

Some comments on the misfit and coherency loss of Al_3Sc particles in Al–Sc alloys

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Abstract

An attempt of refining a recently reported calculation of the temperature dependent misfit between Al and Al_3Sc particles is given. Further, the impact of a temperature dependent misfit on the calculated diameter for coherency loss of Al_3Sc precipitates is demonstrated. The origin of misfit dislocations is also briefly discussed.

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1. Introduction

The research on scandium additions in aluminium alloys has gained some interest over the last decade, due to the beneficial effects that can be obtained by such additions. It has been reported that Sc additions may provide good grain refinement during casting or welding, excellent control of the grain structure in thermomechanical treatments by Al_3Sc dispersoids, and significant particle strengthening due to precipitation of Al_3Sc [1]. Apparently, the precipitation of Al_3Sc particles in the solid state is to a large extent of a homogeneous nature, and it seems that the equilibrium Al_3Sc phase precipitates directly from the supersaturated solid solution without preceding formation of metastable phases. The particles formed in the solid state are coherent with the Al matrix, they normally have a spherical appearance (It has been shown that the equilibrium particle morphology for many conditions is that of a Great Rhombicuboctahedron, which in effect is quite close to

a sphere [2].), and the volume fraction of particles is small. This seemingly simple precipitation behaviour of Al_3Sc has also led to a certain popularity of the binary Al–Sc system as a model system for investigating basic principles in physical metallurgy [3–6]. The aim of the present work is to discuss the misfit and coherency loss of Al_3Sc particles in view of recently published experimental investigations.

2. Misfit between the Al_3Sc particles and the Al matrix

At room temperature the lattice parameters of the Al_3Sc phase and pure Al is 0.4103 nm and 0.4049 nm, respectively, which translates to a misfit of the Al_3Sc particles with the Al matrix of approx. 1.33%. However, the lattice thermal expansion of the Al_3Sc particles is different from that of the Al matrix, thus making the misfit temperature-dependent. The thermal expansion of Al_3Sc has not been measured until recently, but in a recent study [7] the linear thermal expansion was determined to be constant at approx. $16 \times 10^{-6}/\text{K}$ over a wide temperature range. For pure Al the linear thermal

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expansion is dependent on the temperature. A recommended approximation [8] for the linear thermal expansion of Al in the temperature range 300–900 K is given by

$$\begin{aligned} \Delta L^{\text{Al}}/L_0^{\text{Al}} = & 1.8 \times 10^{-4} + 2.364 \times 10^{-5}(T - 300) \\ & + 4.164 \times 10^{-9}(T - 300)^2 \\ & + 8.270 \times 10^{-12}(T - 300)^3 \end{aligned} \quad (1)$$

This thermal expansion is somewhat higher than that of Al_3Sc , which in turn means that the misfit between the Al_3Sc particles and the Al matrix decreases with increasing temperature. The temperature dependent misfit $\delta(T)$ has been calculated from the linear thermal expansion data in [7], and is reproduced by the solid line in Fig. 1:

$$\delta''(T) = \frac{a_{\text{Al}_3\text{Sc}} [1 + (16 \times 10^{-6})(T - 300)]}{a_{\text{Al}} \left(1 + \frac{\Delta L^{\text{Al}}}{L_0^{\text{Al}}}\right)} - 1 \quad (2)$$

It is, however, possible to refine this calculation somewhat. Whereas the thermal expansion of Al_3Sc is expected to be only due to lattice expansion, there is a significant contribution from vacancies on thermal expansion of Al at high temperatures [9]. Thus, the temperature effects on the misfit should be calculated from the changes in lattice parameters rather than from the linear thermal expansion.

