AGEING OF LIQUID-QUENCHED AND SOLID-QUENCHED ALUMINIUM BASE ALLOYS; ANALYSIS OF LATTICE-PARAMETER VARIATIONS

P. VAN MOURIK

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PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, Prof.Drs. P.A. Schenck, in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen op dinsdag 18 oktober 1988 om 16.00 uur

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Multatuli, uit Idee 198.

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Aan Louise Henriëtte

Remco en Elise

STELLINGEN

1. De roosterparameterbepaling via Debije-Scherrer röntgenfoto's is een krachtig en vaak onterecht veronachtzaamd hulpmiddel bij het onderzoek van precipitatieprocessen in legeringen.

Dit proefschrift.

2. Macrorekken en microrekken in een matrix, veroorzaakt door een, door die matrix omgeven, mispassende tweede fase, kunnen kwantitatief beschreven worden door toepassing en uitwerking van Eshelby's theorie, oorspronkelijk opgesteld voor de beschrijving van de elastische vervormingen door puntfouten in een eindige matrix.

Dit proefschrift, hoofdstuk III. J.D. Eshelby, Solid State Phys., 3 (1956), p. 79-114.

3. Uit de roosterparameter van een fase wordt veelal via een uit de literatuur bekend verband tussen de roosterparameter van die fase en samenstelling, de samenstelling van die fase bepaald. Voor een meerfasige legering is dit onjuist, indien geen rekening met de, geheel of gedeeltelijk, elastische accommodatie van de volumemispassingen tussen de fasen wordt gehouden. Om deze reden kunnen vele gepubliceerde fasediagrammen correctie behoeven.

Dit proefschrift, hoofdstuk IV.

4. Bij de berekeningen van Von Heimendahl van de matrixrekken in een preparaat bestaande uit een aluminiummatrix met daarin silicium als gedispergeerde fase wordt de spiegelbeeldkracht ten onrechte over het hoofd gezien.

M. van Heimendahl, Aluminium, 44 (1968), p. 96-101.

5. Faulkner neemt bij de berekening van het gemiddelde kwadraat van de microrek ten onrechte impliciet aan dat de gemiddelde rek in een isotroop kristal altijd nul is.

E.A. Faulkner, Phil. Mag., 5 (1960), p. 519-521.

6. Bij het onderzoek naar de leerprestaties van leerlingen aan het eind van het basisonderwijs wordt de invloed van de leerkracht ten onrechte buiten beschouwing gelaten.

Programmalijn 1; basisonderwijs, overzicht van in 1986/1987 lopend en afgesloten SVO-onderzoek; SVO, Den Haag, 1987.Goed Onderwijs, wat is dat? Voorstudie periodieke peiling van het onderwijsniveau, H. Wesdorp, SVO, Den Haag, 1985.

- 7. Een bakfiets is een milieuvriendelijk transportmiddel met een hoge verhouding van nuttige last tot eigen massa; toepassing van aluminiumlegeringen in bakfietsen met een aangepaste vormgeving kan deze verhouding verder verhogen.
- De verhouding van het ledental van de Vereniging tot behoud van Natuurmonumenten in Nederland tot dat van de ANWB (≡ 1 : 12) geeft de relatieve marktwaarde van natuurbehoud in Nederland.
- 9. Amnesty International komt op voor (onder meer) slachtoffers van de schending van het recht op vrijheid van meningsuiting, dat belangrijk is voor de verspreiding van resultaten van wetenschappelijk onderzoek. Daarom zijn universiteiten en onderzoekorganisaties de natuurlijke bondgenoten en belanghebbenden in deze strijd van Amnesty International.
- 10. Fietsers of wandelaars luisterend naar hun "walkmans" dienen een bord "slecht horend" ter waarschuwing aan hun medeweggebruikers met zich te voeren.

P. van Mourik Delft, 18 oktober 1988

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SUMMARY

SAMENVATTING

RÉSUMÉ

I. INTRODUCTION

Rapidly solidified aluminium alloys form a new class of metastable metallic materials with, in general, very fine microstuctures and enlarged (metastable) solid solubility of alloying elements (1-4). Due to the high cooling and solidification rates, the presence of excess vacancies (5) can be expected after rapid solidification. The transformation of these metastable structures into more stable ones brings about precipitation of solute atoms. The progress of precipitation will be dependent on the excess vacancy concentration. However, the mechanism and the kinetics of the precipitation are only superficially known: apart from the results presented in this thesis, until now only few investigations were devoted to the precipitation in rapidly solidified alminium alloys (3,6).

Rapid solidification techniques mostly yield solids in the shape of ribbons, flakes or powders. These products are all, at least in one dimension, small. So, for practical application, a compaction, e.g. by hot extrusion, is required. During hot extrusion, ribbons, flakes or powders are heated and a part of the alloying elements, originally dissolved in the matrix, will precipitate. For an eventual optimized treatment, knowledge of the precipitation kinetics is necessary.

A considerable part of the aluminium alloys contains silicon and magnesium as major alloying elements. Therefore, binary aluminium alloys with silicon and with magnesium as alloying elements were chosen for the present research project. Furthermore, this choice enabled to compare two types of precipitation:

(i) Direct precipitation of the equilibrium phase:

silicon precipitates from the Al-rich phase as silicon crystals with a diamond crystal structure.

(ii) Precipitation via intermediate phases:

magnesium precipitates from the Al-rich phase evolve by the formation of Guinier-Preston (GP) zones (clusters) and an intermediate precipitate (β), before the equilibrium phase (β) develops (7).

Precipitation in aluminium alloys implies alloying-element (= solute) depletion of the Al-rich phase. Because the lattice parameter of the Al-rich phase (= Al matrix) is related with the amount of solute, measurement of this lattice parameter allows, in principle, quantitative analysis of precipitation processes in (binary) aluminium alloys. Such a procedure is favoured by the high accuracy of the X-ray diffraction lattice parameter determination (in practice 1-2 parts to 40,000). By taking X-ray diffraction Debije-Scherrer (DbS) photographs, the lattice parameter(s) of the Al matrix and, occasionally, of the second (precipitating) phase can be determined and also the broadening of selected diffraction lines can be analysed.

Atoms in the precipitating phase in a binary aluminium alloy can have an atomic volume different from the one they have when they are dissolved in the Al matrix. Further, the precipitating (second) phase can have a thermal expansion coefficient different from that of the Al matrix. These two differences can cause volume-misfit strains resulting in X-ray diffraction line shift and line broadening (3,7, this thesis).

Characterization of the (initial) metastable structures as obtained after liquid quenching is essential for the subsequent study of the precipitation process. A description of the structure of the AlSi and AlMg alloys after liquid quenching is given in the next chapter.

Strains resulting in X-ray diffraction line shift, indicating a change of the lattice parameter as averaged over the diffracting volume are called *macrostrains*. Strains associated with spacing variations on an atomic scale, and giving rise to X-ray diffraction line broadening are described as *microstrains*. Macro- and microstrains due to volume misfits in two-phase systems are analysed theoretically and experimentally in chapter III.

Precipitation phenomena occurring on ageing in quenched AlSi and AlMg alloys are analysed in chapter IV. Thanks to the relation between composition of the Al matrix and its lattice parameter, the kinetics of the precipitation process can be studied by analyzing the behaviour of the Al matrix lattice parameter as a function of the time of ageing at the ageing temperature applied.

By precipitation of a second phase in an initially supersaturated Al matrix, macrostrains can be provoked as the outcome of (i) the difference in volume between atoms dissolved in the Al matrix and in the precipitated phases, and (ii) the difference in thermal shrinkage between matrix and precipitated particles on cooling after ageing. Macrostrains from origin (i), affecting the average Al-matrix lattice parameter, develop at the ageing temperatures applied. A subsequent relaxation is possible. Macrostrains from origin (ii) will be introduced after each cooling. The unraveling of the various contributions to lattice-parameter variations and the study of the kinetics of the precipitation processes occurring on ageing liquid-quenched and solid-quenched AlSi and AlMg alloys is the subject of chapter IV.

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II. STRUCTURES OF LIQUID-QUENCHED ALLOYS

Structural inhomogeneities of AISi alloys rapidly quenched from the melt

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Hypo- and hyper-eutectic AlSi alloys were rapidly quenched from the melt using the melt-spinning technique with two spinning velocities. Structural differences between the wheel (chill) and upper sides of the melt-spun ribbons were investigated by optical and scanning electron microscopy and X-ray diffraction methods (texture- and size-strain analyses). The Al-rich phase of the hypo-eutectic alloys was textured. The textures observed from both sides of the ribbons were different; in neither case was it of fibre type. For the larger spinning velocity applied, the structural imperfection of the wheel side was larger than that of the upper side for both the Al-rich and the Si-rich phases.

1. Introduction

By rapid quenching from the melt, recycling of scrap material may be facilitated because the solid solubility of alloying elements is enlarged and/or a very fine structure is developed [1]. A considerable part of the aluminium scrap consists of alloys with silicon as major alloying element.

It was shown recently [2], that considerable variations in the metastable solid solubility of silicon in aluminium occur as a function of ribbon thickness. Also in view of a possible commercial application of the melt-spinning process, the former analysis is extended to a description of the preferred orientations and micro-structure (sizestrain analysis) of the aluminium and silicon phases present at the wheel (chill) and upper sides of the ribbons.

2. Experimental details

2.1. Specimen preparation

Aluminium-silicon alloys with compositions 0, 2.5, 12.6 and 33.9 at% Si were prepared from 99.998 wt% Al and 99.99 wt% Si by melt-spinning (i.e. impinging a jet of molten alloy onto the cylindrical surface of a rotating copper wheel) as described previously [2]. The ribbons obtained were irregular varying in thickness from ~ 0.1 (not only at the edges) to 150 μ m. Therefore, no

useful information was available for the average thickness.

2.2. Metallography

Optical and scanning electron microscopy were performed with a Neophot-2 (Carl Zeiss Jena) optical microscope and a Jeol JXA-50A scanning electron microscope, respectively. Wheel and upper sides and cross-sections of the ribbons were examined after mechanical polishing and etching in a 5 or 10% KOH solution or Keller and Wilcox's reagent. Applying an accelerating voltage of 20 kV, SEM micrographs were obtained from specimens covered with a vacuum-deposited gold layer to enhance contrast.

2.3. X-ray diffraction

Specimens for the X-ray diffraction analysis were composed of a number of ribbons (as much as possible of uniform and equal thickness in the range $20-150 \ \mu m$) placed parallel to each other with either wheel or upper side at the surface.

2.3.1. Texture analysis

Pole figures were determined according to the Schulz reflection technique [3] using $CoK\alpha$ radiation and a Siemens Lücke-type texture



Figure 1 Optical micrographs in the plane of the ribbon of upper side (a) and wheel side (b) of a melt-spun ribbon of the hypo-eutectic AlSi (2.5 at % Si) alloy.

goniometer. The measured intensities were corrected for background radiation and defocusing effects. The pole figures were plotted according to Love [4]. The low-angle reflections 1 1 1 and 200 were used, because then the X-rays penetrate least into the specimen and discrimination between wheel and upper side is optimal.

2.3.2. Line profile analysis

Line profiles from the aluminium-rich and siliconrich phases were recorded with $CoK\alpha$ radiation. A Siemens type F ω -diffractometer was used, having a graphite monochromator in the diffracted beam and operating at low scanning speed to obtain sufficient counting accuracy. Large portions of the background at both sides of the peaks were recorded. The background was interpolated linearly between the two extremities. For the elimination of the α_2 component [5] the ratio R (where $R = I\alpha_2(\max)/I\alpha_1(\max)$ and $I\alpha_1$ and $I\alpha_2$ are the intensities of the α_1 and α_2 components, respectively) was taken from a high-angle reflection of the standard specimen.

The broadening due to the instrumental aberrations and the X-ray spectrum used was eliminated with the aid of line profiles recorded from a thin silicon standard specimen (prepared as described in [6]). For analysis of the profiles of the aluminium-rich phase, an interpolation was performed on the 2θ -scale between the breadths of the reflections of this silicon standard.

3. Results

3.1. Morphology

Optical micrographs characteristic of the upper and wheel sides of the hypo-eutectic AlSi (2.5 at %



Figure 2 Optical micrographs in the plane of the ribbon of upper side (a) and wheel side (b) of a melt-spun ribbon of the hyper-eutectic AISi (33.9 at % Si) alloy.



Si) and the hyper-eutectic AlSi (33.9 at % Si)alloys were obtained after very slight mechanical polishing and subsequent etching (Figs 1a, b and 2a, b). It can be seen that the structure at the upper side is considerably coarser than at the wheel side.

Optical and SEM micrographs of the crosssections show that, especially at those places where the absence of curvature at the wheel side indicates good contact between wheel and ribbon during solidification, a thin fine-grained region with only a few silicon-rich phase particles is adjacent to the wheel-ribbon interface ("featureless" zone: e.g. Fig. 3c).

On top of this zone, a primary Al-rich solidification structure is observed for the hypo-eutectic alloy (a region of columnar grains as suggested by



Figure 3 SEMs of the cross-section of a melt-spun ribbon of the hypo-eutectic AlSi (2.5 at % Si) alloy: a thin predendritic fine (chill) crystal zone at the wheel side with only a few silicon-rich phase particles (c), which develops into a region of dendritic columnar grains with siliconrich phase particles at the grain boundaries (a, b).

the presence of Si-rich phase particles at the grain boundaries; cf. Fig. 3a and b), whereas a primary Si-solidification structure is observed for the hyper-eutectic alloys (cf. Fig. 4; AlK α and SiK α X-ray emission images demonstrate that the material protruding from the etched surface of the cross-section is Si-rich).

3.2. Preferred orientations

The silicon-rich phase did not show any preferred orientation.

With reference to the surface and the axis of a ribbon, the texture of the aluminium-rich phase in hypo-eutectic alloys can be described as follows:

wheel side: $\{1 \ 1 \ 0\} \langle 1 \ 0 \ 0\rangle;$

upper side: $\{100\}\langle 110\rangle$.

Examples of 11 l-pole figures for the AlSi (2.5 at % Si) alloy are shown in Fig. 5a and b. The 200-pole figures were also determined and gave results consistent with the 11 l-pole figures.

The textures are symmetrical with respect to the longitudinal section. Furthermore, it is seen that the texture of the upper side shows an "off-



Figure 4 SEM of the cross-section of a melt-spun ribbon of the hyper-eutectic AlSi (33.9 at % Si) alloy showing a primary silicon-rich phase (facetted) solidification structure (a). The AlK α and SiK α X-ray emission images (b and c; d is the corresponding electron image) demonstrate that the material protruding from the etched surface is Si-rich.



Figure 5 1 1 1-pole figures of the aluminium-rich phase present at the wheel side (a) and the upper side (b) of melt-spun ribbons of the hypo-eutectic AlSi (2.5 at % Si) alloy. The ribbon axis is indicated by the arrow. The single-crystal orientation designating the preferred orientation observed is indicated. Note the "off-set" for the texture of the upper side as indicated by the difference between for example the positions 1 and 1'.

set" of about $5-10^{\circ}$ with respect to the preferred orientation indicated above (note the difference between, for example, the positions 1 and 1' in Fig. 5b).

Because of the penetration of the X-rays, in the pole figure obtained from one side of the ribbon some phenomena of the pole figure of the other side could be observed too. This effect was stronger for the wheel side than for the upper side. Therefore, it is concluded that the preferred orientation of the wheel side is restricted to a smaller part of the ribbon thickness than the preferred orientation of the upper side.

TABLE I The ratio R of the difference between the maximum and the minimum intensities observed in the 1 1 1-pole figures of the aluminium-rich phase in melt-spun AlSi alloys and the intensity which would be observed from a specimen without preferred orientation

Silicon content	Circumferential	R		
(at.%)	velocity (m sec ⁺¹)	Upper side	Wheel side	
0	38.6	2.5	1.8	
12.6	23.2	1.5	1.5	
12.6	46.2	1.2	1.2	
33.9	46.2	0.8	0.7	

With increasing silicon content of the alloy and increasing circumferential velocity of the wheel, the sharpness of the texture of the aluminium-rich phase decreased, in particular for the upper side of the ribbons. This may be illustrated roughly by the decrease of the difference between the maximum and minimum intensities observed in the 1 1 1-pole figures from either side (Table I). In the hypereutectic alloy practically no texture is present.

3.3. Crystallite size and lattice strain

The crystallite (domain) sizes and the lattice distortions in the aluminium-rich and the silicon-rich phases can be determined by X-ray diffraction line profile analysis. In this paper, a recently developed single-line method is applied [7]. It was justified that the method is valid for the specimens considered here [7]. All line profiles are assumed to be Voigt functions, i.e. convolutions of Cauchy and Gaussian functions. From the profile to be investigated the integral breadths of the Gaussian and Cauchy components of the only structurally broadened profile are obtained. In practice, size broadening is often considered to result into Cauchy-shaped profiles, whereas strain broadening gives rise to Gaussian-shaped profiles [8, 9]. Then one can apply for the determination of size and strain effects [7]:

$$D_{\rm eff} = \lambda/\beta_{\rm c}^{\rm f} \cos \theta$$
 and $e = \beta_{\rm g}^{\rm f}/4 \tan \theta$,

where D_{eff} and e denote the effective crystallite size perpendicular to the reflecting planes and an average microstrain, respectively. β_c^f and β_g^f are the integral breadths of the Cauchy and Gaussian components of the only structurally broadened profile, f.

The aluminium-rich phase showed a dominant strain broadening: the Cauchy components of the standard profile and the instrumentally and struc-

TABLE 11 Size-strain analysis of the aluminium-rich and silicon-rich phases of melt-spun ribbons of the AISi
(12.6 at. % Si) alloy. β^{f} = total integral breadth of the pure profile f; β_{c}^{f} = integral breadth Cauchy component of the
pure profile f; β_{σ}^{f} = integral breadth Gaussian component of the pure profile f; D_{eff} = cifective crystallite (domain) size
and $e = \text{microstrain}$. The microstrain of the Al-rich phase was calculated from the total integral breadth β^{f} . $D_{eff} = \infty$
denotes $D_{eff} > 20 \times 10^3$ nm

Reflection	Circumferential velocity (m sec ⁻¹)	Ribbon side	β ^f (° 20)	$\beta_{c}^{f}(^{\circ}2\theta)$	$\beta_{g}^{f}(^{\circ}2\theta)$	D _{eff} (10 nm)	e × 10 ³
Aluminium-r	ich phase						
200	23.2 46.2	upper wheel upper	0.149 0.134 0.154	0.017 0.020 0.031	0.138 0.121 0.134	60 00 00	1.3 1.2 1.4
Silicon-rich	ohase	wheel	0.192	0.052	0.157	8	1.7
220	23.2	upper wheel	0.369 0.377	0.170 0.223	0.250 0.215	680 520	2.0 1.8
220	46.2	upper wheel	0.690 0.846	0.344 0.317	0.447 0.629	340 370	3.7 5.2

turally broadened profile were equal to within the experimental error. Therefore the microstrain of the aluminium-rich phase was calculated from the total integral breadth of the pure, only structurally broadened, profile. The silicon-rich phase showed both size- and strain-broadening. As an example, results of the AlSi (12.6 at % Si) alloy are gathered in Table II.

