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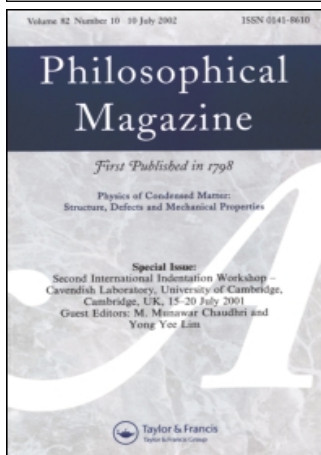
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Unusual lattice parameters in two-phase systems after annealing

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ABSTRACT

The lattice parameter observed at room temperature for the aluminium-rich phase in fully precipitated AlSi alloys has been found to be significantly greater than the expected equilibrium value. This effect increased with silicon content and with annealing temperature. Two possible causes were considered: (i) the difference between the atomic volumes for silicon in the precipitates and in the aluminium matrix; and (ii) the difference between the thermal expansion coefficients of the matrix and the precipitates. A quantitative description is based on the theory of Eshelby developed originally for the case of elastic distortions in a crystal by point imperfections. Distortions due to cause (i) vanished during the anneal. For cause (ii) the theoretical prediction obtained agreed fairly well with the experimental data. The validity of the Eshelby model in this case was discussed. For precipitation studies where the change in lattice parameter is followed, a procedure is proposed to obtain correct solid solubilities.

§ 1. INTRODUCTION

In the course of an investigation of the precipitation phenomena in AlSi alloys rapidly quenched from the melt the lattice parameter of the aluminium-rich phase has been measured at room temperature as a function of annealing time, annealing temperature and silicon content of the alloy. At the precipitation temperatures applied the solid solubility of silicon in aluminium is negligible (Mondolfo 1976) and thus, after ageing times sufficiently long to complete precipitation, one may expect the lattice parameter of the aluminium-rich phase to reach that of pure aluminium. However, the observed lattice parameter always exceeded this limit.

A difference in thermal expansion between two phases in a specimen introduces strains on cooling. From X-ray diffraction line-broadening studies it was found that local variations in the lattice parameter occur due to this effect (Nielsen and Hibbard 1950, Cocks and Cogan 1976). In this paper it is shown experimentally that a significant X-ray diffraction line shift also occurs, implying a change in average lattice parameter. The lattice parameter change is explained on the basis of a theory due to Eshelby (1954, 1956), developed originally for the case of elastic distortions in a crystal by point imperfections.

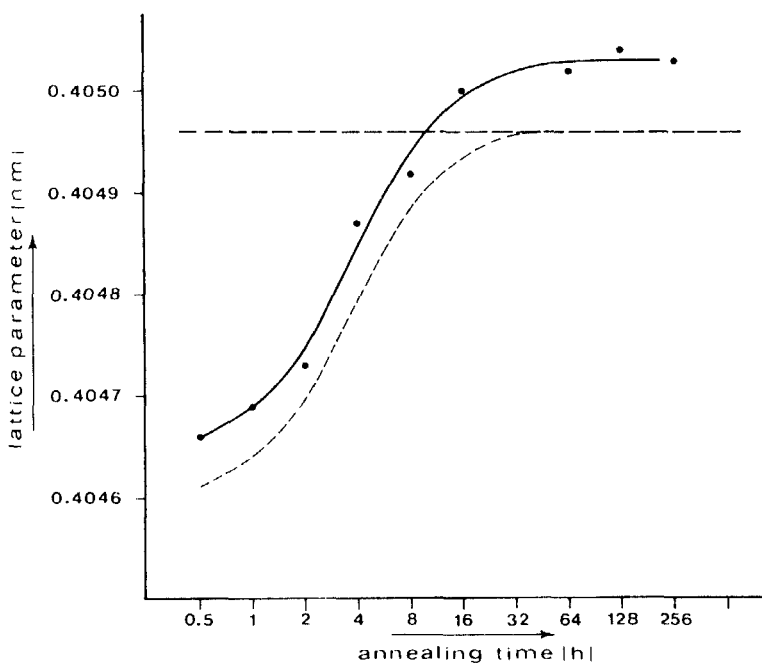
In precipitation studies, where the lattice parameter is used as indication of the progress of precipitation (cf. Krawitz and Sinclair 1975), one should consider the effect of the difference in thermal expansion coefficient between the two phases. A correction procedure is proposed.