The equilibrium concentration of vacancies may be written on the form

$$c_v = e^{S_v/R} e^{-H_v/RT} \quad (3)$$

where c_v is the fraction of vacancies in the matrix, S_v and H_v is the entropy and enthalpy of the formation of vacancies, T is the temperature in K and R is the

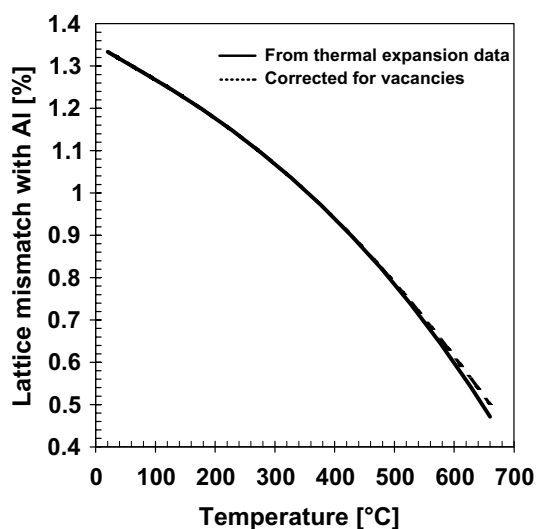


Fig. 1. Lattice mismatch between Al and Al_3Sc as a function of temperature. The solid line represents the calculation based on linear thermal expansion data as given by Eq. (2), whereas the dotted line represents a correction for vacancies as given by Eq. (4).

gas constant. The values of S_v and H_v are found to be 20 J/mol K and 73.2 kJ/mol, respectively.

By subtracting the vacancy effect on the thermal expansion one achieves a temperature-dependent misfit as represented by the dotted line in Fig. 1:

$$\delta'(T) = \frac{a_{\text{Al}_3\text{Sc}} [1 + (16 \times 10^{-6})(T - 300)]}{a_{\text{Al}} \left(1 + \frac{\Delta L^{\text{Al}}}{L_0^{\text{Al}}} - \frac{c_v}{3}\right)} - 1 \quad (4)$$

A second correction that should be taken into account is the effect of Sc in solid solution on the lattice parameter of the Al matrix. With increasing temperature more Sc is brought into solid solution, and it is reported that the lattice parameter of the Al matrix, presumably measured at room temperature, increases linearly with the Sc content in solid solution [10]. These data can be used to calculate the effect on the lattice parameter at elevated temperatures under the assumption that the relative increase in lattice parameter due to Sc in solid solution is independent on temperature. In [10] a figure is presented which shows the measured lattice parameter as a function of Sc content in solid solution, and a value $(da/dc)/a = 0.122$ is reported, where a is the lattice parameter of the Al matrix and c is the Sc content in solid solution in at.%. This reported value for $(da/dc)/a$ is 100 times larger than what is indicated in the corresponding figure. However, if c is taken to mean atomic fraction rather than atomic percent, there is a good match between the reported value and the corresponding figure. Thus, in the present exercise the value for $(da/dc)/a$ of 0.122 is used with the understanding that c represent atomic fraction.

It has been shown that the measured solvus line in the binary Al–Sc system is well described by the regular solution approximation [11,12]:

$$c_{\text{Sc}} = e^{S_{\text{Sc}}/R} e^{-H_{\text{Sc}}/RT} \quad (5)$$

where c_{Sc} is the fraction of Sc atoms in solid solution in the matrix, S_{Sc} and H_{Sc} is the entropy and enthalpy of Sc in solid solution, T is the temperature in K and R is the gas constant. In a recent work the values of S_{Sc} and H_{Sc} were found to be 19 J/mol K and 65 kJ/mol, respectively [12].

Combining these equations one obtains the following expression for temperature dependent misfit:

$$\delta(T) = \frac{a_{\text{Al}_3\text{Sc}} [1 + (16 \times 10^{-6})(T - 300)]}{a_{\text{Al}} \left(1 + \frac{\Delta L^{\text{Al}}}{L_0^{\text{Al}}} - \frac{c_v}{3}\right) (1 + 0.122 \times c_{\text{Sc}})} - 1 \quad (6)$$

The corrections for vacancies and Sc in solid solution relatively to Equation (2) are shown in Fig. 2. These two corrections are of approximately the same magnitude, but with opposite signs. Thus, the resulting (net) correction as incorporated in Equation (6) is close to zero, and it turns out that the first hand approximation of Equation (2) as applied by [7] is very good in this case.