The differences between wheel and upper side were investigated for pure Al and AlSi (12.6 at % Si) and AlSi (33.9 at % Si) alloys^{*}. In general, the broadening from the aluminium-rich phase did not show a significantly systematic difference between the wheel and upper sides. The broadening from the silicon-rich phase was significantly larger for the wheel side than for the upper side (in particular for the AlSi (12.6 at % Si) alloy; cf. Table 11); in general, at the wheel side a smaller crystallite size and a larger microstrain was found than at the upper side.

A large circumferential velocity of the wheel increased the broadening observed from both the aluminium-rich and silicon-rich phases. This held for the wheel sides in particular (see Table II).

4. Discussion

4.1. Hypo-eutectic alloys

From the differences between the results obtained from wheel and upper sides, a subdivision of the cross-section of the melt-spun ribbon is plausible: (i) a thin zone (say $10 \mu m$) at the wheel (chill) side, where an approximately "diffusionless solidification" [10] occurred (the analogue of the massive transformation [11]). During solidification the supercooling was large enough to permit nucleation and growth of the solid phase without an appreciable solute redistribution; only a few silicon-rich phase particles are observed in this region (Fig. 3c). This predendritic fine (chill) crystal zone develops into (ii) a thick zone of columnar, parallel, dendritic grains. At the grain boundaries of this presumably less rapidly solidified material, silicon-rich phase particles are discerned (interdendritic microsegregation; Fig. 3a and b).

Indications for the occurrence of preferred orientations after liquid quenching were rarely obtained [12, 13]. (In splat-cooled aluminium flakes no preferred orientation was observed [14]). The observation of a definite texture *both* at the wheel side and at the upper side of melt-spun ribbons has not been reported before.

The textures observed are not fibre textures, as one may intuitively expect, but they are symmetrical with respect to the longitudinal section of the ribbon. This hints at the presence of anisotropic temperature gradients and/or mechanical stresses during solidification.

The textures observed at the wheel side and at the upper side can be transformed into each other by a 90°-rotation around a (110)-axis parallel to the outer surfaces of the ribbon and perpendicular to the ribbon axis. Because it was found previously that some of the dendrite boundaries in liquid-quenched material are of the twin

*The effect of the silicon content of the alloy on the line broadening observed was discussed in [2].

type [10], we tried to explain the texture of the upper side with respect to the texture of the wheel side by a multiple twinning operation (e.g. [15]), which proved to be impossible.

For the wheel side of melt-spun ribbons, no texture has been observed previously. For the upper side of melt-spun ribbons of nickel-based superalloys it was noted that columnar dendritic grains were aligned approximately along a (100)direction [16], in agreement with the present results from the AlSi alloys. Also, in conventionally cast AlSi alloys, a (100)-direction appears to be favoured by the growing dendrites [17].

The observation of an "off-set" of about $5-10^{\circ}$ for the texture of the upper side can be considered to be related to the columnar crystals angled backwards to the melt pool (cf. [16]), indicating that the temperature gradient makes an angle of $5-10^{\circ}$ with the surface normal (cf. Figs 3a and 5b). This sets an essential difference between melt-spun and splat-cooled material; in the latter case [12] the columnar crystals grow perpendicular to the splat surface.

The (aluminium-rich phase) texture of the upper side, especially, became less sharp as the silicon content of the alloy increased, which may indicate the hindrance of preferred growth by the microsegregated silicon-rich phase particles.

Because in the thin (chill) zone at the wheel side of the ribbons only a very small amount of silicon-rich phase particles is observed, the sizestrain data for the silicon-rich phase taken at the wheel side are related mainly to the lower part of the columnar grain region. Also, because of the penetration of the X-rays, the size-strain data for the aluminium-rich phase taken at the wheel side are an average for the thin (chill) zone and the lower part of the columnar grain region.

Several factors contribute to the presence of microstrains in both the aluminium-rich and silicon-rich phases:

(i) because a silicon atom in its own diamondtype lattice occupies a volume 23% larger than in the aluminium fcc lattice, considerable misfit strains will be invoked in both phases. This effect will increase with increasing silicon content;

(ii) microstrains in both phases may result from the temperature gradient present during quenching. This effect will be larger at the wheel side than at the upper side;

(iii) after solidification the two-phase alloy cools down to room temperature resulting in

thermal strains due to the large difference between the thermal expansions of both phases [18]. This effect will increase with increasing silicon content;

(iv) concentration variations within (solute clustering) and between the diffracting domains lead to apparent strain values [19].

The smaller crystallite (domain) size of the silicon-rich phase at the wheel side as compared to the upper side is presumably related to the larger cooling rate at the wheel side.

A larger spinning velocity of the rotating wheel will cause a larger cooling and solidification rate. Then a less pronounced texture, a larger microstrain and a smaller crystallite size may be expected, as is observed (cf. Tables I and II).

4.2. Hyper-eutectic alloys

As with the hypo-eutectic alloys the hypereutectic alloys also possess a thin "featureless" zone at the wheel side, especially if good contact between ribbon and wheel occurred. On top of this zone the primary silicon phase grew in a facetted manner. A relatively high supercooling is required for this mode of solidification. It may then be expected that a more or less homogeneous and rapid solidification occurs throughout this region. This picture can be consistent with: (i) lattice parameter measurements indicating that a considerable amount of aluminium may be incorporated in the silicon-rich phase of the hypereutectic alloys, in contrast with the hypo-eutectic alloys [2]; (ii) the observed absence of texture in the hyper-eutectic alloys.

The cooling rate at the wheel side will have been larger than at the upper side and this can explain the coarser microstructure (Figs. 2a, b) as well as the smaller line broadening observed from the upper side as compared to the wheel side.

5. Conclusions

(1) Both the hypo-eutectic alloys and the hypereutectic alloys show a thin "featureless" zone at the wheel side. On top of this zone a dendritic region of columnar grains is observed for the hypoeutectic alloys, whereas a region showing a facetted growth is observed for the hyper-eutectic alloys.

(2) In the hypo-eutectic alloys the aluminiumrich phase at the wheel side shows a preferred orientation different from the one at the upper side, whereas the silicon-rich phase is randomly oriented. In the hyper-eutectic alloy no significant texture is observed. (3) The silicon-rich phase at the wheel side has a larger microstrain and a smaller domain size than at the upper side, which is presumably due to the difference in cooling rate between both sides.

(4) A larger circumferential velocity of the rotating wheel is accompanied by a larger cooling and solidification rate and thus "broadens" the texture, decreases the domain size and enlarges the microstrain.

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Structural and compositional variations in aluminium alloys rapidly quenched from the melt

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Rapid quenching of aluminium alloys by meltspinning results in ribbons showing a heterogeneous solidification structure [1, 2]. This structural heterogeneity is expected to result from local differences in cooling rate. Thus, compositional variations due to differences in solidification conditions may be expected. Therefore, the relation between the local concentration of the alloying element and the microstructure has been investigated.

Ribbons of AlSi and AlMg alloys were prepared by applying a melt-spinning technique ([3]; in the present investigation the circumferential velocity was 31.4 m sec^{-1}). The hypo-eutectic alloys used were prepared from 99.994 wt % Al, 99.99 wt % Si and 99.99 wt % Mg. The thickness of the ribbons obtained varied between 40 and 80 μ m. Cross-sections were obtained by preparation of the ribbons along their longitudinal axis. After mechanical polishing and etching in Keller and Wilcox's reagent the cross-sections were examined with a Neophot 2 (Carl Zeiss Jena) optical microscope. X-ray microanalysis was performed with an ARL electron microprobe. The content of alloying element was determined near the wheel side, near the upper side and in the centre as an average value obtained from tracks with a length of about $45 \,\mu\text{m}$ parallel to the outer surfaces.

Cross-sections of melt-spun ribbons are shown in Fig. 1. Three regions can be distinguished.

1. A very finely grained (sometimes "featureless") zone at the wheel (chill) side.

2. A zone of columnar grains.

3. A zone of equiaxed grains at the upper side. The results of the X-ray microanalysis are gathered in Table I. It is concluded that the concentration of alloying element is highest in the centre and lowest near the upper side, whereas the concentration near the wheel side takes an intermediate value.

The results obtained suggest a close relation

TABLE I Local alloying element concentrations in melt-spun ribbons of AlSi and AlMg alloys. Compositions given are average values, obtained from tracks with a length of about 45 μ m parallel to the outer surfaces. The counting statistical standard deviations are indicated. The calculated "overall" concentration equals $\frac{1}{4}$ (concentration wheel side + 2 × concentration centre + concentration upper side) (trapezoidal rule)

Alloy system	"Overall" concentration (at%)	Wheel side concentration (at %)	Centre concentration (at %)	Upper side concentration (at %)
AlSi	1.14	1.14 ± 0.015	1.20 ± 0.016	1.01 ± 0.016
	1.33	1.31 ± 0.013	1.37 ± 0.014	1.28 ± 0.013
	1.30	1.29 ± 0.010	1.31 ± 0.010	1.29 ± 0.010
	2.74	2.74 ± 0.014	2.78 ± 0.014	2.65 ± 0.013
	2.78	2.80 ± 0.014	2.80 ± 0.014	2.73 ± 0.014
	5.29	5.33 ± 0.027	5.36 ± 0.027	5.09 ± 0.025
	5.23	5.10 ± 0.026	5.34 ± 0.027	5.13 ± 0.026
AlMg	2.84	2.84 ± 0.015	2.84 ± 0.015	2.83 ± 0.015
	2.32	2.28 ± 0.014	2.39 ± 0.014	2.21 ± 0.013
	2.36	2.36 ± 0.014	2.37 ± 0.014	2.36 ± 0.014
	9.64	9.65 ± 0.026	9.75 ± 0.027	9.41 ± 0.026
	15.44	15.18 ± 0.035	15.73 ± 0.036	15.13 ± 0.035



between solidification structure and composition. The following picture of solidification on meltspinning may explain the experimental findings.

At the wheel side the highest cooling rate and the largest undercooling are expected, yielding a very finely grained (sometimes "featureless") zone, which is thought to have solidified "diffusionless" [3]. As a consequence the alloying element concentration in this zone should equal the average alloy composition. The results in Table I support this expectation.

After solidification of the (predendritic) chill zone, the columnar (dendritic) zone will develop, accompanied by interdendritic microsegregation. As solidification proceeds from the wheel side, solidification will start from the upper side too. Because the local cooling rate there is relatively small, equiaxed grains can develop. In this region solidification is accompanied by an appreciable solute redistribution and the solidified alloy will have a concentration of alloying element lower than the average alloy composition.

From the above discussion it follows that the ribbon centre solidifies last. Hence a marked enrichment of alloying element occurs in this region. It is suggested that solidification completes after the ribbon has lost contact with the wheel surface.

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EXCESS VACANCIES IN RAPIDLY QUENCHED ALUMINIUM ALLOYS

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A sudden increase of the Al-rich phase lattice parameter of liquid-quenched AlMg and AlSi alloys occurred on short-time ageing. This increase was attributed to the annihilation of excess vacancies, initially retained after liquid quenching. Applying a simple model the initial excess vacancy concentration was calculated from the increase of the Al-rich phase lattice parameter. The excess vacancy concentration was found to increase with solute content, which was interpreted in terms of a solute-concentration dependent apparent free enthalpy of vacancy formation.

1. INTRODUCTION

Many properties of metals depend on the vacancy concentration. Vacancies play an important part in precipitation phenomena^{1,2}. If the quenching rate is sufficiently high (> 10^4 Ks^{-1}), nearly all equilibrium vacancies present at high temperature are retained at low temperature as excess vacancies³. These excess vacancies may annihilate at the low temperature. In pure aluminium the annihilation is completed within one hour at room temperature^{4,5}. In binary aluminium alloys the interaction between solute atoms and vacancies delays vacancy annihilation.

The introduction of vacancies decreases the value of the lattice parameter 1 . Thus, excess vacancy annihilation can be followed by measurement of the lattice parameter on ageing.

2. EXPERIMENTAL

Aluminium alloys with 2.3 and 11.6 at% Si and with 3.18, 10.5, 12.8 and 16.7 at% Mg were prepared from 99.998 wt% Al, 99.99 wt% Si and 99.99 wt% Mg. Meltspinning yielded ribbons with a thickness of 25-50 μ m and a width of about 2 mm⁶. Measurement of dendrite arm spacings⁷ indicated a cooling rate of about 10⁶ Ks⁻¹.

Specimens were cut out half-way the ribbon width parallel to the ribbon axis. Typical

dimensions were: 8 mm length, 1 mm width and local ribbon thickness.

Ageing took place in an oil bath at about 400 K, using specially designed cylinders with three specimens each allowing direct contact between oil and specimens. The ageing temperature was reached within one minute. Lattice parameters at 298 K of the Al-rich phase of the alloys were obtained as a function of ageing time with a precision of 1-2 parts to 40,000 from Debye-Scherrer photographs, taken with Cu-K α radiation and applying Nelson-Riley extrapolation⁸.

3. RESULTS

Fig. 1 shows some examples of the change of the Al-rich phase lattice parameter as a function of ageing time. In all cases the values of the Al-rich phase lattice parameter suddenly increased on short-time ageing. The observed maximum changes, Δa^{max} , are given in Table 1.

For the AlMg alloys as liquid quenched, X-ray diffraction analysis did not reveal any presence of second phases. No precipitation was detected during the present ageing experiments. Thus, the composition of the Al-rich phase was taken equal to the overall alloy composition.

In the AlSi alloys a Si-rich and an Al-rich phase were both present. The composition of the

Al-rich phase could be estimated from its lattice parameter after accounting for the strain effect due to the difference in thermal expansion between the Al-rich phase and the Sirich phase provoked by cooling after ageing¹.

4. DISCUSSION

The increase of the Al-rich phase lattice parameter on short times of ageing can not be attributed to precipitation of a second phase. For the AlSi alloys this follows from previous work¹, where it was shown that precipitation only occurred significantly at later stages of ageing. For the AlMg alloys precipitation would result in a *decrease* of the Al-rich phase lattice parameter, in contrast with the increase observed for short-time ageing. Also, no precipitation of a second phase was found in the present experiments. Further, no such sudden increase of the Al-rich phase lattice parameter occurred in experiments with conventionally quenched AlSi alloys.

Because of the condition of mechanical equilibrium the average stress of the specimens is zero. The resulting Al-rich phase lattice parameter is a weighted average of all occurring lattice parameters in a specimen, because the penetration depth of the X-rays is of the same order of magnitude as the thickness of the specimen and the specimen was fully enclosed by the X-ray beam while the DbS photograph was taken. Thus, the sudden increase of the average Al-rich phase lattice parameter can not be ascribed to stress effects.

Hence, the following conclusions are drawn (cf. Table 1 and Fig. 1):

- (i) The increase of the lattice parameter is caused by the annihilation of excess vacancies initially retained after liquid quenching.
- (ii) The amount of excess vacancies strongly increases with the atomic percentage of solute atoms.

The lattice parameter of a "binary" alloy of a metal and vacancies may be written as:

$$a = c_v a_v + (1 - c_v) a_p$$
 (1)

where a is the lattice parameter of the alloy, a_v is the fictitious vacancy lattice parameter, c_v is the vacancy concentration and a_o is the lattice parameter of the metal without vacancies. If the vacancy volume is half the volume of an aluminium atom⁹, then a_v can be written as:

$$a_v = 2^{-1/3} a_o$$
 (2)

From equations (1) and (2), the change of the lattice parameter Δa due to a change of the vacancy concentration Δc_v can be written as:

$$\Delta a \equiv a_{t=t} - a_{t=0} = (2^{-1/3} - 1) a_0 \Delta c_v$$
 (3)

where $a_{t=t}$ is the value of the lattice parameter after t minutes of ageing and $a_{t=0}$ is the value of the lattice parameter at t = 0, i.e. in this case after liquid quenching.

If the maximum change of the Al-rich phase lattice parameter, Δa^{max} , is caused by annihilation of all excess vacancies, $-\Delta c_V^{max}$, equals the initial excess vacancy concentration c_V^{exc} . Values of c_V^{exc} are presented in Table 1 and Fig. 2 as a function of atomic percentage of solute atoms.

In a pure metal the equilibrium vacancy concentration c, can be given by:

$$c_{v} = \exp - \Delta g_{f} / kT \tag{4}$$

where Δg_f is free enthalpy of formation of a vacancy, exclusive of configurational entropy. In the presence of solute atoms interacting with vacancies the vacancy concentration is different from that in the pure metal. Lomer calculated

Table 1: Maximum change of Al-rich phase lattice parameter (Δa^{max}), excess vacancy concentration (c_v^{exc}) and apparent free enthalpy of formation of a vacancy (Δg_f^s)

	co	mposition						
alloy		Al-rich pha	se ageing temperatur	e ^a t=0	$\Delta a^{max} \times 10^5$	cv ^{exc} x 10 ⁴	Τq	∆g ^s f
(at%)		(at%)	(K)	(nm)	(<i>nm</i>)		(K)	(eV)
2.30	Si	1.41 Si	399 + 4	0.40470	3	4	900	0.61
10.6	Si	3.53 Si	399 <u>+</u> 4	0.40434	7	8	850	0.52
3.18	Mg	3.18 Mg	404 + 4	0.40634	4	5	900	0.59
10.5 I	Mg	10.5 Mg	404 + 4	0.40978	6	7	825	0.52
10.5	Mg	10.5 Mg	411 + 2	0.40975	6	7	825	0.52
12.8	Mg	12.8 Mg	411 + 4	0.41027	10	12	800	0.46
16.7 I	Mg	16.7 Mg	404 + 4	0.41220	34	40	760	0.36
16.7	Mg	16.7 Mg	411 + 2	0.41215	50	59	760	0.34





The change of the Al-rich phase lattice parameter, Δa , as a function of ageing time t (alloy composition and ageing temperatures are indicated)



The excess vacancy concentration in liquidquenched AlSi and AlMg alloys, c_v^{exc} , and the apparent free enthalpy of formation of a vacancy, Δg_f^s , as a function of atomic percentage of solute atoms, c_B (the estimated quench temperatures, T_q , are indicated).

the equilibrium vacancy concentration for diluted substitutional binary solid solutions with less than 1 at% of solute atoms^{3,10}. Theoretical treatments for concentrated alloys were proposed too^{11,12,13}. However, these models do not allow easy application because of lack of data.

