small compared to our typical first-neighbor bond energies of 0.07 to 0.10 eV/atom. We believe that the values in reference [4] may be high, although their trends agree with the experimental observation that the highest melting points are observed for the DO_{22} structure within each transition metal group; see Table II. More recently Fu [3] used the full-linear-augmented-planewave (FLAPW) method to obtain ~ 0.03 eV/atom for the energy difference between the DO_{22} - L1_2 for Al_3Ti . This latter value is about one-third our calculated value of 0.093 eV/atom for the Al-Ti bond for Al_3Ti in the L1_2 structure. The effect of the second neighbor pair potentials on T_c can be estimated with the expanded version of Cowley's formula [8],

$$T_c = (3/2 k) (V_1 - 3/2 V_2), \quad (3)$$

where V_2 is the second neighbor pair potential. Nicholson et al.[5] calculated that $V_1 = 0.102$ eV and $V_2 = -0.082$ eV for the L1_2 form of Al_3Ti . Thus, the second neighbor pair potential, V_2 , would contribute as much to the ordering temperature as V_1 . Our assumption that the melting temperature is not sensitive to the structural differences between L1_2 , DO_{22} , and DO_{23} and that only the nearest neighbor potential is important can lead to errors of a factor of two in our bond values. We recognize that nearest neighbor bonding forces alone are not sufficient to describe in detail the phase stability of ordered intermetallic alloys; however, general trends are predictable [11]. It is not our intent to attach too much significance to the quantitative values of these potentials. Their relative values, however, could give us the relative strengths of the Al-M bonding which, we believe, provides a useful parameter for understanding their mechanical behavior.

Because the ordering (melting) temperature reflects the large bonding energy between Al-M pairs, we suggest that the melting temperature of the trialuminides gives a measure of their

stability. By the addition of one metal atom M to three Al atoms, the bonding compared to pure Al has been altered in a major way, mainly because of the very strong Al-M bonds and not by changes in the Al-Al bonds. As these strong bonds between Al-M and weak bonds between Al-Al neighbors could control the mechanical properties of the trialuminides, their intrinsic brittleness may be related to this disparity. No trialuminides to date have shown a degree of ductility useful for engineering application. We suggest that the Al-M bonds must be weakened or disordered by alloying with a resultant drop in melting temperature or a major fraction of Al-Al bonding replaced by alloying to achieve useful ductility.

CONCLUSIONS

Observations show that trialuminides phases are brittle. Their conversion to L1₂ by ternary alloying has also proven insufficient to ductilize the trialuminides to date. We have used the melting temperature of these intermetallic alloys from which a pairwise bond energy for Al-M first-neighbor pairs was calculated and found to have reasonable values compared with advanced theoretical calculations. This leads us to believe that the high melting temperature of the ordered trialuminides is important to their mechanical behavior. The strong bonding reflected in their high melting points compared to that of pure Al produces a large disparity in strength between Al-M and Al-Al bonds which are of equal number for first-neighbor pairs. An alloying effort aimed at reducing the melting point of the trialuminides and weakening the Al-M bonds or strengthening the Al-Al bonds may help increase their ductility.

ACKNOWLEDGEMENTS

The research was managed by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors express their appreciation to D. M. Nicholson, E. P. George, C. T. Liu, and C. L. Fu for helpful discussions, and C. A. Carmichael, Jr., for preparation of the alloys.

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