§ 2. EXPERIMENTAL

Aluminium alloys with 2.4, 11.0, 22.4 and 34.8 wt% silicon were prepared from 99.998 wt% Al and 99.99 wt% Si. By the melt-spinning technique ribbons with a non-uniform thickness varying from 10 to 150 μm were obtained (Bendijk, Delhez, Katgerman, de Keijser, Mittemeijer and van der Pers 1980). The cooling rate was in the range 10^6 to 10^7 K s^{-1} .

The lattice parameter of the aluminium-rich phase was determined as a function of annealing time until its value became constant (fig. 1).

Fig. 1



The lattice parameter a_m , at a reference temperature of 298 K, of the aluminium-rich phase, as observed at room temperature, for an AlSi alloy with 11 wt% Si as a function of annealing time at 425 K. The lattice parameter corrected for the effect due to the difference in thermal expansion is presented by the dashed line. The dashed bold line represents the equilibrium value of the lattice parameter of pure aluminium.

From each ribbon a section, 0.5 mm in width and 10 mm in length, was cut for use as a specimen, which stayed in a specimen holder during the whole course of the annealing treatment. After certain annealing times this specimen holder, with the specimen, could be mounted reproducibly in a Debije-Scherrer camera (diameter 114.7 mm). Applying the Nelson-Riley extrapolation procedure (Klug and Alexander 1974), the lattice parameters were determined with a precision of one part in 40 000. Lattice parameters

were measured at room temperature; as a reference temperature, 298 K was chosen.

The heat treatments were performed in an oil bath (temperature control within 4 K) at temperatures of 397, 425 and 448 K in an atmosphere of 90% nitrogen and 10% hydrogen. During annealing the specimen holder with the very vulnerable specimen was enclosed in a cylinder (pervious to oil) for protection against deformation. Further the cylinder permitted two specimens (of, for example, different composition) to be annealed at precisely the same temperature.

As a reference, the lattice parameter of melt-spun pure aluminium was determined: no change with annealing time at 425 K was detected and the value found for the lattice parameter was 0.40496 nm, in agreement with literature data (see, for example, Pearson 1967). This experiment also proved that the unusual lattice parameters found cannot be attributed to conditions of specimen preparation, chemical contamination, etc.

§ 3. RESULTS

As an example the measured lattice parameter of the aluminium-rich phase as a function of ageing time at 425 K is shown in fig. 1 (bold line) for the AlSi alloy with 11.0 wt% Si.

After complete precipitation the equilibrium phases can be considered as pure aluminium and pure silicon (Mondolfo 1976). The difference Δa between the lattice parameter a_m of the aluminium matrix after complete precipitation and the equilibrium value of the lattice parameter a_{Al} of pure aluminium, both measured at room temperature, is given in table 1 for different annealing temperatures and various silicon contents.

Table 1. Values of the difference Δa as a function of silicon content of the AlSi alloys and annealing temperature.

Silicon content of alloy		Precipitation temperature (K)	a_m (nm)	$\Delta a \times 10^{+5}$ (nm)
(weight %)	(volume %)			
2.4	2.8	397	0.40496	(0.3)
11.0	12.5	397	0.40502	6
2.4	2.8	425	0.40497	1
11.0	12.5	425	0.40503	7
2.4	2.8	445	0.40498	2
2.4	2.8	448	0.40499	3
11.0	12.5	448	0.40503	7
22.4	25.1	445	0.40511	15
34.8	38.2	445	0.40516	20

$\Delta a = a_m - a_{Al}$ (reference temperature 298 K).

a_m = lattice parameter of the aluminium-rich phase after completed precipitation, measured at room temperature (about 294 K).

a_{Al} = lattice parameter of pure aluminium = 0.40496 nm (Pearson 1967).