Generally the equilibrium vacancy concentration in a binary solid solution, c_y^s , can be written as:

$$c_v^s = exp - \Delta g_f^s / kT$$
 (5)

where Δg_f^s is an apparent free enthalpy of formation of a vacancy, analogously to Δg_f in eq. (4); however, part of the configurational entropy change is included in Δg_f^s . Assuming that the excess vacancy concentration at room temperature equals the vacancy concentration at the quench temperature, T_q , i.e. $c_v^S(T_q) = c_v^{exc}$ with T_q = the appropriate solidus temperature of the alloy concerned¹⁴, values for Δg_f^s can be calculated for the present experiments (cf. Table 1 and Fig. 2). Clearly, the values for Δg_f^s decrease roughly linear with the atomic percentage of solute atoms in the composition range studied, which corresponds with an exponential increase of the vacancy concentration.

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III. X-RAY DIFFRACTION LINE SHIFT AND LINE BROADENING DUE TO MISFIT STRAINS IN TWO-PHASE ALLOYS

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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.

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§ 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 μ m were obtained (Bendijk, Delhez, Katgerman, de Keijser, Mittemeijer and van der Pers 1980). The cooling rate was in the range 10⁶ to 10⁷ 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 aluminiumrich 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_{AI} of pure aluminium, both measured at room temperature, is given in table 1 for different annealing temperatures and various silicon contents.

Silicon con	tent of alloy	of alloy		
(weight %)	(volume %)	temperature (K)	a_m (nm)	$\Delta a \times 10^{+3}$ (nm)
2.4	2.8	397	0.40496	(0.3)
11.0	12.5	397	0.40202	6
2.4	2.8	425	0.40497	1
11.0	12.5	425	0.40203	7
2.4	2.8	445	0.40498	2
2.4	2.8	448	0.40499	3
11.0	12.5	448	0.40203	7
22.4	25.1	445	0.40511	15
34.8	38.2	445	0.40516	20

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

 $\Delta a = a_m - a_{AI}$ (reference temperature 298 K). $a_m =$ lattice parameter of the aluminium-rich phase after completed precipitation, measured at room temperature (about 294 K).

 $a_{A1} =$ lattice parameter of pure aluminium = 0.40496 nm (Pearson 1967). The volume % silicon holds for the case where all the silicon is precipitated.

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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 ($\alpha_{Al} = 23.5 \times 10^{-6} \text{ K}^{-1}$ (Smithells 1976); $\alpha_{Si} = 3.0 \times 10^{-6} \text{ K}^{-1}$ (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

$$\boldsymbol{\epsilon} = (r_0^{\mathbf{B}} - r_0^{\mathbf{A}})/r_0^{\mathbf{A}}, \qquad (1)$$

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[†] 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))

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

with

$$C = \frac{\mu_{\mathsf{A}}}{K_{\mathsf{A}}} \frac{K_{\mathsf{B}}}{3K_{\mathsf{B}} + 4\mu_{\mathsf{A}}},\tag{3}$$

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

$$\Delta a \equiv \Delta a_{\rm A} = 4Ca_{\rm A} \frac{\epsilon}{\left(1+\epsilon\right)^3} y_{\rm B} \,. \tag{4}$$

4.2. Application to AlSi

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

(a) $\epsilon_{\mathbf{V}}$, 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):

$$\epsilon_{\rm V} = (a_{\rm Si} - a_{\rm Al}\sqrt[3]{2})/a_{\rm Al}\sqrt[3]{2} = 0.0643, \tag{5}$$

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:

$$\epsilon_{\rm T} = (\alpha_{\rm Al} - \alpha_{\rm Si})(T_{\rm a} - T_{\rm r}) = 20.5 \times 10^{-6} \Delta T, \qquad (6)$$

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



 $\Delta a/\Delta T$ 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 $\epsilon_{\rm V} (=0.064)$ and $\epsilon_{\rm T} (=0.003$ 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).

Lattice parameters in two-phase systems after annealing

	Particle size of silicon from reflection			
Alloy composition (wt% Si)	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	

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)).

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 $(x_{si} = 0)$. 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 $x_{\rm B} = 0$ 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

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

where $x_{\rm B}$ is the atomic fraction of component B in solid solution in the A-rich matrix and $y_{\rm B}$ 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 $f_{\rm S}(x_{\rm B})$ and the effect due to the difference in thermal expansion between the dispersed B-rich phase and the A-rich matrix is represented by $f_{\rm T}(y_{\rm B})$. The term $f_{\rm S}(x_{\rm B})$ follows from experimental data. Often $f_{\rm S}(x_{\rm B})$ can be approximated by $px_{\rm B}$, where p is a constant (a second-order approximation has been proposed by Moreen, Taggart and Polonis (1971)). The term $f_{\rm T}(y_{\rm B})$ can be written as $qy_{\rm B}$ (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).

Lattice parameters in two-phase systems after annealing

The unknowns $x_{\rm B}$ and $y_{\rm B}$ 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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ON MISFIT-INDUCED LATTICE SPACING VARIATIONS IN TWO-PHASE ALLOYS:

THE CASE OF COOLING-INDUCED MICROSTRAINS IN THE AI-MATRIX OF FULLY AGED AISI ALLOYS

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1.Introduction

On the ageing of supersaturated solid solutions, elastic strains develop as a result of the volume misfit between the precipitating disperse (non-equilibrium) phase(s) and the, continuous, matrix phase. This is the basis of the well known, but not fully understood, precipitation hardening of alloys. Knowledge of the development of internal strain distributions may be of great use for the understanding of the macroscopic mechanical properties of multiphase materials.

Consider a specimen composed of a matrix A and homogeneously distributed particles B. Elastic strains in such an assembly occur if the B-particles do not fit without deformation into the holes provided by the Amatrix. The origin of such a misfit can be various, e.g. atomic volume changes caused by precipitation of the B-particles or differences in shrinkage between the A-matrix and the B-particles on cooling after a heat treatment.

From an experimental point of view, one can distinguish macro- and microstrains. By definition, a macrostrain is related to the *average* lattice spacing of a phase, whereas a microstrain corresponds to an average of the variations in the lattice spacing. Therefore, both macro- and microstrains can be detected by X-ray diffraction: macrostrains cause shifts of the diffraction lines and microstrains induce broadening of the diffraction lines.

The occurrence of *macrostrains* in a matrix containing misfitting second phase particles was investigated earlier (1,2). On the basis of a theory developed by Eshelby (3) for the elastic strains in a continuous isotropic matrix due to misfitting inclusions and originally applied to crystals containing point imperfections, a relation was derived (see Section 2) between the macrostrain, the volume fraction y_B of B-particles, a misfit parameter ε and a constant C_A reflecting the elastic properties of both the matrix and the inclusions (1,4). In the case of point imperfections the theory has its limitations (5). However, these may be less significant for inclusions composed of a number of atoms.

An experimental test was performed on two-phase AlSi and FeN alloys. Because precipitation stresses due to differences in molar volume were completely relaxed in the fully aged AlSi alloys (Al-matrix + Siparticles) (1,4), the misfit solely stemmed from the difference in shrinkage between the Al-matrix and the precipitated Si-particles on cooling from the ageing temperature T_a to room temperature T_r and the misfit parameter ε could be quantified easily (see Section 4). A fair agreement between theory and experiment was established (1). A very good agreement between theory and experiment was obtained for the fully aged twophase FeN alloys (α -Fe matrix + α "-Fe₁₆N₂ particles), where the misfit was solely due to differences in molar volume (2).

To our knowledge a quantitative interpretation of *microstrains*, i.e. of diffraction line broadening, in a matrix containing misfitting particles has not been given before. The aim of the present study is to describe the microstrain quantitatively and to perform an experimental test on fully aged AlSi alloys.

2. Theory

In Eshelby's theory the distinction between an infinite and a finite A-matrix is essential.

Inserting a misfitting spherical B-particle into a cavity of an *infinite*, continuous and isotropic A-matrix causes stresses in all directions. Taking the origin in the centre of the B-particle and considering only the displacements in the A-matrix it can be shown that, in polar coordinates (r,φ,θ) , the mutually perpendicular local strain components are given by (5):

$$\mathbf{e}_{rr} = -2 \, C \, \varepsilon \, (\mathbf{r}_{o}^{A})^{3} / \mathbf{r}^{3} ; \qquad \mathbf{e}_{\phi\phi} = \mathbf{e}_{\theta\theta} = C \, \varepsilon (\mathbf{r}_{o}^{A})^{3} / \mathbf{r}^{3} \qquad (\mathbf{r} > \mathbf{r}_{o}^{A})$$
[1]
where $C = 3K_B/(3K_B + 4\mu_A)$ with μ and K denoting the shear and the bulk modulii and where - with r_0^A and r_0^B as the radii of the undeformed cavity in the A-matrix and of the undeformed B-particle - the misfit parameter ε is given by: $\varepsilon = (r_0^B - r_0^A)/r_0^A$. The B-particle is only subjected to a uniform hydrostatic stress, implying the absence of microstrains. As the relative volume change of the matrix $\Delta V_A/V_A$ equals $e_{rr} + e_{\phi\phi} + e_{\theta\theta}$, it follows directly from eq. [1] that for an infinite A-matrix no volume change, and therefore no macrostrain, occurs at all on inserting a misfitting B-particle. Hence, the stress components for the A-matrix can be written in terms of the shear modulus μ_A :

$$X_{rr} = -4\mu_A C \varepsilon (r_0^A)^3 / r^3; \qquad X_{\phi\phi} = X_{\theta\theta} = 2\mu_A C \varepsilon (r_0^A)^3 / r^3 \qquad (r > r_0^A)$$
 [2]

A finite spherical assembly of an A-matrix with a spherical B-particle has a traction-free bounding surface. To fulfil this requirement, the stress along the radius vector \mathbf{I} has to be compensated by a hydrostatic stress equal to $-X_{\Gamma\Gamma}$ (r = R) where R is the radius of the assembly. This hydrostatic stress changes the volume of the matrix (1,4) and therefore macrostresses occur in a finite matrix. For a cubic matrix with lattice parameter a_A the macrostrain $e_u = \Delta a_A/a_A$ follows, via $\Delta V_A/V_A = 3\Delta a_A/a_A = -X_{\Gamma\Gamma}$ (r = R)/K_A, from eq. [2]:

$$e_{u} = 4 C_{A} \varepsilon (r_{o}^{A})^{3} / R^{3} = 4 C_{A} \frac{\varepsilon}{(1+\varepsilon)^{3}} y_{B}$$
[3]

where $C_A = C \mu_A/3K_A$ and y_B is the volume fraction of B. Equation [3] also holds for a matrix containing a number of B-particles whose strain fields are independent.

The strain e_u is uniform throughout the finite matrix and therefore does not contribute to the broadening of matrix reflections. The breadth of an X-ray diffraction line is connected with $\langle e^2 \rangle$, i.e. the volume average of the square of the position-dependent part of the strain in the direction perpendicular to the diffracting planes (hkl) (6). For an elastically isotropic matrix in which the strain field has spherical symmetry it holds that (i) $\langle e^2 \rangle$ is the same for all (hkl) and (ii) the average over a sphere of radius r around the origin of the squared position-dependent strains perpendicular to the diffracting planes, $\langle e^2(r) \rangle$, is equal to the average over all directions (φ, θ) of the squared strains at a point (r, φ, θ). Then it follows:

$$\langle e^{2}(\mathbf{r}) \rangle = \frac{1}{5} \left(e^{2}_{\mathbf{r}\mathbf{r}} + e^{2}_{\phi\phi} + e^{2}_{\theta\theta} \right) + \frac{2}{15} \left(e_{\mathbf{r}} e_{\phi\phi} + e_{\mathbf{r}} e_{\theta\phi} + e_{\phi\phi} e_{\theta\theta} \right)$$
[4]

Substitution of eq. [1] yields:

$$\langle e^{2}(\mathbf{r}) \rangle = \frac{4}{5} C^{2} \varepsilon^{2} (r_{o}^{A})^{6} / r^{6}$$
 [5]

By averaging over the total volume, i.e. over all distances $r^B \le r \le R$, one obtains (see also eq. [3]):

$$\langle e^2 \rangle = \frac{4}{5} C^2 \frac{\varepsilon^2}{(1+\varepsilon)^6} y_{\rm B}$$
 [6]

Eq.[6] also holds for a matrix containing a number of B-particles, whose strain fields in the matrix are independent (see eq. [3]).

This result can also be obtained in an indirect way from the energy E_A , associated with the strain field in an infinite matrix (no uniform strain). From eqs. [1] and [2] it is obtained (cf. Ref. 5):

$$E_{A} = 6\mu_{A} C^{2} \frac{\varepsilon^{2}}{(1+\varepsilon)^{6}} y_{B}$$
[7]

According to the reasoning by Faulkner (7), it follows for the present symmetry:

 $E_{A} = \frac{15}{2} \mu_{A} < e^{2} >$ [8]

From eqs. [7] and [8], eq. [6] follows directly.

The integral breadth of a strain-broadened line profile, i.e. integral intensity divided by maximum intensity, is related to the microstrain $\langle e^2 \rangle^{1/2}$ by:

$\langle e^2 \rangle^{1/2} = k \beta \cot \theta_B$

where $\theta_{\rm B}$ is Bragg's angle and k is a proportionality constant, which, as usual, is taken here as 1/4 (6).

3. Experimental Procedures

Ribbons (thickness 20-50 mm) of AlSi alloys with 0, 2.3, 4.2, 5.9, 11.9 and 18.2 at% Si were prepared by meltspinning from 99.998 wt% Al and 99.99 wt% Si (8). According to dendrite arm spacing measurements the cooling rate was in the range of $10^6 - 10^7 \text{ Ks}^{-1}$. To be sure of a completed silicon precipitation ((9);see also Section 4), sections of the ribbons were (fully) aged during 1841 h at 447 ± 2 K in an oil bath and cooled in air. The preparation of specimens for X-ray diffractometry consisted of placing pieces of ribbon parallel to each other on a flat plastic turntable with the aid of adhesive tape, alternating up- and wheelsides. So, the data obtained are averages for the up- and wheelsides (10).

The X-ray diffraction line profiles were chosen on the following grounds: (i) high $2\theta_B$ reflections to improve accuracy, (ii) different crystallographic directions to investigate effects due to a possible lack of isotropy, and (iii) minimal disturbance by neighbouring diffraction lines from Si-particles. The Al{400}-, Al{331}- and Al{420}-line profiles were selected; only the Si{531}-reflection was situated between the Al{331}- and the Al{420}-line profiles. The profiles were recorded using a Siemens ω -diffractometer employing CuK α -radiation (45 kV, 25 mA). The profiles were measured by the preset-time method with steps of 0.02°20. Large portions of the background at both sides of the peak were recorded.

To remove the so-called instrumental broadening and the broadening due to the X-ray wavelength distribution the corresponding line profiles of co-aged pure aluminium ribbons served as references (10). The background was linearly interpolated between the extremities of the profile measured. The analysis of the line profiles was performed by the so-called single-line Voigt method, assuming that both the reference profile and the line profile to be analysed could be described by a Voigt-function (11). As the recorded profiles were relatively sharp, no corrections for the angle dependence of the Lorentz-polarisation and the absorption factors were considered to be necessary. Before applying the single-line Voigt method, the α_2 -components of the profiles were eliminated.

In practice it is often considered that a finite crystallite size results in Cauchy-shaped profiles and that microstrains result in Gaussian-shaped profiles (11). In the present case, it appeared that the Al-matrix line profiles corrected for instrumental effects were almost entirely of Gaussian shape. Therefore, the structural line broadening of the Al-matrix line profiles investigated was interpreted as only caused by microstrains.

For the presence of overlapping tails of the Si{531} reflection the following correction procedure was applied to the Al{331} and Al{420} profiles. For the alloy with the highest silicon content the overlapping Si{531} tails were eliminated by an educated guess, which gave an increase of 10% of the microstrain as compared to the microstrain obtained without elimination. Then for the remaining alloys the microstrain values obtained from the Al{331} and Al{420} reflections, without elimination of the overlapping Si{531} tails, were increased in proportion to the silicon content of the alloy concerned.

4. Results and Discussion

In fully aged AlSi alloys, consisting of an Al-matrix and dispersed Si-particles, a contribution to the broadening of the Al-matrix line profiles can be expected from (i) composition variations in the Al-matrix, (ii) lattice defects as dislocations, and (iii) misfit phenomena. Composition variations in decomposing alloys would generally result in asymmetrical Al-matrix line profiles (12). However, the observed Al-matrix profiles are symmetrical. Further, at the ageing temperature applied the silicon equilibrium solubility in the Al-matrix is negligible (13). So, it is concluded that cause (i) does not contribute to the line broadening observed. A

[9]

substantial density of lattice defects as dislocations in the Al-matrix is not expected since the motion of dislocations is not much obstructed in the matrix of almost pure Al at the relatively high ageing temperature applied: 447 ± 2 K, which is almost half the melting point of Al. Further, one should expect about the same lattice defect density in the pure Al reference specimen (see Section 3) and by the line profile analysis technique applied here (relative determinations, see Ref. 14), a possible presence of lattice defects is not reflected in the values for the microstrains obtained.

Misfit phenomena can be caused by:

- a. the difference in atomic volume between silicon dissolved and silicon precipitated;
- b. the difference in thermal shrinkage between the Al-matrix and the Si-particles on cooling from the ageing temperature T_a to room temperature T_r.

The difference in atomic volume causes strains during silicon precipitation (4,9), that relax during and after precipitation (15). At about 450 K this process of silicon precipitation and stress relaxation in melt-spun AlSi alloys has been completed after 32 h of ageing (4,9). The applied ageing treatment in this investigation was 1841 h at 447 ± 2 K. So, the only origin of Al-matrix line broadening is the difference in thermal shrinkage between the Si-particles and the surrounding Al-matrix.

[10]

The misfit parameter ε then reads (1):

 $\varepsilon = (\alpha_{A1} - \alpha_{Si})(T_a - T_r) = \Delta \alpha \Delta T$

where α_{A1} and α_{S1} are the thermal linear expansion coefficients of the Al-matrix and the Si-particles.

- The fully aged melt-spun AlSi alloys can be regarded as a model system for the study of the elastic effects due to the presence of misfitting second phase particles since:
- (i) the large difference in thermal expansion coefficients of the Al-matrix and the Si-particles $(\Delta \alpha = 20.5 \times 10^{-6} \text{ K}^{-1}$ (4)) yields a large misfit parameter.
- (ii) the Al-matrix can be regarded as elastically isotropic (16).
- (iii) the Si-particles in melt-spun AlSi alloys can be considered as small spheres (1).