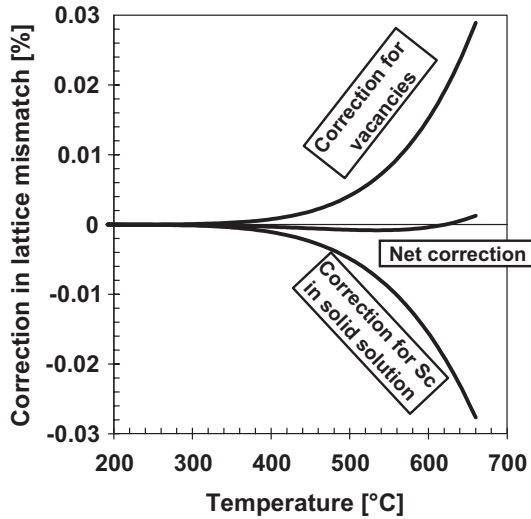


Fig. 2. Corrections relative to Eq. (2) due to vacancies and to Al lattice expansion from Sc in solid solution.

3. Critical diameter for loss of coherency

When an Al₃Sc particle grows it will sooner or later reach a critical size where it will be energetically more favourable to introduce an interface dislocation at the Al/Al₃Sc interface than to increase the matrix strain. A simple approximation for the critical size can be derived from the lattice parameters, assuming that the critical size is reached when the misfit over the whole particle diameter equals the burgers vector of the Al matrix:

$$d_{\text{crit}} = b/\delta \quad (7)$$

where b is the burgers vector of Al and δ is the misfit between Al and Al₃Sc. This approximation yields a critical diameter of approx. 21.5 nm at ambient temperature. Applying the calculated temperature dependent misfit $\delta(T)$ from Equation (6) (and not forgetting that also b is temperature dependent) with this simple approximation for a critical diameter for loss of coherency, one gets a temperature dependent critical diameter as shown by the lower curve in Fig. 3.

A more refined analysis on the transition from coherent to incoherent particles has been performed in [13]. This analysis is based on the balance between the increase in particle/matrix interface energy due to interfacial dislocations and the relaxation in elastic energy due to the same dislocations:

$$\pi d_{\text{crit}}^2 \sigma_{\text{disl}} = \pi d_{\text{crit}}^3 G \delta^2 \frac{(1 + \nu)}{3(1 - \nu)} \quad (8)$$

where σ_{disl} is the energy of a interface dislocation network per unit area and G and ν are the shear modulus and the Poissons ratio of the Al matrix, respectively. The energy of the dislocation network is expressed by

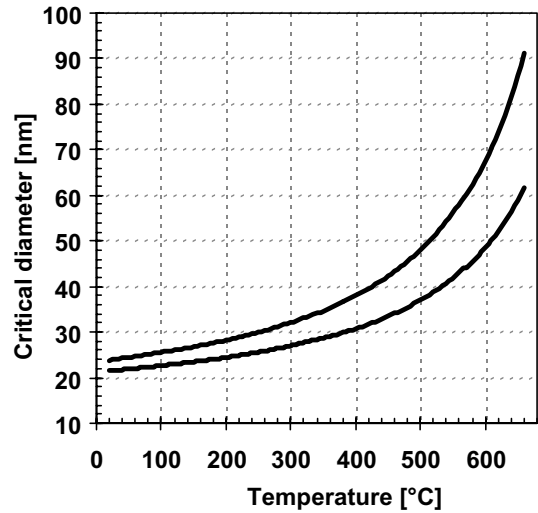


Fig. 3. Approximations for the temperature-dependent critical particle diameter for the introduction of dislocations to the Al/Al₃Sc interface. The lower curve represents Eq. (7), whereas the upper curve represents Eq. (11).

$$\sigma_{\text{disl}} = \frac{Gb}{2\pi^2} \left[1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln(2\beta(1 + \beta^2)^{1/2} - 2\beta^2) \right] \quad (9)$$

where

$$\beta = \frac{\pi\delta^*}{1 - \nu} \quad (10)$$

in which δ^* is the decrease in lattice misfit when interfacial dislocations are introduced.