The volume % silicon holds for the case where all the silicon is precipitated.

The results can be summarized as follows.

- (i) After complete precipitation a lattice parameter significantly larger than the lattice parameter of pure aluminium is observed ($\Delta a > 0$).
- (ii) Δa increases with increasing silicon content of the alloys.
- (iii) Δa increases with increasing annealing temperature.

§ 4. INTERPRETATION

To explain Δa one might think at first of impurities dissolved in the aluminium matrix. There are a few metallic elements which enlarge the lattice parameter of aluminium ($\Delta a > 0$), of which magnesium is the most notable (Helfrich and Dodd 1962, Poole and Axon 1952, Ellwood 1952). However, a careful chemical analysis showed that no contaminating elements were present in an amount which might explain the observed values of Δa (see also the end of § 2).

In our opinion the observed Δa is due to strains in the aluminium-rich matrix. These strains may originate from two causes.

- (a) The silicon occupies a considerable larger volume when precipitated than when dissolved in the matrix (a relative volume expansion of about 23% occurs (Saulnier 1961)).
- (b) The difference in thermal linear expansion coefficient α of aluminium and silicon ($\alpha_{\text{Al}} = 23.5 \times 10^{-6} \text{ K}^{-1}$ (Smithells 1976); $\alpha_{\text{Si}} = 3.0 \times 10^{-6} \text{ K}^{-1}$ (Roberts 1978))† implies that, after cooling from the annealing temperature to room temperature, the volume available to the silicon precipitate is too small.

Both effects will distort the aluminium matrix in the same manner. The strains will be greater the larger the silicon fraction precipitated (causes (a) and (b)) and the higher the annealing temperature (cause (b)). Causes (a) and (b) may operate simultaneously or separately. Eshelby (1954, 1956) has proposed a model for the elastic distortion of a crystal by point imperfections. We suggest that this model may be adopted for the calculation of the elastic distortion of a matrix by small inclusions.

4.1. Volume change of the matrix

The model for the elastic distortion by point imperfections has its limitations (Christian 1975). However in the present case of an inclusion composed of a number of atoms this model will be better than in the case of an individual misfitting atom.

For a spherical inclusion of phase B (Si) in a continuous matrix of phase A (Al) the misfit parameter ϵ is defined by

$$\epsilon = (r_0^{\text{B}} - r_0^{\text{A}})/r_0^{\text{A}}, \quad (1)$$

† In fact the thermal expansion coefficient is temperature dependent and more accurately eqn. (6) can be written in integral form. For the present purpose an Average value suffices.

where r_0^B and r_0^A are the radii of the 'free' undeformed inclusion B and of the empty undeformed cavity in the matrix A respectively. In the model, the distinction between an infinite and a finite matrix A is essential, since for an infinite assembly no volume changes of the matrix itself occur, whereas for a finite assembly volume changes of the matrix occur as a consequence of the requirement of a stress-free bounding surface. Assuming elastically isotropic material containing n inclusions per unit volume, the fractional volume change $\Delta V_A/V_A$ of the finite matrix can be written as (cf. eqn. (8.12) of Eshelby (1956) and eqn. (25.10) of Christian (1975))

$$\frac{\Delta V_A}{V_A} = 16\pi C \epsilon (r_0^A)^3 n, \quad (2)$$

with

$$C = \frac{\mu_A}{K_A} \frac{K_B}{3K_B + 4\mu_A}, \quad (3)$$

where μ and K represent the shear and the bulk moduli respectively. Considering a volume fraction y_B of inclusions B ($y_B = 4\pi(r^B)^3 n/3$, where r^B is the actual radius of the inclusion) and approximating r^B by r_0^B and $\Delta V_A/V_A$ by $3\Delta a_A/a_A$, where a_A denotes the lattice parameter of the matrix, it follows from eqns. (1) and (2) that

$$\Delta a \equiv \Delta a_A = 4Ca_A \frac{\epsilon}{(1 + \epsilon)^3} y_B. \quad (4)$$