In Fig. 1 the theoretical and experimental values of $\langle e^2 \rangle^{1/2} / \Delta T$ as obtained for the fully aged melt-spun AlSi alloys from the different Al-matrix reflections are plotted as a function of $(y_{Si})^{1/2}$ (The volume fraction y_{Si} was calculated from the overall composition of the alloy concerned; the value of C in eqs. [1] and [6] was obtained from the elastic constants of the elements (16), giving a theoretical value of Cth = 0.73). For the ageing temperature applied the value of $(1 + \varepsilon)$ can be put equal to one. As prescribed by eq. [6], the experimental data lie on a straight line through the origin, the slope of which is only slightly different from the predicted value. As a function of y_{Si} (the alloy composition) no distinct differences occur between the values of $\langle e^2 \rangle^{1/2} / \Delta T$ obtained from the different Al-matrix line profiles {400}, {331} and {420}. This justifies the assumption of elastic isotropy.

The value for C in eqs. [1] and [6] as deduced from the straight line through the experimental data in Fig. 1 equals $C^{exp} = 0.67$ which is about 10% smaller than $C^{th} = 0.73$. The proportionality constant C_A in eq. [3] for the *macrostrain* as deduced from experiments was about 30% larger than the one calculated from literature data: $C_A^{exp} = 0.112$ to compare with $C_A^{th} = 0.086$ (4). Considering the simplicity of the model applied, the compatibility of the used literature data for the elastic

Considering the simplicity of the model applied, the compatibility of the used literature data for the elastic constants with the model and the uncertainties in the line profile analyses, e.g. about the value of k in eq. [9], a satisfactory correspondence occurs between theory and experiment, not only for the *macrostrain* (1,2), but also for the *microstrain* (present work).

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FIGURE 1- The microstrain in the Al-matrix of fully aged AlSi alloys per Kelvin difference between ageing and room temperature, $\langle e^2 \rangle^{1/2} / \Delta T$, as a function of the square root of the volume fraction of Si-phase, $(y_{Si})^{1/2}$.

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IV. PRECIPITATION AND THE DEVELOPMENT AND RELAXATION OF MISFIT STRAINS IN LIQUID-QUENCHED AND IN SOLID-QUENCHED AISI AND AIMg ALLOYS

On precipitation in rapidly solidified aluminium-silicon alloys

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The precipitation of silicon in rapidly solidified AISi alloys was studied. For alloys with 2.4 and 11.0 wt % Si (2.3 and 10.3 at % Si, respectively) the lattice parameters of the Alrich and of the Si-rich phases were measured after ageing at 397, 425 and 448 K. For alloys with 2.6 and 13.0 wt % Si crystallite sizes and lattice strains were determined by analysis of the X-ray diffraction line broadening. After ageing the lattice parameters of the Al-rich and the Si-rich phases were influenced by the difference in thermal expansion between both phases. After correction for this effect the amount of silicon dissolved in the Al-rich phase was estimated as a function of ageing time. Quenched-in (excess) vacancies influenced the precipitation kinetics. Activation energies for precipitation appeared to depend on the extent of transformation. Further, quenched-in vacancies caused anomalous maxima in the lattice parameter curves. The behaviour of the lattice microstrains on ageing was explained as a result of the disappearance of stresses due to quenching and the introduction and subsequent dissipation of stresses due to precipitation. After completed precipitation stresses due to the difference in thermal expansion between both phases still exist at room temperature.

1. Introduction

Alloys of aluminium and silicon form an important part of aluminium scrap. Liquid quenching [1, 2], as compared to solid quenching, enlarges the solid solubility of the alloying elements, thus facilitating the recycling of scrap material. Although the precipitation of silicon in solid-quenched AlSi alloys was the subject of several studies [3-8], few investigations were devoted to precipitation in liquid-quenched AlSi alloys [1, 9]. This paper presents results on processes occurring during precipitation in liquid-quenched AlSi alloys. By liquid quenching the silicon solubility may be extended up to the eutectic composition [2], whereas the maximum equilibrium solubility equals 1.58 at % at 850 K. On liquid quenching all silicon present can rarely be kept in solid solution (cf. Discussion in [2]). Further, vacancies present at elevated temperatures will be retained after quenching. Therefore, the precipitation kinetics are determined by the amount of silicon in solid solution as well as by the excess vacancy concentration.

2. Excess vacancies in aluminium and its alloys

From the literature the following picture of the behaviour of excess vacancies during quenching and ageing may be obtained.

In case the quenching rate is sufficiently high $(>10^4 \text{ K sec}^{-1} [10-12])$ nearly all vacancies present at high temperatures will be retained at room temperature as excess vacancies. In pure aluminium excess vacancies cluster into voids which can collapse into loops during quenching and during ageing subsequent to quenching. The occurrence of voids preceding loop formation was first suggested by Kuhlmann-Wilsdorf and Wilsdorf [13] and was experimentally supported by Kiritani [14, 15]. The observation of vacancy loops only was reported in $[13, 16]^*$. Since the recovery of quenched pure aluminium has been completed after 1 h of ageing at room temperature [17-19], the excess vacancies are expected to annihilate at room temperature within the same time.

In the presence of dissolved alloying elements interacting with vacancies, the concentration of excess vacancies can be higher than in pure aluminium [20, 21]. According to Westmacott et al. [22] the size of the vacancy loops depends on the nature of the alloying element. Alloying with zinc, copper, silver, magnesium and silicon resulted in smaller loops in the order given, indicating an increasing interaction from zinc to silicon between (clusters of) dissolved alloying atoms and vacancies. The majority of the excess vacancies is bound to alloying atoms. This amount will be larger as the interaction between alloying atoms and vacancies increases [20, 21]. In the case of the AlSi system the "free" excess vacancies will precipitate into vacancy loops during quenching or subsequent ageing. Indeed, it can be deduced from experimental data for aluminium alloys [3, 11, 22] that only a small fraction of the total excess vacancy concentration, as theoretically calculated according to [20, 21], precipitates into vacancy loops. To our knowledge no void formation preceding loop formation has been reported until now for aluminium alloys*. Due to the affinity between vacancies and silicon vacancy loops in AlSi alloys may be stabilized up to rather high temperatures $[6, 7]^{\dagger}$. Therefore, in contrast with the case of pure aluminium no significant vacancy annihilation occurs at room temperature (cf. [11] p. 39).

During ageing vacancies are moving through the crystal. According to Ozawa and Kimura [7] vacancy loops can act as temporary sinks. In the presence of a low density of permanent sinks[‡] the excess vacancies firstly condense into loops. This process continues until a quasi-equilibrium concentration of excess vacancies in the matrix is established. From that moment on a net loss of excess vacancies occurs at permanent sinks which is compensated by the evaporation of the loops.

Because silicon precipitation proceeds via a vac-

ancy diffusion mechanism, the annihilation of the excess vacancies will have a great influence on the kinetics of the silicon precipitation. Liquid quenching generally results in higher excess vacancy concentrations than solid quenching does [23, 24].

Initial experiments with liquid-quenched AlSi alloys demonstrated the influence of the excess vacancy concentration: as compared to solidquenched specimens, precipitation in liquidquenched specimens can proceed more rapidly (cf. [3, 4] to [1, 9]). In accordance with this picture, the activation energy for precipitation after liquid quenching can be lower than after solid quenching (cf. [8] to [1, 9]).

3. Experimental procedures

Aluminium alloys with 2.4 and 11.0 wt % Si were prepared [2] from 99.998 wt % Al and 99.99 wt % Si. By the melt-spinning technique ribbons with a non-uniform thickness varying between 20 and $150 \,\mu\text{m}$ were obtained [2]. According to dendritic arm spacing measurements the cooling rate was in the range 10^6 to 10^7 K sec⁻¹.

The kinetics of the silicon precipitation were studied by the measurement of the lattice parameter of the Al-rich phase (with a precision of 1 part to 40 000) as a function of ageing time at 397, 425 and 448 K[§]. The measurement procedure and the heat treatment applied were described earlier [25]. Further, short-time experiments were performed, using a specially designed cylinder to enclose two specimen holders with the very vulnerable specimens. With the new cylinder it was found that ageing temperatures of 397 and 448 K were reached within one minute.

Crystallite size and microstrain of the aluminium matrix and the silicon precipitates were studied by X-ray diffraction line profile analysis for two liquid quenched AlSi alloys, with 2.6 wt %Si and with 13.0 wt % Si, respectively, as a function of ageing time at 445 K. Sections of the ribbons obtained after melt spinning were placed parallel to each other on a piece of flat glass with the aid of adhesive tape, alternating up- and wheelsides. Thus, the effects that might originate from

§ All lattice parameter values presented in this paper are valid at 298 K.

^{*}This may be due to the collapse of voids during preparation at about room temperature of electron microscope specimens.

[†]In this context it is remarked that according to Rosenbaum and Turnbull [4] silicon precipitates after ageing show a density of the same order of magnitude as the vacancy loop density.

[‡]Vacancy loops having a diameter of about 10 nm and a density of about 10^{16} cm⁻³ [4, 5, 22] possess an estimated loop line length of 3×10^{4} cm⁻².

differences between the up- and wheel-side are averaged [26]. After the X-ray investigation the sections were removed from the glass in trichloroethane, followed by cleaning in acetone. Then, the sections were put into a specimen holder which enabled two collections of ribbon sections of different compositions to be aged simultaneously at precisely the same temperature. After heat treatment the ribbon sections were cleaned in trichloroethane, acetone, trichloroethane and acetone in the order given, and then dried.

X-ray diffraction line profiles were recorded using a Siemens ω -diffractometer employing CuK α radiation (45 kV; 24 mA). The profiles were recorded by the preset-time method employing steps of 0.02° 2 θ and counting times of 100 sec. Large portions of the background at both sides of the peak were recorded. The background was interpolated linearly between both extremities, except in the case of the silicon {220} reflection were a correction for a tail of the aluminium {200} reflection, present in the background, was performed.

The $\{400\}$ and $\{422\}$ line profiles of the Alrich phase were recorded. In the case of AlSi 13.0 wt % alloy the $\{111\}$, $\{220\}$, $\{311\}$ and $\{422\}$ profiles of the Si-rich phase were measured as a function of the ageing time. Due to weak intensities these profiles from the AlSi 2.6 wt % alloy were only measured after 730 h ageing. The Si-rich phase $\{111\}$ profile from this alloy in the liquid-quenched condition was measured as well, although with a very low accuracy due to the low intensity. The line profiles obtained were analysed using a single-line technique, described elsewhere [27].

4. Results

4.1. Lattice parameters

4.1.1. Anomalous effects at initial stages

Figs. 1 and 2 show the lattice parameter of the Alrich phase as a function of ageing time (times shorter than 120 min) for two alloy compositions at the ageing temperatures 399 and 445 K. Two types of anomalous humps are observed in the curves of lattice parameters against ageing time at the start of ageing (the reason of this subdivision is outlined in the discussion (Section 5.3)):

(a) Hump I is observed at the lower ageing temperature, whereas Hump II is observed at the higher ageing temperature.

(b) Hump II is higher than Hump I.

(c) Hump II occurs after longer ageing times than Hump I.

(d) Both effects increase with silicon content (note the different scales of Figs. 1 and 2).

Ribbons obtained by melt spinning generally show local variations of the amount of silicon dissolved in the Al-rich [2, 26]. This explains differences in the Al-rich phase lattice parameter at the start of ageing and an exact correspondence between the curves of the Al-rich phase lattice parameter against ageing time cannot be expected (Figs. 1 to 4).

4.1.2. The lattice parameter of the Al-rich phase

The lattice parameter of the Al-rich phase as a function of ageing time at different temperatures is shown in Figs. 3 and 4. These results were obtained from Debye-Scherrer photographs by Nelson-Riley extrapolation [28]. As shown for the first time in [25], a difference in thermal



Figure 1 The lattice parameter of the Al-rich phase in the AlSi 2.4 wt % alloy after short times of ageing.



Figure 2 The lattice parameter of the Al-rich phase in the AlSi 11.0 wt % alloy after short times of ageing.

expansion between two phases in a system can cause macrostrains. A correction for this effect can be performed (see Section 5.1). Resulting curves for the Al-rich phase lattice parameter against ageing time are presented by dash-dot lines in Figs. 3 and 4.

4.1.3. The lattice parameter of the Si-rich phase

Because of the small amount of silicon, present in the hypo-eutectic alloys of this investigation, the determination of the Si-rich phase lattice parameter by applying a Nelson-Riley procedure [28] was impossible. In these cases the Si-rich phase lattice parameter was studied as a function of ageing time and temperature by measuring a selected reflection on a Debye-Scherrer photograph; precision was improved by a tenfold measurement of the line. In Table I the results are shown. The comparison of results from different reflections is justified in view of the zero slope of the Nelson-

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Riley plot obtained for hypereutectic alloys. The following observations can be made:

(a) The value of the Si-rich phase lattice parameter after ageing is smaller than after liquid quenching, and is also smaller than the equilibrium value of silicon (0.54307 nm; [29]).

(b) The silicon lattice parameter after completed precipitation decreases with increasing ageing temperature (this trend is best seen from the results for the AlSi 11.0 wt% alloy; these data were taken from high angle reflections).

In addition, for the hypereutectic alloys AlSi 22.4 wt % and AlSi 34.8 wt % the Si-rich phase lattice parameter was investigated (now by Nelson-Riley extrapolation [28]) before and after ageing at 445 K. In Table I these results are gathered too. The following observations can be made:

(c) In the hypereutectic alloys the Si-rich phase lattice parameter is considerably larger than in the hypo-eutectic alloys.

Figure 3 The lattice parameter of the Al-rich phase in the AlSi 2.4 wt% alloy as a function of ageing time; dash-dot lines indicate the results obtained after correction for the difference in thermal expansion between the Al-rich and Si-rich phase (cf. Section 5.1). The equilibrium value is indicated too.



Figure 4 The lattice parameter of the Al-rich phase in the AlSi 11.0 wt% alloy as a function of ageing time; dash-dot lines indicate the results obtained after correction for the difference in thermal expansion between the Al-rich and Si-rich phase (cf. Section 5.1). The equilibrium value is indicated too.

(d) In agreement with the hypo-eutectic alloys the value of the Si-rich phase lattice parameter after ageing is smaller than after liquid quenching, but in contrast with the hypo-eutectic alloys the silicon lattice parameter remains after 128 h ageing larger than the equilibrium value.

4.2. Crystallite sizes and lattice strains

X-ray diffraction line broadening is caused by instrumental aberrations, the wavelength distribution and the structural defects in the specimen. The broadening by instrumental aberrations and by the wavelength distribution can be determined by measuring corresponding line profiles of appropriate standard specimens. In this paper it is assumed that the profiles of both the specimen to be investigated and the standard specimen can be described by a Voigt function [27]. A Voigt function is the outcome of the folding of Cauchy and Gaussian components. In practice it is often considered that size broadening results in Cauchyshaped profiles and that strain broadening results in Gaussian-shaped profiles [27, 28, 30].

The crystallite size and the microstrain were followed as a function of ageing time at 445 K. The results have been collected in Figs. 5 to 8 and in Table II. For the aluminium matrix the following observations can be made:

(a) For the AlSi 2.6 wt % the line broadening is almost entirely of Gaussian shape. For the AlSi 13.0 wt % alloy the Gaussian component dominates strongly.

(b) Interpreting the total line broadening for both alloys as due to microstrains it is found that the microstrain decreases with increasing ageing time. The microstrains in a [100] direction are

Alloy (wt % Si)	Selected	After liquid quenching a _{Si} (nm)	After ageing		
	reflection ΣH^2		Time (h)	Temperature (K)	^a Si (nm)
	11	0.5432 (± 5)	256	397 ± 3	0.5429 (± 2)
2.4	8	0.5431 (± 2)	256	425 ± 4	0.5425 (± 2)
	11	0.5435 (± 2)	256	448 ± 5	0.5428 (± 1)
11.0	11	0.5430 (± 4)	256	397 ± 3	0.5429 (± 1)
	24	0.5428 (± 2)	256	425 ± 4	0.5427 (± 1)
	24	0.5429 (± 1)	256	448 ± 5	0.5426 (± 1)
TABLEIBT	he lattice parameter o	of the Si-rich phase in hyper	eutectic alloys		
22.4	NR*	0.54395 (± 9)	128	445 ± 2	0.5437 (± 2)
34.8	NR	0.5444 (± 2)	128	445 ± 2	0.5437 (± 2)

TABLE IA The lattice parameter of the Si-rich phase in hypo-eutectic alloys

*NR = Nelson - Riley extrapolation.



larger than in a [211] direction, especially for the AlSi 13.0 wt % alloy (cf. Figs. 5 and 6).

Due to the weak intensities observed for the Sirich phase, an appreciable scatter is present on the size-strain values for the Si-rich phase as derived from the Cauchy and Gaussian components, respectively. The best results are, of course, obtained after completed precipitation. Nevertheless, for the Si-rich phase the following observations can be made:

(c) The crystallite size of the Si-rich precipitates increases with ageing time. The domain size in a [111] direction is in general smaller than in [220], [311] and [211] directions.

(d) In case of the AlSi 13.0 wt % alloy, in particular the microstrain in a [111] direction shows an anomalous behaviour: first a decrease, than an increase; at last followed by a continuous decrease in the coarsening stage (Fig. 7). After 730 h ageing the microstrain in the Si-rich precipitates of the AlSi 13.0 wt % alloy is smaller than in the Si-rich precipitates of the AlSi 2.6 wt % alloys (Table II).

5. Discussion

5.1. The correction of the Al-rich phase lattice parameter for the effect caused by the difference in thermal expansion between the Al-rich phase and the Si-rich phase

From the value of the Al-rich phase lattice parameter the amount of silicon dissolved can be calculated. For this, normally a Végard-type equation is used. However, as shown earlier [25] a difference in thermal expansion between two phases in a specimen. can also change the average lattice parameter of the matrix after annealing. The total difference, Δa , between the measured lattice parameter of the Al-rich phase, a_m , and the lattice parameter of pure aluminium a_{Al} can be written as [25]:



Figure 6 The microstrain, $(c^2)^{1/2}$, of the Al-rich phase in the AlSi 13.0 wt% alloy as a function of time of ageing at 445 K.

Figure 5 The microstrain, $\langle e^2 \rangle^{1/2}$, of the Al-rich phase in the AlSi 2.6 wt% alloy as a function of time of ageing at 445 K.