This analysis as reported in [13] yields a predicted critical diameter of 24.6 nm for transition from coherent to semi-coherent particles at ambient temperature. The temperature dependency of the critical diameter is not treated in [13]. However, solving Equations (8) and (9) for the critical diameter d_{crit} one gets

$$d_{\text{crit}} = \frac{b}{\delta^2} \frac{3(1 - \nu)}{2\pi^2(1 + \nu)} \left[1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln(2\beta(1 + \beta^2)^{1/2} - 2\beta^2) \right] \quad (11)$$

and from the temperature dependencies on b and δ as discussed above, one gets a temperature dependent critical diameter as shown by the upper curve in Fig. 3.

The analysis of [13] is based on the following simplifications [14]:

1. The precipitate and the matrix have the same crystal structure and the same elastic constants (G and ν).
2. The interface between the precipitate and the matrix is planar.

It should thus be possible to further refine this analysis by evaluating whether taking the measured elastic constant of Al₃Sc [15] and the spherical interface into account has any impact on the predicted critical

Table 1
Some reported critical diameters for coherency loss in binary Al–Sc

Reference	d_{crit} [nm]	C_{Sc}^0 [wt.%Sc]	T_{trans} [°C]	d_{crit} Eq. (7) [nm]	d_{crit} Eq. (11) [nm]
Drits '83 [16]	38–40	0.5			
Berezina '90 [17]	28–30	0.3	400	30.8	38.0
Riddle '00 [18]	>32	0.2	400, 450	30.8, 33.5	38.0, 42.3
Riddle '01 [19]	50	0.2			
Jones '01 [20]	40	0.12, 0.25			
Jones '03 [21]	40	0.25	450–500	33.5–37	42.3–48.0
Marquis '01 [2]	40	0.3	400, 450	30.8, 33.5	38.0, 42.3
Iwamura '02 [13]	40	0.2	400–460	30.8–34.1	38.0–43.3
Watanabe '04 [22]	40	0.28	400–450	30.8–33.5	38.0–42.3

diameter. A further refinement should also look into the temperature dependency on the elastic constants.

Some examples from the literature of experimentally observed critical diameters in binary Al–Sc alloys [2,13,16–22] are summarized in Table 1, along with some predictions for critical diameters from Equation (7) and Equation (11) (Fig. 3). There is a fairly good consistency between the observations, and the measured diameter is quite close to the simple predictions above. Taking the temperature dependency of the misfit into account clearly improves the theoretical predictions.

4. Misfit dislocations

One should keep in mind that the discussion above only considers for what particle sizes it is energetically favourable to introduce misfit dislocations to the particle/matrix interface, whereas the origin of such dislocations has not been treated. There are several possible origins of misfit dislocations:

1. A possible formation mechanism of misfit dislocations, referred to as prismatic punching of dislocation loops, is discussed in the literature [23]. Such a mechanism requires large stresses at the particle/matrix interface. The maximum stress at the interface is only depending on the precipitate misfit δ , not on the precipitate size. It has been suggested that misfits in excess of approx. 0.1 is necessary for this mechanism to operate [24], which is an order of magnitude higher than the misfit of Al/Al₃Sc.
2. Another possibility of formation of misfit dislocations is through the accumulation of vacancies on the particle/matrix interface. Computer simulations have shown that vacancies at the interface may reduce the lattice strain [25], and it is suggested that collapsing vacancy clusters may form misfit dislocations [26].
3. Formation of dislocation loops inside particles has been observed [26].
4. Matrix dislocations in the vicinity of the precipitates.