4.2. Application to AlSi

The misfit parameters for the two possible explanations of Δa mentioned in § 4.1 are (cf. eqn. (1))

- (a) ϵ_V , which accounts for the difference between the volume of a silicon atom as precipitated (diamond structure, lattice parameter a_{Si}) and the volume available to a silicon atom in the undeformed aluminium matrix (cubic-close-packed structure):

$$\epsilon_V = (a_{Si} - a_{Al}\sqrt[3]{2})/a_{Al}\sqrt[3]{2} = 0.0643, \quad (5)$$

where the factor $\sqrt[3]{2}$ originates from the difference in atomic volume between the diamond and cubic-close-packed structures; and

- (b) ϵ_T , which accounts for the difference in thermal linear expansion coefficients α between the aluminium matrix and the silicon inclusion:

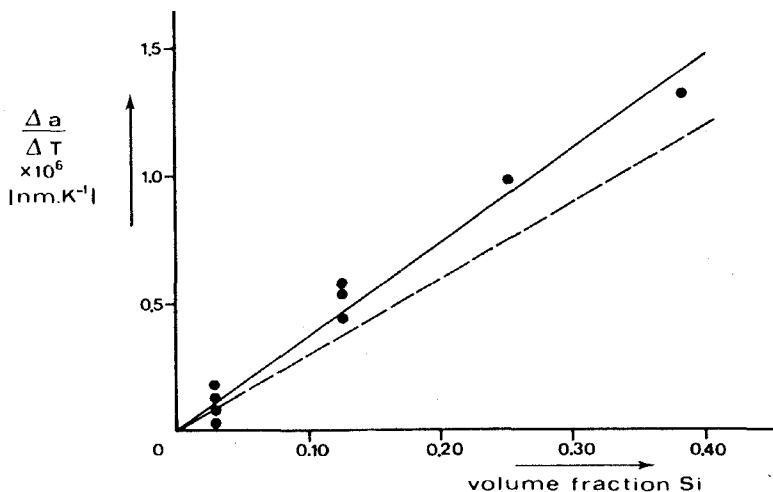
$$\epsilon_T = (\alpha_{Al} - \alpha_{Si})(T_a - T_r) = 20.5 \times 10^{-6} \Delta T, \quad (6)$$

where T_a and T_r are the annealing temperature and room temperature respectively and the thermal linear expansion coefficient is taken independent of temperature.

From eqns. (5) and (6) it follows that both misfit parameters are positive and hence, according to eqn. (4), a dilatation of the aluminium matrix is expected ($\Delta a > 0$), which is in agreement with experiment (see table 1).

It will be made probable below that only the difference in thermal expansion coefficient (see (b) above) is responsible for the Δa -effect observed. Then the experimental data for $\Delta a/\Delta T$ as a function of volume

Fig. 2



$\Delta a/\Delta T$ as a function of volume fraction silicon precipitated. Bold line: experimental data (cf. table 1). Dashed line: calculated from eqns. (3), (4) and (6).

fraction y_B of precipitated silicon should fall on a straight line passing through the origin (cf. eqns. (4) and (6)). This is indeed observed (solid line in fig. 2). A calculation of C from eqn. (3) with literature data for the elastic constants (Smithells 1976) yields $C = 0.09$. Subsequently a theoretical line for $\Delta a/\Delta T$ versus y_B is obtained (dashed line in fig. 2). Considering the simplicity of the model and in view of the question about the compatibility of the elastic data used with the model, there is a fair agreement between theory and experiment.

From the large difference between the values for $\epsilon_V (=0.064)$ and $\epsilon_T (=0.003$ for $\Delta T = 150$ K) it is obvious that cause (a) (see above) cannot be responsible for the Δa -effect observed. This implies that relaxation occurs at the annealing temperatures. This relaxation was confirmed experimentally by subsequently annealing the *same* specimen of a completely precipitated 11 wt% Si alloy at two temperatures. The values observed for $\Delta a/\Delta T$ agreed with the experimental line in fig. 2. Also the work by Itagaki, Giessen and Grant (1968) indicates a relaxation of misfits occurring at the annealing temperatures.