Figure 7 The microstrain, $(e^2)^{1/2}$, of the Si-rich phase in the AlSi 13.0 wt% alloy as a function of time of ageing at 445 K.

$$\Delta a \equiv a_{\rm m} - a_{\rm Al} = f_{\rm s}(x_{\rm Si}) + f_{\rm T}(y_{\rm Si}) \qquad (1)$$

where the change of the average lattice parameter due to an atomic fraction of silicon dissolved in the Al-rich phase, x_{Si} , is represented by $f_s(x_{Si})$ and the change of the average lattice parameter due to the difference in thermal expansion between the dispersed Si-rich phase (with a volume fraction of y_{Si}) and the aluminium matrix is given by $f_T(y_{Si})$.

The term $f_s(x_{Si})$ follows from experimental data. Often $f_s(x_{Si})$ can be approximated by px_{Si} (Végard), where p is a constant. The term $f_T(y_{Si})$ can be written as qy_{Si} , where q follows from experimental data [25]. According to [25] the values of p and q are, respectively:



with $\Delta T = T_{\text{ageing}} - T_{\text{room}}$.

However, it should be realized, that the proportionality constant p was obtained from solidquenched specimens [31]. In fact it incorporates contributions due to dissolved silicon atoms and to quenched-in vacancies. Contributions to the lattice parameter due to silicon atoms dissolved and to quenched-in vacancies may be in different proportion after liquid quenching as compared to solid quenching. Hence, use of the above mentioned value of p in this work may introduce uncertainties in calculated values of x_{Si} .



Figure 8 The crystallite size, D_{eff} , of the Si-rich phase in the AlSi 13.0 wt% alloy as a function of time of ageing at 445 K.

	Reflection						
	AI{400}	Al{422}	Si{111}	Si{220}.	Si{311}	Si{422}	
Silicon content (wt%)	(X 10 ³)	(× 10 ³)	(X 10 ³)	(× 10 ³)	(X 10 ³)	(× 10 ³)	
2.6	0.44	0.43	1.4	2.9	2.7	2.0	
13.0	0.68	0.67	1.0	1.2	1.1	1.0	

TABLE II Microstrain values, (e²)^{1/2}, of the Al-rich and Si-rich phases after 730 h ageing at 445 K

With the aid of Equation A2 (see Appendix) x_{si} can be calculated from Equation 1. The values of the lattice parameter corrected for thermal strains, $a_{cor} = a_{A1} + px_{Si}$, are presented by dash-dot lines in Figs. 3 and 4.

5.2. The composition of the aluminium matrix after liquid quenching

For the study of precipitation kinetics (see Section 5.4) knowledge of x_{si} after liquid quenching is required. This value of x_{si} might be obtained from the lattice parameter as measured after liquid quenching. However, a correction of the lattice parameter for the effect to thermal strains cannot be performed at the start of ageing, since the solidification temperature and thus ΔT (see Section 5.1) is unknown. Therefore, the value of x_{si} at t = 0 was determined by extrapolation of x_{si} against ageing time t to t = 0 (Table III). This extrapolation procedure is accompanied by some uncertainties. Firstly, the effects due to Humps I and II can be accounted for by an educated guess only. Secondly, the rate of the precipitation process at the highest ageing temperature is higher than at the lowest temperature. Therefore, extrapolation down to t = 0 from the plot x_{si} against ageing time is much more reliable for the lowest ageing temperature than for the highest one.

Inspection of the values of x_{si} at t = 0, obtained from the above extrapolation, in terms of the corresponding Al-rich phase lattice parameters shows (Table III), that in most cases the measured lattice parameters are lower than the extrapolated ones (see also Figs. 1 and 2). This finding may be understood as follows: the ribbons after liquid quenching possess a high excess vacancy concentration. Excess vacancies lower the lattice parameter.

5.3. The behaviour of the Al-rich phase lattice parameter during initial stages of ageing

5.3.1. Hump I

The increase of the Al-rich phase lattice parameter at the very start of ageing at 399 K (Figs. 1 and 2) can be attributed to the annihilation of excess vacancies (e.g. at sinks and by the creation of vacancy loops; Section 2). This assertion is made plausibly below.

The lattice parameter of a "binary" alloy of pure aluminium and vacancies may be written as:

$$a = c_{v}a_{v} + (1 - c_{v})a_{A1}$$
 (2)

where a is the lattice parameter of the alloy, a_v is the fictitious vacancy lattice parameter and c_v is the fraction of atomic sites occupied by vacancies.

Suppose, the volume of a vacancy is half of the volume of the aluminium atom [32], then a_v can be written as:

$$a_{\rm v} = 2^{-1/3} a_{\rm Al}.$$
 (3)

From Equations 2 and 3, the change of the alu-

Alloy	Ageing	$x_{Si} \times 10^2$	Lattice parameter	
(wt % Si)	temperature (K)	extrapolated	Extrapolated (nm)	Measured (nm)
	(397 ± 3	1.67	0.40467	0.40468
2.4	425 ± 4	1.75	0.40466	0.40461
	448 ± 5	1.17	0.40476	0.40470
	(397 ± 3	3.81	0.40430	0.40427
11.0	$\begin{cases} 425 \pm 4 \end{cases}$	2.18	0.40458	0.40453
	448 ± 5	1.9	0.40463	0.40464

TABLE III The lattice parameter of the Al-rich phase after liquid quenching

minium lattice parameter Δa_v due to a change of the excess vacancy concentration Δc_v can be written as:

$$\Delta a_{\rm v} = (2^{-1/3} - 1)a_{\rm Al}\Delta c_{\rm v}.$$
 (4)

In case Hump I is attributed to the annihilation of excess vacancies, then for both alloys the change of the excess vacancy concentration may be estimated from the respective heights of Hump I by using Equation 4 (cf. Figs. 1 and 2):

AlSi 2.4 wt %:

$$\Delta a (\text{Hump I}) = (0.3 \pm 0.2) \times 10^{-4} (\text{nm})$$
$$\Delta c_v = -(3.6 \pm 2.4) \times 10^{-4}.$$

AlSi 11.0 wt %:

$$\Delta a (\text{Hump I}) = (0.5 \pm 0.2) \times 10^{-4} (\text{nm})$$
$$\Delta c_v = -(6.0 \pm 2.4) \times 10^{-4}.$$

Due to the strong interaction between silicon and vacancies a large fraction of the excess vacancies will be bound to silicon atoms dissolved after quenching (cf. Section 2). However, a small fraction of "free" excess vacancies will exist. The concentrations of free and bound excess vacancies differ by an order of magnitude [22]. Obviously, the concentration of the "free" vacancies, c_v^{A1} , will depend on the silicon content of the aluminiumrich phase. c_v^{A1} may be estimated by (cf. [21]):

$$c_{\rm v}^{\rm Al} = (1 - x_{\rm Si})^2 A \exp(-E_{\rm f}/kT)$$
 (5)

where z is the coordination number (for fcc z = 12). The pre-exponential factor A and the vacancy formation energy E_f have been taken from [33]. The temperature T was taken equal to the appropriate melting temperature. With $x_{Si} = 1.41 \times 10^{-2}$ and $x_{Si} = 3.53 \times 10^{-2}$ for the AlSi 2.4 wt% and the AlSi 11.0 wt%, respectively, as obtained after extrapolation to t = 0, one obtains

AlSi 2.4 wt %: $c_v^{A1} = 5.4 \times 10^{-4}$ AlSi 11.0 wt %: $c_v^{A1} = 2.3 \times 10^{-4}$.

These values of free excess vacancy concentration c_v^{A1} are of the same order of magnitude as the change of excess vacancy concentration calculated above from the heights of Hump I in Figs. I and 2. It might be argued that the loss of "free" excess vacancies is suppleted by excess vacancies bound to (clusters of) dissolved silicon atoms. For kinetic reasons this process is unlikely to occur

substantially at the start of ageing, as has been found for other aluminium alloys in [11] (this is also supported by the present investigation; see Section 5.4). Thus, one is tempted to conclude that the rise of the Al-rich phase lattice parameter at the start of ageing can be attributed to the annihilation of "free" excess vacancies. Considering this in more detail, the experimental Δc_v seems larger for the AlSi 11.0 wt% alloy than for the AlSi 2.4 wt% alloy, whereas theoretically a reverse trend is suggested. However, in view of the experimental errors and the uncertainties inherent to the theoretical calculation (Equation 5) and to the choice of its parameters detailed conclusions are unjustified.

The lowering of the lattice parameter after Hump I may be caused by the relaxation of quenching stresses. The occurrence of stress of this kind has been demonstrated earlier for solidquenched aluminium alloys [34-36].

Annihilation of the free excess vacancies proceeds by diffusion. The diffusion constant for vacancy migration can be written as

$$D = D_0 \exp\left(-E_{\rm m}/kT\right),$$

with $E_{\rm m}$ as the migration energy for a vacancy. Substituting $E_{\rm m} = 0.65 \, {\rm eV}$ [18] it follows that the vacancy diffusion constant at 445 K is seven times greater than at 399 K. Therefore, as compared to Hump I, Hump II observed at the highest ageing temperature at larger ageing times will have another origin.

5.3.2. Hump II

In our opinion a similar phenomenon to Hump II (Figs. 1 and 2) was observed by Itagaki et al. [1]. It was suggested that the transformation stresses induced by the silicon precipitation were not readily dissipated by the accompanying recovery process. At a lower ageing temperature this effect can be smaller, even undetectable, since the precipitation proceeds more slowly. This can explain the absence of Hump II at the lowest ageing temperature. It can be expected that Hump II will be larger the more silicon has been dissolved in the Al-rich phase in the as-liquid-quenched condition, which agrees with the experimental finding (note the difference in scale between Figs. 1 and 2). As precipitation proceeds, per unit of time less transformation strain is introduced because less silicon precipitates and the recovery process can catch up the strains induced. This explains why a

lowering of the Al-rich phase lattice parameter after Hump II occurs (cf. Figs. 1 and 2).

5.4. The precipitation of silicon from the supersaturated Al-rich phase after liquid quenching

For the study of the kinetics of precipitation a parameter X_t (the fraction transformed) is defined by:

$$X_{t} = (c_{0} - c_{t})/(c_{0} - c_{e})$$
(6)

where c_0 is the silicon concentration in the Al-rich phase at time t = 0, c_e is the equilibrium concentration of silicon in the Al-rich phase per unit volume and c_t is the silicon concentration in the Alrich phase after ageing time t.

At the commonly applied ageing temperatures for the AlSi alloys $c_e \simeq 0$ [37]. Using atomic fractions, Equation 6 transforms into:

$$1 - X_{t} = (a_{0}^{3} x_{\mathrm{Si}}^{t=t}) / (a_{\mathrm{m}}^{3} x_{\mathrm{Si}}^{t=0})$$
(7)

where a_0 is the Al-rich phase lattice parameter measured at t = 0, a_m is the Al-rich phase lattice parameter after ageing time t, $x_{Si}^{t=0}$ and $x_{Si}^{t=t}$ are the atomic fraction of silicon in solid solution in the Al-rich phase at time t = 0 and t = t, respectively. The values of $x_{Si}^{t=t}$ and $x_{Si}^{t=0}$ are obtained as described in Sections 5.1, 5.2 and the Appendix. The resulting $(1 - X_t)$ -curves are plotted in Figs. 9 and 10.

Assuming that the precipitation process proceeds in the same manner at the three ageing tem-



Figure 9 The reaction parameter, $(1 - X_t)$, for the precipitation on the AlSi 2.4 wt % alloy as a function of ageing time.



Figure 10 The reaction parameter, $(1 - X_t)$, for the precipitation in the AlSi 11.0 wt % alloy as a function of ageing time.

peratures applied, the activation energy can be calculated by plotting the time needed to reach a certain value of $(1 - X_t)$ against the reciprocal temperature. The results for progressive values of X_t are gathered in Table IV. (The values of X_t chosen were not affected by Hump I and/or Hump II). Notwithstanding inaccuracies inherent in the approximations made in the procedures followed, it may be concluded that the values of the activation energy for precipitation

(a) are smaller than the value reported for precipitation of silicon in solid-quenched AlSi alloys (i.e. 1.27 ± 0.03 eV; [8]);

(b) increase as the precipitation process proceeds.

In the following discussion it is assumed that the dominant step in the precipitation process is the diffusion of silicon atoms in the Al-rich phase*.

The activation energy for the diffusion of silicon in aluminium at thermal equilibrium corresponds

TABLE IV The activation energy E_A for silicon precipitation at constant values of $(1 - X_t)$

Alloy	$1-X_t$	<i>E</i> _A (eV)
	$\begin{pmatrix} 0.8\\ 0.6 \end{pmatrix}$	0.9
AlSi 2.4 wt %	{ 0.4 0.2	1.1 1.2
	0.6	0.8
AlSi 13.0 wt %	0.4	0.9 0.9

*The progress of precipitation can be described only approximately by the Avrami equation $(1 - X_t = \exp(-kt)^n)$. Best fitting can be expected for the first stage of precipitation [38]. From our experimental results values of the time constant n in the range 0.7 to 1.1 are obtained. From the review given in [38] it may be concluded that the obtained values of n indicate diffusion-controlled growth, which supports the assumptions made. to 1.32 eV [37, 39]. Therefore, it can be concluded that the activation energy of precipitation in solid-quenched AlSi alloys, as determined by Köster and Knorr [8] at a late stage of precipitation, corresponds to the diffusion of silicon in aluminium in the presence of the thermal equilibrium concentration of vacancies.

For a quenched AlSi specimen of a certain composition the same excess vacancy concentration will be present at the start of precipitation at each of the ageing temperatures applied. Hence, the energy of formation of a vacancy is absent in the activation energy for silicon diffusion and the activation energy at the start of precipitation will be given by the activation energy of migration of a vacancy (neglecting the temperature dependence of the correlation factor [40]). As the precipitation process proceeds, the excess vacancies associated with silicon are annealed out gradually (see Section 2) and thus at different ageing temperatures different vacancy concentrations will be present. This effect enhances the activation energy for precipitation, which corresponds with the experimental findings (at the end of the precipitation the activation energy equals the sum of $E_{\rm f}$ and E_{m}).

A larger supersaturation with respect to excess vacancies and dissolved silicon will enhance the precipitation kinetics. For the AlSi 11.0 wt % alloy the amounts of excess vacancies and of dissolved silicon are larger than for the AlSi 2.4 wt % alloy. Indeed, precipitation in the AlSi 11.0 wt % alloy proceeds faster than in the AlSi 2.4 wt % alloy (cf. Figs. 9 and 10).

Further, assuming that on ageing the fractional decrease of the excess vacancy concentration is approximately the same for both alloys, it can be expected that at the same X_t the activation energy for precipitation in the AlSi 11.0 wt % will be smaller (see discussion above) than in the AlSi 2.4 wt % alloy, as is observed.

5.5. The precipitation of aluminium from the supersaturated Si-rich phase after liquid quenching

The equilibrium solid solubility of aluminium in silicon is uncertain [37, 41]. According to

Wamich's data [41] the dissolution of aluminium in silicon enlarges the lattice parameter of the Sirich phase. Thus, the decrease of this lattice parameter observed on ageing (see Table I) may be interpreted as a result of the precipitation of aluminium from the Si-rich phase*.

In the hypo-eutectic alloys the Al-rich phase solidifies primarily, whereas in the hypereutectic alloys the Si-rich phase solidifies primarily. According to the phase diagram [37] it may be expected that, after liquid quenching, the Si-rich phase of the hypereutectic alloys contains more aluminium (retrograde solidus) than the Si-rich phase of the hypo-eutectic alloys. Indeed, the value of the Si-rich phase lattice parameter after liquid quenching is significantly larger for the hypereutectic, than for the hypo-eutectic alloys (see Table 1).

5.6. Unusual lattice parameters of the Si-rich phase after completed precipitation

After 256 h ageing at the three ageing temperatures applied the lattice parameter of the Si-rich phase in the hypo-eutectic alloys is smaller than the lattice parameter of pure silicon[†]. This may be caused by the difference in thermal expansion between the Al- and Si-rich phases. As discussed in Section 5.1 the same effect caused an increase of the Al-rich phase lattice parameter after complete precipitation. Analogously, a decrease of the Si-rich phase lattice parameter as compared to the lattice parameter of pure silicon can be expected, as is observed (cf. Table I).

According to Eshelby's theory on point imperfections [25, 38, 42] the volume change of a misfitting spherical inclusion depends on its radius and on the elastic constants of the inclusion and of the surrounding matrix. For a spherical inclusion of phase B (silicon) in a continuous matrix of phase A (aluminium), the misfit parameter ϵ is defined by

$$\epsilon = (r_0^{\mathbf{B}} - r_0^{\mathbf{A}})/r_0^{\mathbf{A}}$$
(8)

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. Assuming

^{*}The amount of aluminium dissolved, as estimated from the decrease of the Si-rich phase lattice parameter using Wamich's data [41], can be neglected in calculating x_{Si} (see Appendix).

[†]The hyper-eutectic alloys were aged for only 128 h at 445 K. It is suggested that the aluminium precipitation in these alloys has not finished. Thus the lattice parameter of the Si-rich phase at this stage can be still larger than that of pure silicon.

$\Delta T = T_{\mathbf{a}} - T_{\mathbf{r}}$	Experiment (cf	Theory			
(K)	AlSi 2.4 wt % Selected reflection ΣH^2	$\Delta a_{\rm Si} \times 10^4$ (nm)	AlSi 11.0 wt % Selected reflection ΣH ²	$\Delta a_{\rm Si} \times 10^4$ (nm)	(cf. Equation 10) ∆a _{Si} × 10 ⁴ (nm)
99	11	- 2 (± 2)	11	$-2(\pm 1)$	- 8
127	8	$-6(\pm 2)$	24	$-4(\pm 1)$	- 10
150	11	- 3 (± 1)	24	$-5(\pm 1)$	- 12

TABLE V The effect on the silicon lattice parameter after completed precipitation resulting from the difference in thermal expansion between the Al-rich phase and the silicon phase (for symbols see text)

elastically isotropic material, the fractional volume change $\Delta V_{\rm B}/V_{\rm B}$ of a misfitting spherical inclusion B in a finite matrix A can be written as (cf. Equation 25.7 [38]):

$$\frac{\Delta V_{\rm B}}{V_{\rm B}} = 4\pi C \epsilon \, \frac{(r_0^{\rm A})^3}{V_{\rm B}} \tag{9}$$

with $C = 3K_B/(3K_B + 4\mu_A)$, where K and μ denote the bulk and shear modulus, respectively, and V_B , the volume of the "free" undeformed inclusion = $(4/3)\pi(r_0^B)^3$.