Observations in [13] indicate that misfit dislocations at Al/Al₃Sc interfaces may form without the participation of matrix dislocations. It could be worthwhile to do some experimental work in order to determine the mechanism of formation of misfit dislocations in Al–Sc alloys. This would improve the understanding of the precipitation behaviour, not only in Sc-containing Al alloys but in all alloys containing coherent precipitates.

5. Conclusions

The attempt of refining the calculation of the temperature dependent misfit between Al and Al₃Sc lead to only negligible corrections.

It is shown that by taking the temperature dependent misfit into account, there is a much better match between calculated values and observed values of critical particle diameter for loss of coherency.

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References

- [1] Røyset J, Ryum N. *Int Mater Rev* 2005;50:19.
- [2] Marquis EA, Seidman DN. *Acta Mater* 2001;49:1909.
- [3] Hyland Jr RW. *Metall Trans A* 1992;23A:1947.
- [4] Rohrer CL, Asta MD, Foiles SM, Hyland Jr RW. *Mater Res Soc Symp Proc* 1996;398:477.
- [5] Novotny GM, Ardell AJ. *Mater Sci Eng A* 2001;A318:144.
- [6] Robson JD, Jones MJ, Pragnell PB. *Acta Mater* 2003;51:1453.
- [7] Harada Y, Dunand DC. *Scripta Mater* 2003;48:219.
- [8] Touloukian YS, Kirby RK, Taylor RE, Desai PD, editors. *Thermal expansion: metallic elements and alloys*. Plenum: New York; 1975.
- [9] Simmons RO, Balluffi RW. *Phys Rev* 1960;117:52.
- [10] Očko M, Babić E, Krsmik R, Girt E, Leontić B. *J Phys F Met Phys* 1976;6:703.
- [11] Fujikawa SI, Sugaya M, Takei H, Hirano KI. *J Less-Common Met* 1979;63:87.
- [12] Røyset J, Ryum N. *Mater Sci Eng A* 2005;A396:408.
- [13] Iwamura S, Miura Y. *Acta Mater* 2004;52:591.
- [14] Jesser WA. *Phil Mag* 1969;19:993.
- [15] George EP, Horton JA, Porter WD, Schneibel JH. *J Mater Res* 1990;5:1639.
- [16] Drits ME, Toropova LS, Bikov UG, Anastaseva. In: Kedves FJ, Beke DL, editors. *DIMETA-82 diffusion in metals and alloys*. Trans Tech Publications; 1983. p. 616.
- [17] Berezina AL, Volkov VA, Domashnikov BP, Ivanov SV, Chui-tov KV. *Phys Metals* 1990;10:296.
- [18] Riddle YW, Sanders Jr TH. *Mater Sci Forum* 2000;331–337: 939.

- [19] Riddle YW, McIntosh M, Sanders Jr TH. In: Jata K, Lee EW, Frazier W, Kim NJ, editors. *Lightweight alloys for aerospace application VI*. Warrendale, PA: TMS; 2001. p. 25.
- [20] Jones MJ, Humphreys FJ. In: Gottstein G, Molodov DA, editors. *Recrystallization and grain growth*. Springer Verlag; 2001. p. 1287.
- [21] Jones MJ, Humphreys FJ. *Acta Mater* 2003;51:2149.
- [22] Watanabe C, Kondo T, Monzen R. *Metall Mater Trans A* 2004;35A:3003.
- [23] Weatherly GC. *Phil Mag* 1968;17:791.
- [24] Brown LM, Ham RK. In: Kelly A, Nicholson RB, editors. *Strengthening methods in crystals*. Elsevier; 1971. p. 45.
- [25] Easterling KE, Johannesson T. *Phil Mag* 1971;24:981.
- [26] Weatherly GC. *Phil Mag* 1968;17:801.