The theory applied assumes spherically shaped precipitates. The crystallite sizes of the silicon precipitates were investigated by X-ray diffraction line-profile analysis. As can be seen from table 2 about the same crystallite size is derived from different reflections. Thus it is concluded that the silicon precipitates are approximately spherical.

4.3. Discussion

To our knowledge neither a Δa -effect in the matrix has previously been reported nor has the theory of Eshelby for point singularities been applied to the case of elastic distortions in the matrix resulting from a difference in thermal expansion coefficient between matrix and inclusion (precipitate).

Table 2. Particle size of silicon in different splat-cooled AlSi alloys as obtained from X-ray diffraction line-profile analysis (for the method used see de Keijser, Langford, Mittemeijer and Vogels (1981)).

Alloy composition (wt% Si)	Particle size of silicon from reflection		
	111 (nm)	220 (nm)	311 (nm)
2.4	43	34	45
11.0	24	30	46
22.4	38	37	29
34.8	35	39	30

In the AlSi system the lattice parameter of the aluminium-rich phase decreases with increasing silicon content. Hence the observation of a lattice parameter larger than that of pure aluminium is unexpected. On reflection, the AlSi system is especially suited for the observation of the effect: the two-phase boundary in the AlSi phase diagram (aluminium-rich side) almost coincides with the ordinate ($x_{\text{Si}} = 0$). In other systems where larger solid solubilities occur the lattice parameter observed may still fall within the 'possible' range of lattice parameter values, set by $x_{\text{B}} = 0$ and the solubility limit at the annealing temperature, and thus, although present, a Δa -effect may be ignored. Therefore, solubilities (two-phase boundaries) determined from lattice parameter measurements after cooling to room temperature may be in error (for the AlSi system $\Delta\alpha$ is large, but in the present experiments ΔT was small). Therefore in decomposition studies where the change in lattice parameter is followed (see discussion by Krawitz and Sinclair (1975)) erroneous conclusions may be obtained. Correct results can be obtained by the procedure given below.

§ 5. CORRECTION FOR THE Δa -EFFECT

The difference between the measured lattice parameter a_{m} of the A-rich phase and the lattice parameter a_{A} of the pure component A can be written as

$$a_{\text{m}} - a_{\text{A}} = f_{\text{S}}(x_{\text{B}}) + f_{\text{T}}(y_{\text{B}}), \quad (7)$$

where x_{B} is the atomic fraction of component B in solid solution in the A-rich *matrix* and y_{B} is the volume fraction of the dispersed B-rich phase in the *specimen*. The change in lattice parameter due to dissolving of B in A is represented by $f_{\text{S}}(x_{\text{B}})$ and the effect due to the difference in thermal expansion between the dispersed B-rich phase and the A-rich matrix is represented by $f_{\text{T}}(y_{\text{B}})$. The term $f_{\text{S}}(x_{\text{B}})$ follows from experimental data. Often $f_{\text{S}}(x_{\text{B}})$ can be approximated by px_{B} , where p is a constant (a second-order approximation has been proposed by Moreen, Taggart and Polonis (1971)). The term $f_{\text{T}}(y_{\text{B}})$ can be written as qy_{B} (cf. eqn. (4)), where q can be obtained from experiment (cf. fig. 2). If no experimental data are available q can be calculated from eqns. (3), (4) and (6).

The unknowns x_B and y_B are calculated from the measured lattice parameter (eqn. (7)) and the known overall composition of the specimen.

For the AlSi system it follows that $p = -1.74 \times 10^{-2}$ nm (derived from data by Axon and Hume-Rothery (1948)) and $q = 3.73 \times 10^{-6} \Delta T$ nm (derived from the experiment: fig. 2). Then, the effect due to the difference in thermal expansion can be eliminated from the measured lattice parameters. As an example, the change in lattice parameter due to precipitation alone has also been given in fig. 1 (dashed line).

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