Supposing that an individual inclusion experiences no interaction with other inclusions, then the fractional volume change is independent of the volume fraction of the inclusions present. Approximating the actual radius of the inclusion by $r_0^{\rm B}$ and $\Delta V_{\rm B}/V_{\rm B}$ by $3\Delta a_{\rm B}/a_{\rm B}$ and substituting $r_0^{\rm A}$ by $r_0^{\rm B}/(1 + \epsilon)$ (cf. Equation 8) one obtains:

$$\Delta a_{\mathbf{B}} = a_{\mathbf{B}} C \epsilon / (1+\epsilon)^3 \simeq a_{\mathbf{B}} C (\alpha_{\mathbf{B}} - \alpha_{\mathbf{A}}) (T_{\mathbf{a}} - T_{\mathbf{r}})^*$$
(10)

where α_B and α_A are the linear thermal expansion coefficients of B and A, respectively.

In Table V the theoretically obtained Δa_{Si} values for the Si-rich phase (calculated using the elastic constants according to [43]) are presented, together with the experimentally obtained differences between the measured lattice parameter, a_m , and the equilibrium value, a_{Si} , for both alloys. The following can be remarked:

(i) According to Equation 10 the value of Δa_{si} is independent of the amount of silicon present and it increases with increasing values of $\Delta T = T_a - T_r$. This corresponds with the experimental data.

(ii) In view of the large experimental errors (silicon is the minority phase), the simplicity of the model applied and considering the question of the compatability of the elastic constants used, a quantitative agreement between experiment and theory cannot be expected. The differences between experiment and theory may be interpreted such, that in the theoretical calculations "modified" elastical constants should be used instead of literature data (see also [25]).

5.7. Lattice microstrains and crystallite size

5.7.1. Lattice microstrains

5.7.1.1. As-liquid-quenched. Quenched-in stresses, lattice defects, concentration variations and misfit between constituting phases [2, 26] give rise to strain broadening. Since for the Al-rich phase $(1/E)_{100} > (1/E)_{211}$ [43], larger strains may be expected in a [100] direction than in a [211] direction (see Figs. 5 and 6 at t = 0).

For the studied crystallographic directions of the Si-rich phase (1/E) is smallest in a [111] direction and largest in a [311] direction [43]. Hence, the largest strain may be expected in a [311] direction and the smallest in a [111] direction (see Fig. 7 at t = 0).

5.7.1.2. During precipitation. At the start of ageing the quenched in stresses disappear, which contributes to the decrease of the microstrain. On the other hand precipitation will introduce transformation stresses which are not readily dissipitated at an ageing temperature of 445 K. (cf. Section 5.3.2).

The fraction of the volume affected by the transformation strains will be larger for the (minority) Si-rich phase than for the Al-rich phase. Hence, the average microstrain of the Si-rich phase will be more influenced by the transformation strains than the average microstrain of the Al-rich

^{*}In case of the AISi system $a_{\rm B}$ equals $a_{\rm Si} = 0.54307$ (nm) and $(\alpha_{\rm B} - \alpha_{\rm A}) = (\alpha_{\rm Si} - \alpha_{\rm AI}) = -20.5 \times 10^{-6} \, {\rm K}^{-1}$ [29, 43, 44].

phase. Accordingly, after an initial decrease of the microstrains in the Si-rich phase these microstrains may increase again, as is observed for the [111], [110] and [311] direction (Fig. 7). The magnitude of this effect is largest in a [111] direction, which may be related to the preference of silicon particles in line their $\{111\}$ planes parallel to the interface with the Al-rich phase (cf. [4]).

After completed precipitation no effects due to transformation strains are expected. Indeed, for ageing times $> 8\frac{1}{4}$ h at 445 K the microstrains in the silicon phase start to decrease again.

5.7.1.3. During coarsening. After completed precipitation (time > about $8\frac{1}{4}h$ at 445 K) the microstrains decrease with increasing ageing time (Figs. 5 to 7). However, a substantial microstrain remains even after 730 h ageing at 445 K (Table II). In our opinion this phenomenon is due to the difference in thermal expansion between the Al-rich phase and silicon precipitates (which effect was also responsible for the macrostrains observed in the aluminium matrix and silicon precipitates after completed precipitation (see [25] and Sections 5.1 and 5.6). Thus it may be expected that the microstrains in the Al-rich phase increase with increasing silicon content of the alloy. This corresponds with the experimental result (Table II; and compare Figs. 5 and 6).

As the ripening process proceeds the area of interface between the Al-rich phase and silicon particles decreases. Hence, on coarsening the fraction of the volume affected by the thermal stresses will diminish for both phases. Accordingly these microstrains should decrease with increasing coarsening time, as is observed (Figs. 5 and 6).

A quantitative prediction of $\langle e^2 \rangle^{1/2}$ after 730 h at 445 K (i.e. an average value for the phase considered), is difficult to make. The microstrain due to the difference in thermal expansion will be largest near the interface of the Al-rich and Si-rich phase. An order of magnitude for this local microstrain may be obtained by equating the tensile stress along the interface in the Al-rich phase to the compressive stress along the interface in the Sirich phase [cf. 45]. Thus, the following estimates are obtained:

$$e_{A1} = \frac{E_{Si}}{(E_{Si} + E_{A1})} \epsilon = +0.9 \times 10^{-3}$$

$$e_{Si} = \frac{E_{A1}}{(E_{Si} + E_{A1})} \epsilon = -2.1 \times 10^{-3}.$$
(11)

The value of the misfit ϵ due to the difference in thermal expansion can be obtained from Equation 10. The elastic data are taken from [43]. Indeed, (i) after 730 h ageing at 445 K the average microstrain values, $\langle e^2 \rangle^{1/2}$, are in general smaller than the above estimated local strains and (ii) the $\langle e^2 \rangle^{1/2}$ -values observed for the Al-rich phase are smaller than for the Si-rich particles (Table II), but the averaging noted in Section 5.7.1.2 also contributes to this effect. The latter effect also suggests that the microstrain in the Al-rich phase will be larger for the AlSi 13.0 wt % alloy than for the AlSi 2.6 wt % alloy (Table II and Figs. 5 and 6) and vice versa for the Si-rich phase (Table II).

5.7.2. Crystallite size

On ageing the crystallite (domain) size of the silicon precipitates increases (Fig. 8). The domain sizes measured in a [111] direction are the smallest, which may be related to the preference of silicon particles to line their $\{111\}$ planes parallel to the interface with the Al-rich phase [4].

At the start of precipitation the growth rate of the average domain size is low, as nucleation of new crystallites occurs. After nucleation the growth of the silicon particles is facilitated by the presence of remaining excess vacancies which enhance the silicon diffusion through the aluminium matrix (see Section 5.4).

According to [22] silicon precipitate needles grow along [110] directions. This corresponds to a larger growth rate in this direction (Fig. 8).

At later, coarsening stages, less or no excess vacancies will be present. During the coarsening stage particle growth proceeds by dissolving small particles in favour of large particles (Ostwald ripening). Thus, silicon atoms contributing to particle growth have to cover larger diffusion distances in the coarsening stage as compared to the precipitation stage. The above considerations both suggest, that in the coarsening stage the growth rate of the average crystallite is smaller than during precipitation. This is supported by Fig. 8 (note logarithmic time scale).

6. Conclusions

1. "Free" excess vacancies, i.e. not bound to silicon, are induced by liquid quenching. At the start of ageing these "free" excess vacancies are annihilated. At relatively low ageing temperatures this gives rise to the anomalous Hump I in the curve of the Al-rich phase lattice parameter against ageing time.

2. The large difference between the atomic volume of silicon as dissolved in the Al-matrix and of silicon as precipitated evokes precipitation stresses. At high ageing temperatures these stresses are not readily dissipated by the accompanying recovery. This causes Hump II in the curve of the Al-rich phase lattice parameter against ageing temperature.

3. At the start of ageing quenched-in vacancies give rise to rather low values of the activation energy for precipitation. As precipitation proceeds, excess vacancies initially bound to silicon are annihilated gradually, thus enhancing the activation energy for silicon precipitation.

4. Liquid quenching of hyper-eutectic AlSi alloys yields a Si-rich phase, supersaturated with aluminium, as indicated by a decrease of the Si-rich phase lattice parameter on ageing.

5. The microstrain in the Al-rich phase decreases with increasing ageing time. The influence of the precipitation stresses on the microstrain is not observed: being the majority phase, only a small volume fraction of the Al-rich phase is affected by the precipitation stresses, in contrast with the Sirich phase.

6. The microstrain in the Si-rich phase initially decreases on ageing, since quenched-in stresses are dissipated. Then as a result of the precipitation stresses induced, the microstrain increases, in particular in the [111] direction. During coarsening the microstrain decreases again. The remaining microstrain as observed at room temperature is determined by the difference in thermal expansion between the aluminium and silicon phases. During precipitation the growth of the Si-particles is largest in the [110] direction.

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Appendix

Consider 1 gram mole alloy with an overall atomic fraction x_0 of silicon. If s gram mole silicon has been dissolved in the Al-rich phase then the atomic fraction, x_{Si} , dissolved is given by:

$$x_{Si} = s/(1-x_0+s)$$
 and thus
 $s = x_{Si}(1-x_0)/(1-x_{Si}).$ (A1)

Assuming that at the ageing temperatures applied a negligible amount of aluminium will be dissolved in the silicon phase ([37]; Section 5.5) the amount of Al-rich phase reads: $(1 - x_0 + s) = (1 - x_0)/(1 - x_{si})$.

Accordingly, the quantity of silicon not dissolved in the Al-rich phase equals: $(x_0 - s) = (x_0 - x_{Si})/(1 - x_{Si})$.

The volumes of the Al-rich phase and the silicon phase are given by $(1-x_0)(N/4)a_m^3/(1-x_{Si})$ and $(x_0 - x_{Si})(N/8)a_{Si}^3/(1-x_{Si})$, respectively, where N is Avogadro's number, a_{Si} is the lattice parameter of the silicon phase and a_m is the lattice parameter of the Al-rich phase.

The volume fraction of the silicon can now be written as:

$$y_{\rm Si} = \frac{a_{\rm Si}^3}{2a_{\rm m}^3(1-x_0)/(x_0-x_{\rm Si})+a_{\rm Si}^3}$$
. (A2)

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Precipitation of Silicon in a Solid Quenched Aluminium-Silicon (1.3 at%) Alloy Studied by Positron Annihilation

By

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Doppler broadening of the positron annihilation line was measured for quenched and aged specimens of an aluminium-silicon (1.29 at% Si) alloy. One set of specimens was aged at room temperature (set A) and one set was isochronally (t = 30 min) aged at temperatures ranging from 347 to 884 K (set B). The lineshape parameter S measured in the as-quenched condition was larger than that of well-annealed pure aluminium. S decreased with time of ageing at room temperature, which might be ascribed to the formation of vacancy loops decorated with silicon atoms. After 1320 h at room temperature the specimens of set A were aged for 30 min at 353 K in vacuo. Then, the lineshape parameter S decreased further, which is interpreted as due to a further disappearance of the earlier formed vacancy loops. The behaviour of the lineshape parameter S for set B can be described as follows: 1. 350 to 450 K. Constant value of S, about the same as found for pure aluminium. 2. 450 to 580 K. Increase of S, ascribed to precipitation of vacancies near the Si aggregates/matrix interface relieving transformation strains. 3. above 580 K. Decrease of S to the pure-aluminium value. This effect is ascribed to the growth of silicon precipitates accompanied by annihilation of vacancies. The misfit between the silicon precipitates and the Al-rich matrix is accommodated by dislocations.

Die Dopplerverbreiterung der Positron-Annihilations-y-Linie wird für abgeschreckte und gealterte Proben einer Aluminium-Silizium-(1,29 At% Si) Legierung gemessen. Ein Probensatz wird bei Zimmertemperatur gealtert (Satz A) und ein Satz wird isochron (t = 30 min) bei Temperaturen von 347 bis 884 K gealtert (Satz B). Der Linienformparameter S, der sofort nach dem Abschrecken gemessen wird, ist größer als der für gut getempertes reines Aluminium. S nimmt mit der Alterungsdauer bei Zimmertemperatur ab, was der Bildung von Leerstellenloops zugeschrieben werden kann, die mit Siliziumatomen dekoriert sind. Nach 1320 h bei Zimmertemperatur werden die Proben des Satzes A für 30 min bei 353 K im Vakuum gealtert. Dann sinkt der Linienformparameter S weiter ab, was als Folge eines weiteren Verschwindens der vorher gebildeten Leerstellenloops interpretiert wird. Das Verhalten des Linienformparameters S für den Satz B kann wie folgt beschrieben werden: 1. 350 bis 450 K. Ein konstanter Wert für S, etwa der gleiche wie für reines Aluminium. 2. 450 bis 580 K. Ein Anstieg von S, der der Präzipitation von Leerstellen in der Nähe der Grenzfläche Si-Aggregate-Matrix zugeschrieben wird und Transformationsspannungen beseitigt. 3. oberhalb 580 K. Die Abnahme von S auf den Wert des reinen Aluminium. Dieser Effekt wird dem Wachstum von Siliziumpräzipitaten zugeschrieben und ist begleitet von Leerstellenannihilation. Das Misfit zwischen Siliziumpräzipitaten und Al-reicher Matrix wird durch Versetzungen ausgeglichen.

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1. Introduction

Positron annihilation spectroscopy has become a useful method to investigate defects in solids [1]. Vacancies, voids, and dislocations in pure metals have been studied by the measurement of Doppler broadening and lifetime, and by angular correlation methods. The influence exerted by atoms of alloying elements on the positron annihilation behaviour in defects has been employed by several authors to study defects associated with the alloying element. Measurements have been reported of the vacancy solute (Gibbs free) binding energy (see e.g. [2, 3]) as well as measurements on precipitation phenomena (see e.g. [4, 5]).

With regard to aluminium-silicon alloys several indications exist for appreciable silicon-defect interaction. Lindberg et al. [6] attributed one of the three lifetime components in neutron-irradiated aluminium to voids associated with transmutationproduced silicon. Small angle neutron scattering experiments performed by Hendricks et al. [7] indicated interaction of silicon with vacancy clusters. As the solubility of silicon at the temperatures applied is negligible [8], silicon resulting from the neutron irradiation always exceeds the solid solubility. According to Lindberg et al. [6] voids are stabilized by the decoration with silicon atoms up to about 580 K. Dlubck et al. [9] observed an average lifetime in well-annealed pure aluminium similar to that in a well-annealed aluminium-silicon alloy (0.5 at% Si). However, they found distinctly different lifetimes in Al-Si after a quench from 873 K into water at room temperature. This experimental result indicated that silicon dissolved in the aluminium matrix increased the defect concentration. Recent work by van Mourik et al. [10] revealed that due to the interaction between dissolved silicon atoms and vacancies, the kinetics of silicon precipitation in melt-spun ribbons of Al-Si alloys are influenced by the presence of excess vacancies.

This paper reports on experimental work dealing with the ageing of the quenched-in silicon-vacancy aggregates. The defects are monitored by the Doppler-broadening technique because of its relatively easy and fast data accumulation compared to the other positron annihilation techniques.

Section 2 shortly outlines the experimental procedure followed. The results are presented in Section 3 and these results are discussed in terms of the transition of silicon-vacancy aggregates to silicon precipitates in Section 4.

2. Experimental Procedure

2.1 Specimen preparation

An aluminium-silicon (1.29 at% Si) alloy was prepared from 99.998 wt% Al and 99.99 wt% Si. The alloy castings were rolled. Two sets of specimens were made: specimens 1.7 mm thick (type A) and specimens 2.5 mm thick (type B). To minimize positron trapping at grain boundaries a large grain size is desirable.

Specimens A were annealed for 96 h at 849 K. The grain diameter was about 1.5 mm. Additional polishing reduced the specimens' thickness to 1.2 mm. Final homogenizing and quenching treatment consisted of annealing at 848 K for 120 h and fast cooling in water (273 K) and in liquid nitrogen successively. Specimens A were stored in liquid nitrogen.

Specimens B were annealed at 788 K for 80 h, followed by a homogenizing heat treatment of 19 h at 853 K and a subsequent water quench (273 K). After the quench the grain diameter was about 1.5 mm. An X-ray diffraction pattern (Debye-Scherrer) was taken from filings of the quenched specimens B. In order to determine the amount

of silicon dissolved in the aluminium matrix specimens B were stored at room temperature.

In the as-water-quenched condition of specimens B light microscopy was performed as well as a determination of the overall composition by X-ray microanalysis.

2.2 Ageing treatment

Two specimens A were aged up to 1320 h at room temperature. Hereafter, these two specimens A were aged at 353 K for 30 min in a vacuum furnace (vacuum better than 5×10^{-3} Pa). Two specimens B were isochronally (t = 30 min) aged at temperatures ranging from 350 to 884 K. Ageing and cooling took place in the same way as applied for specimens A at 353 K. Temperature control was within ± 1 K.

After each ageing treatment the positron annihilation measurement was performed.

2.3 Positron annihilation measurement

The 511 keV annihilation line was measured with a Ge(Li) Ortec detector with an efficiency of 18%. A linear amplifier (Ortec model 571) was fed by the signal of the pre-amplifier. An Ortec model 800 ADC was used. A Camac interface provided the link with a PDP 11/70 on-line computer. The resolution of the system was 1.5 keV at the 514 keV γ -line of ⁸⁵Sr at a count rate of about 10 kHz. The measuring system was one-point stabilized on the 511 keV annihilation line itself. A 10 μ Ci ²²Na source deposited on Ni foils was used.

The positron annihilation line was characterized by the S-parameter [11] representing the fraction of full energy counts in a central integration window. At least 2×10^6 counts were accumulated in each spectrum (annihilation line countrate ≈ 550 s⁻¹). Each measurement was performed at room temperature.

3. Results

3.1 Composition and microstructure

The microstructure after water (273 K) quenching is shown in Fig. 1. It appears that nearly all silicon has been dissolved in the Al-rich matrix: the Debye-Scherrer photograph from filings taken after the quench did not reveal any silicon reflections. The lattice parameter of the Al-rich matrix was determined from the photograph by a Nelson-Riley extrapolation [12]. With a calculation as described elsewhere [10, 13] the silicon content of the Al-rich phase was obtained. It equalled (1.17 ± 0.05) at% Si. Chemical analysis yielded the overall content of the alloy: (1.29 ± 0.04) at% Si. The analogous determination by X-ray microanalysis resulted in (1.25 ± 0.12) at% Si.

3.2 Ageing at room temperature

The lineshape parameter S is presented as a function of ageing time in Fig. 2. The value for well-annealed pure aluminium is also indicated. The following observations can be made:

(i) The S-parameter of the water (273 K)/liquid nitrogen quenched specimens at the start of ageing is larger than that of well-annealed pure aluminium.

(ii) The S-parameter decreases with ageing time, it reaches a constant value after about 140 h, but it remains larger than the S-parameter of pure aluminium (note logarithmic time scale).



Fig. 1. The microstructure of Al-Si (1.29 at%) after the quench from 853 K into water of 273 K (magnification $1000 \times$)





Fig. 3

Fig. 2. The lineshape parameter S as a function of ageing time at room temperature (specimens A). The value for pure, well-annealed aluminium is indicated (P)

Fig. 3. The lineshape parameter S as a function of isochronal (t = 30 min) ageing temperature. The value for well-annealed, pure aluminium is indicated (P). Open circles denote values obtained from specimens A after 1320 h ageing at room temperature (1) and 30 min ageing in vacuo at 353 K (2)



Fig. 4. The microstructure after completed isochronical ageing. Small silicon precipitates throughout the grains and few large silicon precipitates along the grain boundaries can be discerned (magnification $1000 \times$)

3.3 Isochronal ageing at temperatures between 350 and 884 K

The lineshape parameter S as a function of ageing temperature is shown in Fig. 3. The values of the S-parameter for specimens A obtained after 1320 h ageing at room temperature and after ageing at 353 K (in vacuo), respectively, are given too. The S-parameter for well-annealed pure aluminium is also indicated.

The following observations can be made:

(i) In the range from 350 to 450 K the S-parameter, after a decrease, maintains a constant value, similar to that for pure aluminium.

(ii) In the range from 450 to 580 K the S-parameter increases to reach a maximum at about 580 K.

(iii) Beyond 580 K the S-parameter decreases again to reach at about 750 K the value for pure aluminium.

The microstructure after completed isochronal ageing is shown by Fig. 4, which reveals silicon precipitation throughout the specimen.

4. Discussion

As the S-parameter after the water (273 K)/liquid nitrogen quench is larger than that of well-annealed pure aluminium, it is concluded that defects capable of trapping positrons are formed on quenching. The amount of these defects decreases with increasing ageing time (Fig. 2).

An estimate of the vacancy concentration in a dilute alloy can be obtained by inserting literature data for the binding entropy and binding energy⁵) into the Lomer equation [16]. In our case with $T_q \approx 850$ K and with an atomic fraction of dissolved silicon equal to 1.2×10^{-2} (see Section 3.1) the vacancy concentration is about 10×10^{-4} , to be compared with 3×10^{-4} in pure aluminium at the same temperature. From the results of Alam and West [17] it can be deduced that the relative increase of S for polycrystalline pure aluminium quenched from 850 K is about $\Delta S/S \approx 0.021$. The relative increase measured for specimens A (Fig. 2) only amounts 0.008. Although the value of $\Delta S/S$ depends on the choice of integration limits [18], this measured value suggests that the concentration of free vacancies surviving after the quench is rather small.

Saulnier showed [19] that in a quenched Al-Si 1.2 wt% alloy vacancy loops are overwhelmingly present. As (i) the atomic fraction of silicon atoms dissolved is large compared to the estimated vacancy concentration $(1.2 \times 10^{-2} \text{ and } < 0.1 \times 10^{-2},$ respectively) and (ii) the interaction between vacancies and silicon increases with increasing temperature (see footnote 5), vacancy-silicon complexes will be formed at the quenching temperature. When vacancies cluster to form voids, these voids will be associated with silicon atoms as already has been suggested by Lindberg et al. [6]. Thus, vacancy loops formed by the collapse of these voids [20 to 22] will be decorated with silicon atoms.

The behaviour of the S-parameter can now be explained as follows: during and after the quench vacancy loops decorated with silicon are formed from vacancysilicon complexes. Because such vacancy loops represent a much smaller free trapping volume than that corresponding to the contributing vacancies, the S-parameter is much smaller than expected from the above-estimated total vacancy concentration at the quenching temperature. On ageing at room temperature vacancy loop formation continues, implying a further decrease of the S-parameter, as is observed. Vacancy loops in aluminium are stable at room temperature [19 to 22]. Because the S-parameter reaches a constant value slightly larger than that of well-annealed pure aluminium (Fig. 2), it is concluded that aluminium with decorated vacancy loops possesses a free trapping volume slightly larger than that of well-annealed pure aluminium.

Vacuum ageing at 353 K for 30 min followed by furnace cooling results in a further decrease of S (see open circles in Fig. 3), which can be interpreted as a further disappearance of the earlier formed loops.

Experiments on the precipitation phenomena in melt-spun Al-Si alloys [10] show that on ageing formation of vacancy loops precedes the actual silicon precipitation, which becomes detectable only after 2 h of ageing at about 400 K. In an investigation by transmission electron microscopy of a solid quenched Al-Si (1.2 at% Si) alloy [19] silicon precipitation on ageing at 473 K becomes detectable after about 30 min. Thus, the times and temperatures of ageing until now are too low to permit a detectable precipitation of silicon from the supersaturated Al-rich matrix.

The atomic volume of silicon precipitated — having the diamond structure — is significantly larger ($\approx 23\%$ [19]) than that of silicon dissolved in the Al-rich matrix having the f.c.c. structure. Therefore, silicon precipitation inevitably introduces large transformation stresses [10]. Russell [23] suggested that vacancies may precipitate near the precipitate/matrix interface, thus relieving transformation strains. Also according to Kanazawa et al. [5] precipitation in aluminium-germanium alloys implies

⁵) From these data follows that the binding entropy rather than the binding energy is connected with the increase of the vacancy concentration in dilute alloys of Al and Si, as compared to pure aluminium [7, 14, 15].

vacancies to aggregate to Ge precipitates in order to relax their stress fields. (Germanium, as silicon, has the diamond crystal structure and the phase diagram of Al-Ge is analogous to that of Al-Si [8].)

As discussed above silicon atoms have initially gathered near the vacancy loops. Therefore, it may be suggested that on ageing vacancy loops provide a source for such strain-relieving vacancies (vacancy emission by vacancy loops has been suggested by Ozawa and Kimura [24, 25]). This could explain the increase of S observed on annealing in the range between 450 and 580 K.

Raising the ageing temperature promotes the growth of silicon precipitates. Then the misfit between precipitates and the Al-rich matrix may be accommodated by (misfit) dislocations introduced into the precipitate/matrix interface. Consequently, the vacancies near the interface, originally relieving the misfit stress field, are annihilated in this stage and a decrease of the S-parameter is observed (Fig. 3, at T >> 600 K). Accordingly, after completed ageing the S-parameter equals the value for well-annealed pure aluminium.

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KINETICS OF PRECIPITATION AND OF RELAXATION OF PRECIPITATION-INDUCED STRESSES IN ALUMINIUM-SILICON ALLOYS

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1. Introduction

Liquid guenching as well as solid quenching of aluminium-silicon alloys yields an aluminiumrich matrix supersaturated with silicon. Ageing of guenched alloys implies silicon precipitation (cf. phase diagram in Ref. 1).

Since the atomic volume of silicon as precipitated (diamond structure) is much larger than as dissolved in the Al-rich matrix, large stresses will develop in the Al-rich phase on ageing. This is clearly demonstrated by the behaviour of the Al-rich phase lattice parameter, a_{Al} , as a function of ageing time, t, cf. Fig. 1 (2, 3). Silicon precipitation from the Al-rich phase causes an overall increase of the Al-rich phase lattice parameter, but precipitation-induced stresses and their subsequent relaxation cause a hump, $\Delta a_{Al}^V(t_{max})$, (3). This hump occurs at much shorter times for liquid-quenched (LQ) than for solid-quenched (SQ) alloys (compare Fig. la to Fig. lb). For the LQ alloys the determination and interpretation of $\Delta_{Al}^V(t_{max})$ is hardly possible because of the interwoven effects on the Al-rich phase lattice parameter of silicon precipitation, precipitation-induced stresses and relaxation stresses.

In this letter the silicon precipitation and subsequent relaxation of precipitation-induced stresses in solid-quenched AlSi alloys are investigated by measurement of the Al-rich phase lattice parameter as a function of temperature and time of ageing.

2. Experimental

Alloys of aluminium with 1.4, 2.4 and 10.0 at% silicon were conventionally produced as described earlier (3). Measurements were performed using wire specimens with a diameter of 0.38 mm. The specimens were annealed for 0.5 h at 836 \pm 5 K in air and guenched in ice water. At 836 K the equilibrium solid solubility of silicon in aluminium is about 1.4 at% (1). After guenching the Al-rich phase grain size was 300 µm, 120 µm and 20 µm for the 1.4, 2.4 and 10.0 at% i alloy, respectively.

The Al-rich phase lattice parameter was determined at room temperature from Debye-Scherrer photographs, using Nelson-Riley extrapolation (for details see Ref. 4), with an accuracy of 1-2 parts in 40,000. Ageing was conducted in an oil bath at 402 \pm 4, 450 \pm 2 and 492 \pm 2 K. All lattice parameter values presented here are valid at 298 K: they were derived from the values measured at room temperature using the appropriate thermal expansion coefficient (3).

3. Evaluation of data

The Al-rich phase lattice parameter as a function of ageing time and temperature is shown in Figs. 2-4. The mere precipitation of silicon atoms from the Al-rich solid solution results in an increase of the Al-rich phase lattice parameter. At the ageing temperatures applied the equilibrium solid solubility of silicon in aluminium is virtually zero (1) and thus the



Fig. 1: Schematic representation of the behaviour of the Al-rich phase lattice parameter, a_{Al} , as a function of ageing time, t, for liquid-quenched (a) and solid-quenched (b) AlSi alloys. The Al-rich phase equilibrium lattice parameter, a_{Al}^{Al} , is indicated.





Fig. 2: The Al-rich phase lattice parameter, a_{A1} , as a function of ageing time, t, for the solid quenched AlSi 1.4 at alloy; the equilibrium value, a_{A1}^{eq} , and the ageing temperatures applied are indicated.





Fig. 4: The Al-rich phase lattice parameter, a_{Al} , as a function of ageing time, t, for the solidquenched AlSi 10.0 at% alloy; the equilibrium value, a_{Al}^{eq} , and the ageing temperatures applied are indicated.

equilibrium value of the Al-rich phase lattice parameter equals that of pure aluminium (see (Figs. 2-4). As discussed earlier (3-5), after completed precipitation and relaxation, the Al-rich phase lattice parameter is still larger with an amount $\Delta a_{AI}^{T}(\infty)$ than its equilibrium value, a_{AI}^{EQ} (see Fig. 1). This results from the difference in shrink between the Al-rich and the Si-rich phase during cooling from the ageing temperature to room temperature.

Values of $\Delta a_{\lambda 1}^{T}(\infty)$ can be calculated by adopting Eshelby's theory on elastic distortion by point defects in a finite matrix (cf. eq. 15 in Ref. 3):

$$\Delta a_{A1}^{T}(\infty) = 3.73 \times 10^{-6} \Delta T y_{Si}(\infty)$$
 (nm)

where ΔT is the difference between ageing and room temperature and $y_{Si}(\infty)$ is the volume fraction of all silicon phase present in the alloy after completed precipitation. For ageing times >> t_{max} (cf. Fig. 1) the silicon precipitation is practically completed and thus $\Delta a_{AI}^{T}(t >> t_{max})$ can be taken equal to $\Delta a_{AI}^{T}(\infty)$. Then it holds for the change of the Al-rich phase lattice parameter due to the precipitation-induced stresses, $\Delta a_{AI}^{T}(t)$:

$$\mathbf{a}_{\mathbf{A}1}^{\mathbf{X}}(\mathbf{t}) = \mathbf{a}_{\mathbf{A}1}(\mathbf{t}) - (\mathbf{a}_{\mathbf{A}1}^{\mathbf{E}1} + \Delta \mathbf{a}_{\mathbf{A}1}^{\mathbf{X}}(\infty))$$
⁽²⁾

(1)

A maximal value of Δa_{A1}^V would occur if no relaxation took place. This maximal value can be calculated on the same basis as used for eq. 1 (cf. eq. 18 in Ref. 3):

$$\Delta a_{\lambda}^{\nu}(max) = 0.0117 \text{ y} g^{\text{rec}}(\infty) \quad (nm) \tag{3}$$

where $y_{S1}^{prec}(\infty)$ denotes the volume fraction of silicon which has precipitated at $t = \infty$ since the start of ageing^{*)}. It is assumed that at the ageing temperatures applied the solid solubilities of silicon in aluminium and vice versa are zero (1). Then, from a mass balance the volume fraction $y_{S1}^{prec}(\infty)$ can be closely approximated by:

$$y_{Si}^{\text{prec}}(\infty) = \frac{x_{Si}(o)}{x_{o}} \frac{(1 - x_{o})}{(1 - x_{Si}(o))} y_{Si}(\infty)$$
(4)

where x_0 denotes the overall atomic fraction of silicon in the alloy and $x_{Si}(0)$ denotes the atomic fraction of silicon in solid solution in the Al-rich phase at t = 0. The value for $x_{Si}(0)$ is equal to the silicon solid solubility in the Al-rich phase at the quenching temperature (1).

Beyond t_{max} (cf. Fig. 1b) the extent of the relaxation process of an ageing time t can be represented by the ratio $\Delta a_{\lambda_1}^V(t)/\Delta a_{\lambda_1}^V(max)$.

4. Activation energy for precipitation of silicon

The amount of silicon to precipitate during the ageing treatment applied is constant, because (i) the homogenizing temperature was the same for all the alloys and (ii) the solid solubility at the ageing temperatures is virtually zero and thus also the same.

It can be assumed that at early stages of precipitation no appreciable relaxation has occurred. Then the Al-rich phase lattice parameter as measured after an ageing time t, $a_{Al}(t)$, can be written as:

$$AI(t) = a_{AI}^{EI} - p x_{Si}(t) + \Delta a_{AI}^{T}(t) + \Delta a_{AI}^{V}(t)$$
(5)

where p is a Végard-like constant and $x_{Si}(t)$ is the atomic fraction of silicon in the Al-rich phase after an ageing time t. The lattice parameter changes $\Delta a_{A1}^{T}(t)$ and $\Delta a_{A1}^{V}(t)$ linearly depend on the amount of silicon precipitated since the start of ageing (cf. eqs. 1 and 3). This implies that, for the three ageing temperatures considered, an equal change of the Al-rich phase lattice parameter (with respect to its value at t = 0) corresponds to an equal stage of the precipitation process. The kinetics of this process can be described by the state variable c_{pt} with $c_{p} = c_{o,p} \exp - E_{p}/kT_{a}$, where $c_{o,p}$, E_{p} , k and T_{a} are a pre-exponential factor, the activation energy for precipitation, Boltzmann's constant and the ageing temperature, respectively. If t_{p} denotes the time to achieve an Al-rich phase lattice parameter of 0.40485 nm at the ageing temperature T_{a} , $c_{p}t_{p}$ corresponds to an equal stage of the precipitation. Now the activation energy for precipitation can be derived from the slope of the straight line through the data points in a plot of ln t_{p} versus $1/T_{a}$ (Fig. 5). For the three alloys considered the following average value of the activation energy for precipitation is found:

$E_{D} = 1.3 \text{ eV}$

* $\Delta a_{\lambda_1}(\max)$ should not be confused with $\Delta a_{\lambda_1}(t_{\max})$.

The result corresponds well with that obtained by Koster and Knorr (6) from resistometry and thermo-electrical analysis. Considerably smaller values of the activation energy for silicon precipitation are found for liquid-quenched AlSi alloys (0.8-1.2 eV depending on the extent of silicon precipitation (5)), where large amounts of excess vacancies are present at the start of precipitation. The activation energy for precipitation found here is close to the sum of the energy for formation and for migration of a vacancy in aluminium (7). Apparently, in the (present) solid-quenched AlSi alloys a much lower concentration of excess vacancies is present than in liquid-quenched AlSi alloys (but see also Ref. 8).

5. Activation energy for relaxation of precipitation-induced stresses

Precipitation of silicon precedes relaxation of the precipitation-induced stresses. Hence, no starting time of the relaxation can experimentally be established. However, for advanced stages of relaxation, where precipitation is virtually complete, the kinetics of the relaxation process can be described by the state variable $c_r(t - t_0)$, with $c_r = c_{0,r} \exp -E_r/kT_a$ and where t_0 denotes a fictitious starting time of relaxation, $c_{0,r}$ is a pre-exponential factor and E_r is the activation energy for relaxation (cf. Ref. 9).

Considering the same two states of relaxation for all ageing temperatures, i.e. the same two values of $\Delta a_{A1}^V(t)/\Delta a_{A1}^V(t_{max})$, the lapse of time, Δt , between the corresponding two ageing times obeys:

$\Delta t = const. exp E_r/kT_a$

Thus, from a plot of ln (Δt) versus $1/T_a$ a value for E_r can be obtained (Fig. 6). To avoid "contributions" from precipitation (see above) the smallest possible values of $\Delta a_{A1}^V(t)/\Delta a_A^V(max)$ were chosen: 0.5 and 0.4, respectively. Then, it was obtained for the AlSi 1.4 at% and AlSi 2.4 at% alloys:

 $E_{r} = 1.2 \text{ eV}$

For the AlSi 10.0 at% alloy the magnitudes of $\Delta a_{A1}^V(t)$ were too small to allow a quantitative analysis.

Creep and stress relaxation in a metal can be caused by the movement of dislocations by climb. Such a process has an activation energy equal to that for self-diffusion (10), which for aluminium ranges from 1.2 to 1.5 eV (11). Further, stresses enhance dislocation movement, and therefore the activation energy for stress relaxation can be somewhat smaller than for selfdiffusion (10). This provides an explanation for the value of the activation energy for relaxation found in the present work (1.2 eV). It is also noted that the activation energy for creep in high purity aluminium is about 1.3 eV for the corresponding temperature range (12). The changes of the Al-rich phase lattice parameter due to precipitation-induced stresses in

the AlSi 10.0 at% alloy were much smaller than in the two other alloys. This can be ascribed to its relatively small grain size (cf. Section 2): relaxation will be enhanced by the presence of many grain boundaries. A very small grain size also accounts for the very rapid relaxation of precipitation-induced stresses in liquid-quenched alloys (see Fig. 1a and Ref. 3).

6. Conclusions

- On ageing the lattice parameter of the Al-rich phase increases owing to silicon depletion and precipitation-induced stresses. A subsequent partial decrease of the Al-rich phase lattice parameter is caused by stress relaxation.
- 2. For the early stages of precipitation the activation energy for silicon precipitation in solid-quenched AlSi alloys is 1.3 eV, whereas the corresponding value in liquid-quenched AlSi alloys is about 0.8 eV.
- 3. After completed silicon precipitation in solid-quenched AlSi alloys the activation energy for stress relaxation is 1.2 eV indicating dislocation climb as a main process of relaxation.
- Stress relaxation in liquid-quenched alloys is greatly facilitated by the large amount of grain boundaries in these alloys.

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Fig. 5: The value of $\ln[t_p(h)]$ (see text) as a function of the reciprocal ageing temperature, $1/T_a$.

Fig. 6: The value of $\ln[\Delta t(h)]$ (see text) as a function of the reciprocal ageing temperature, $1/T_a$.

MISFIT STRAINS AND EXCESS VACANCIES IN LIQUID-QUENCHED AND SOLID-QUENCHED ALSI ALLOYS ON AGING

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ABSTRACT

Rapidly solidified AlSi alloys were prepared by melt-spinning. For comparison, wires of conventionally cast AlSi alloys were homogenized below the eutectic temperature and quenched in icewater. Precipitation processes occurring on ageing were studied by the X-ray diffraction determination of the Al-rich and Si-rich phase lattice parameters. On short-time ageing a rapid annihilation of excess vacancies occurred in the liquid-quenched alloys, whereas such a phenomenon was absent in the solid-quenched alloys. Misfit effects caused changes of the Al-rich phase and the Si-rich phase lattice parameters. Misfits originated from the precipitation itself and from the cooling from the ageing temperature to the room temperature. From a model the magnitudes of the lattice parameter changes were calculated, assuming isotropy and elastic accommodation of misfits. For the coolinginduced changes of the Al-rich phase and Si-rich phase lattice parameters a fair quantitative agreement exists between theory and experiment. The transformation-induced shifts of the lattice parameter were partly dissipated by relaxation. Differences in relaxation behaviour could be ascribed to grain-size differences.

UNTIL NOW ONLY FEW INVESTIGATIONS were devoted to precipitation in liquid-quenched (LQ) AlSi alloys (1-3), whereas several studies were devoted to precipitation in solid-quenched (SQ) AlSi alloys (4-9).

Liquid quenching yields a larger silicon solubility (1,10), a higher excess vacancy concentration (11) and much smaller grain sizes (13) than solid quenching does. In LQ aluminium alloys the increase of the excess vacancy concentration has been interpreted in terms of a solute-content dependent free enthalpy of vacancy formation (12).

Silicon precipitation in AlSi alloys implies

diffusion of silicon atoms by the vacancy mechanism. Thus, excess vacancies can lower the apparent activation energy for silicon precipitation (2, 3).

It can be expected that large stresses develop during the silicon precipitation: the atomic volume of silicon as precipitated (diamond structure) is much larger than as dissolved in the fcc Al-rich matrix (6). Indications for the occurrence of such stresses were obtained for LQ AlSi alloys (1, 3).

This paper presents a comparative study on precipitation in LQ and SQ AlSi alloys. Since vacancies and stresses act on the lattice parameter, Al-rich phase and Si-rich phase lattice parameter changes were analysed using Debye-Scherrer (DbS) method.

1. EXPERIMENTAL PROCEDURES

Liquid-quenched (LQ) AlSi alloys with 2.3 and 10.6 at% Si were prepared from 99.998 wt% Al and 99.99 wt% Si by the melt-spinning technique (10). According to dendrite arm spacing measurements the cooling rate of the melt-spun ribbons was in the range 10^6 to 10^7 Ks⁻¹. The grain size of the Al-rich phase was of the order of 3 µm (13). Specimens for the DbS camera were cut out parallel to the ribbon axis half-way the ribbon width. Typical dimensions were: length 8 mm, width 1 mm and thickness equal to the local ribbon thickness.

Conventionally produced AlSi alloys with 1.4, 2.4 and 10.0 at% Si were prepared from 99.998 wt% Al and 99.99 wt% Si by melting and casting in a metal mould. The alloys were annealed at 820 K for 24 h and extruded at 733 K, thereby reducing the diameter from 19 mm to 3 mm. By cold drawing and intermediate annealing at 650 K the diameter was further reduced to 0.38 mm, which is a suitable diameter for recording of DbS photographs. The quenching treatment consisted of 0.5 h annealing at 836 \pm 5 K in air followed by an ice-water quench (solid quenching = SQ). After SQ the Al-rich



Fig. 1: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for the SQ AlSi 1.4 at% alloy. The equilibrium value a_{S1}^{eq} , the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, $x_{S1}^{e=0}$, are indicated.



Fig. 2: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for (a) the LQ AlSi 2.3 at% alloy and (b) the SQ AlSi 2.4 at% alloy. The equilibrium value, $a_{A1}^{e.g.}$, the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, $x_{S1}^{t=0}$, are indicated.



Fig. 3: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for (a) the LQ AlSi 10.6 at% alloy and (b) the SQ AlSi 10.0 at% alloy. The equilibrium value, a_{A1}^{eq} , the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, x_{S1}^{eq} , are indicated.

phase grain size was 300 μ m, 120 μ m and 20 μ m for the 1.4 at%, 2.4 at% and 10.0 at% Si alloys, respectively.

The LQ and SQ specimens were mounted in specimen holders which fitted in the DbS camera. The same DbS camera was used throughout this investigation. A heat-treatment cylinder, designed to enclose three specimen holders, was applied to age the quenched specimens in an oil bath simultaneously. Ageing temperatures were reached within one minute.

The kinetics of the Si-precipitation were studied by the measurement of the lattice parameter of the Al-rich phase (with a precision of 1-2 parts to 40,000) as a function of ageing time at 397 \pm 3 K, 425 \pm 4 K and 448 \pm 5 K for the LQ



Fig. 4: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for the SQ AlSi 1.4 at% alloy. The equilibrium value, a_{eA}^{eA} , the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, x_{EA}^{eaO} , are indicated.





Fig. 5: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for (a) the LQ AlSi 2.3 at% alloy and (b) the SQ AlSi 2.4 at% alloy. The equilibrium value, a_{A1}^{eq} , the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, $x_{S1}^{t=0}$, are indicated.





Fig. 6: The Al-rich phase lattice parameter, a_{A1} , versus ageing time, t, for (a) the LQ AlSi 10.6 at% alloy and (b) the SQ AlSi 10.0 at% alloy. The equilibrium value, a_{A1}^{eq} , the ageing temperature and the Si-content of the Al-rich phase at the start of ageing, $x_{S1}^{t=0}$, are indicated.

ribbons and as a function of ageing time at 404 \pm 4 K, 450 \pm 2 K and 492 \pm 2 K for the SQ $_{\rm vires}$

The Si-rich phase lattice parameter was studied as a function of ageing time and temperature as far as it was possible to observe and to interprete the DbS reflections of this minority phase.

All lattice parameter values presented in this paper are valid at 298 K. They were derived from the measured values by using the appropriate thermal expansion coefficients as given in section 3.3. Measurements were performed at room temperature.

2. RESULTS

2.1 THE AL-RICH PHASE LATTICE PARAMETER -The Al-rich phase lattice parameter as measured (Nelson-Riley extrapolation (3)) at temperatures in


Fig. 7: The Si-rich phase lattice parameter, a_{Si} , versus ageing time, t, for the SQ AlSi 10.0 at% alloy. The equilibrium lattice parameter, a_{Si}^{eg} , and the ageing temperature are indicated.

the range 400-500 K is shown in Figs. 1-3 for short (t \leq 120 min) and in Figs. 4-6 for prolonged ageing times^{*}). In these figures the silicon content of the Al-rich phase after quenching, $x_{1=0}^{t=0}$, and the equilibrium value of the Al-rich phase lattice parameter, a^{eq} , are indicated. The values of $x_{1=0}^{t=0}$ for the LQ alloys were obtained as described in (3); for the SQ alloys $x_{51}^{t=0}$ was taken equal to the solid solubility (15) at the quench temperature.

At the ageing temperatures applied the equilibrium silicon solubility in the Al-rich matrix is negligible (15). Therefore, a_{A1}^{eq} , equals the value of the lattice parameter of pure aluminium, which is 0.40496 (nm) (16).

On short-time ageing at about 400 K the LQ Al-rich phase lattice parameter shows a sudden increase to a maximum (Figs. 2a and 3a). On ageing at about 450 K the LQ Al-rich phase lattice parameter also shows a maximum, but at longer ageing times as compared to the maxima at 400 K (Figs. 2a and 3a). On prolonged ageing the LQ Al-rich phase lattice parameters reach a

*) Ribbons obtained by melt spinning generally show local variations of the amount of silicon dissolved in the Al-rich phase. This explains differences in the Al-rich phase lattice parameter at the start of ageing and an exact correspondence between the curves of the Alrich phase lattice parameter against ageing time cannot be expected. stationary value larger than the equilibrium value (Fig. 5a,6a).

For the SQ Al-rich phase lattice parameter at about 400 K no sudden increase as for the LQ Al-rich phase lattice parameter is observed. For all ageing temperatures the SQ Al-rich phase lattice parameters show maxima at longer ageing times than for the maxima of the LQ alloys of corresponding ageing temperatures and compositions (see Figs. 4-6). Beyond these maxima the Al-rich phase lattice parameters decrease to reach stationary values larger than equilibrium values. For the SQ AlSi 10.0 at% alloy these maxima are less pronounced than for the other alloys.

2.2 THE SI-RICH PHASE LATTICE PARAMETER -In the LQ AlSi alloys investigated the Si-rich phase is a very finely dispersed minority phase (14). As a consequence DbS reflections are veak and broadened. Therefore, the LQ Si-rich phase lattice parameter could not be determined using the Nelson-Riley extrapolation. Thus, the LQ Sirich phase lattice parameter was determined from a selected reflection on a DbS photograph; this was only possible after prolonged ageing (precision was improved by a tenfold measurement of the line). Table 1 shows the results.

In the case of the SQ alloys, it was possible for the AlSi 10.0 at% alloy to obtain the Si-rich phase lattice parameter as a function of time at the ageing temperatures applied using Nelson-Riley extrapolation (Fig. 7). The other SQ alloys provided too weak Si-reflections to determine the Si-rich phase lattice parameter.

To obtain a reference value the lattice parameter of NBS SRM 640-a silicon (17) was determined applying CuKa₁ radiation. The resulting value was $a_{1}^{eq} = 0.54309(\pm 1)$ (nm). For the LQ alloys it can be observed that

For the LQ alloys it can be observed that the Si-rich phase lattice parameter is smaller than the reference value.

For the SQ AlSi 10.0 at% alloy it is observed that after the quench the Si-rich phase lattice parameter equals the reference value quoted above. On ageing the SQ Si-rich phase lattice parameters decrease to reach a minimum (see Fig. 7). Beyond this minimum the Si-rich phase lattice parameters increase to reach stationary values below the reference value.

The differences between the reference value and the stationary Si-rich phase lattice parameter are significantly less for the SQ alloys than for the LQ alloys (see Table 1).

3. DISCUSSION

3.1 ANNIHILATION OF EXCESS VACANCIES - The lattice parameter of a "solid solution" of metal atoms and vacancies may be described by a Vegardtype equation. By assuming that the vacancy volume is a constant fraction of the metal atomic volume, the fictitious vacancy lattice parameter can be written as a fraction of the lattice parameter of the metal without vacancies. As a consequence the average lattice parameter of the



Fig. 8: Cooling-induced change of the Al-rich phase lattice parameter per degree of cooling, $\Delta a \frac{T}{A1}(\omega)/\Delta T$, as a function of the volume fraction Si precipitated, $y_{S1}(\omega)$ for LQ and SQ AlSi alloys after completed precipitation.



Fig. 9: Schematic representation of the Al-rich lattice parameter versus ageing time; estimation of cooling-induced $\Delta a_1^{T}(\infty)$ and precipitation-induced $\Delta a_2^{V}(t_{max})$ lattice parameter changes for (a) LQ and (b) SQ AlSi alloys.



Fig. 10: Precipitation-induced change of the Alrich phase lattice parameter versus the grain size of the Al-rich phase in SQ AlSi alloys with equal Si content of the Al-rich phase at the start of ageing: $x_{Al}^{t=0} = 1.4 \times 10^{-2}$; Δa_{Al}^{U} at t_{max} .

alloy decreases with increasing vacancy concentration.

On the above basis, the sudden increase of the LQ Al-rich phase lattice parameter on shorttime ageing at the lowest temperature can be ascribed to the annihilation of excess vacancies retained after liquid quenching. A more extended and quantitative discussion of this effect for LQ AlMg and LQ AlSi alloys was given in (12).

For the SQ alloys such a sudden increase of the Al-rich phase lattice parameter was absent. This does not contradict the above interpretation, since the excess vacancy concentration after solid quenching is smaller than after liquid quenching (11). Apparently, the effect of the annihilation of the lower concentration of excess vacancies is too small to be detected in the SQ alloys.

3.2 MISFIT STRAINS IN A TWO-PHASE SYSTEM -The specimens in this study consist generally of two misfitting phases: the continuous Al-rich phase and the dispersed Si-rich phase. Eshelby developed a theory to describe the elastic distortions by point imperfections in a finite matrix (18-20). This model is now applied for the calculations of the distortions in the case of misfitting second phase particles embedded in a matrix phase (14,21).

Shift of the Lattice Parameter of the Continuous Phase - Consider a spherical particle of phase B and a continuous finite matrix of phase A with a cavity. The misfit parameter c is defined by:

$$\varepsilon = (r_0^B - r_0^A)/r_0^A \tag{1}$$

where r_0^B = the radius of the free undeformed oparticle B;

A = the radius of the empty undeformed cavity in the matrix A. Introduction of particle B into the cavity induces elastic strains in both matrix and particle (= inclusion) as a result of the misfit between inclusion and cavity. Assuming elastically isotropic materials and n inclusions per unit volume, the fractional volume change $\Delta V_A/V_A$ of the finite matrix can be written (see eq. 8.12 in (9) and eq. 25.10 in (20)) as:

$$\Delta V_{\rm A}/V_{\rm A} = 16 \ \text{m C}_{\rm A} \ \varepsilon (r_{\rm O}^{\rm A})^{3} \ \text{m} \qquad (2)$$

with
$$C_A = \frac{V_A}{K_A} \frac{K_B}{3K_B + 4V_A}$$

where μ and K represent the shear and bulk modulus. With ${}^{V}_{B}$ being the volume fraction of the inclusions B (${}^{V}_{B} = 4 \, \mathrm{m}(rB)^{3} \, \mathrm{m}/3$, where r^{B} is the actual radius of the inclusion) and by approximating r^{B} by r^{A}_{A} and $\Delta V_{A}/V_{A}$ by $3\Delta a_{A}/a_{A}$, where a_{A} is the lattice parameter of the matrix, it follows for the shift of the matrix lattice parameter:

$$\Delta a_{A} = 4 C_{A} \in y_{B} a_{A}$$
(3)

It is essential that the matrix is of finite dimensions. For an infinite assembly no volume changes of the matrix occur, whereas for a finite assembly volume changes of the matrix occur as a result of the image forces required to obtain a stress-free surface.

Shift of the Lattice Parameter of the Dispersed Phase - After the free undeformed particle has been placed in the cavity, the inclusion itself is in a state of hydrostatic stress. Taking into account the effect of image forces, the fractional volume change $\Delta V_B / V_B$ of the second phase (n particles per unit volume) can be written (see eqs. 25.4 and 25.9 in (20); eq. 25.9 was originally derived for the matrix and is now transposed for the inclusion) as:

$$\Delta v_B / v_B = 3(C-1) \epsilon + \frac{16}{3} \pi \frac{\mu_A}{\kappa_B} C \epsilon (r_O^A)^3 n$$
 (4)

with C = $\frac{3K_B}{3K_B+4\mu_A}$

For a volume fraction Y_B of inclusions B, and by approximating r^B by r^A and $\Delta V_B/V_B$ by $3\Delta a_B/a_B$, where a_B is the lattice parameter of the inclusion, it follows for the shift of the inclusion lattice parameter:

$$\Delta a_B = -4 C_B \epsilon (1 - y_B) a_B$$
(5)
th C_B = $\frac{\nu_A}{3K_B + 4\mu_A}$

Note that Eq. (5) is an improved version of eq. 9 in (3).

3.3 MISFIT PARAMETERS FOR AlSi ALLOYS -Two sources of elastic distortions in the Alrich phase and in the Si-rich phase can be indicated:

a. The difference in linear thermal expansion coefficient, α , of Al-rich and Si-rich phase implies that after cooling from the ageing temperature to room temperature the volume available to the silicon inclusion is too small. Taking $\alpha_{Al} = 23.5 \times 10^{-6} \text{ K}^{-1}$ (22) and $\alpha_{Si} = 3 \times 10^{-6} \text{ K}^{-1}$ (23), it is obtained for the cooling-induced misfit, ε^{T} :

$$T = (a_{A1} - a_{S1})(T_a - T_r) = 20.5 \times 10^{-6} \Delta T$$
 (6)

where \mathbf{T}_{a} and \mathbf{T}_{r} are the ageing temperature and room temperature, respectively.

b. Silicon has a larger atomic volume as precipitated than as dissolved in the Al-rich phase (6). For the calculation of the misfit parameter accounting for this effect, the change of the Al-rich phase lattice parameter due to the change in silicon content by precipitation can be neglected. Using the lattice parameters, a_{Si} and a_{AL} , for pure aluminium and pure silicon at 298 K, it is obtained for the precipitation-induced misfit, t^{V} .

$$\varepsilon^{v} = (a_{S1} - a_{A1} \sqrt[3]{2})/a_{A1}\sqrt[3]{2} = 0.064$$
 (7)

where the factor $\sqrt{2}$ arises from the difference between atomic packing in the silicon diamond structure and in the aluminium fcc structure.

3.4 SHIFT OF THE A1-RICH PHASE LATTICE PARAMETER DURING PRECIPITATION - Both misfit parameters mentioned in section 3.3. are positive. Hence according to Eq. (3) positive Δa_{A1} -effects are expected. The value of C_A can be calculated from literature data for the elastic constants (22), giving $C_{A1} = 0.086$. Then for the coolinginduced increase of the A1-rich phase lattice parameter after an ageing time t, $\Delta a_{A1}^{\Gamma}(t)$, it is obtained from Eqs. (3) and (6)

$$\Delta a_{A1}^{T}(t) = 2.86 \times 10^{-6} \Delta T y_{S1}^{(t)} (nm)$$
(8)

where y(t) is the volume fraction of the Si-rich phase (= pure Si) present in the alloy after an ageing time t. Note that for most alloys investigated here applies that y(q) > 0. It follows from Ref. (3), that: 3

$$y(t) = \frac{a_{Si}}{2(1-x_0)(a(t))^3/(x_0-x(t)) + a_{Si}^3}$$
(9)

where a(t) is the Al-rich phase lattice parameter at 298 K after an ageing time t, x_0 is the overall atomic fraction Si of the alloy and x(t) is the atomic fraction Si of the Al-rich phase after an ageing time t.

For the precipitation-induced increase of the Al-rich phase lattice parameter after an

vi

alloy at% Si	y(_∞) Si x 10 ²	selected	ageing		τ .	Δa_{1}^{T} (=) x 10 ⁴	
		reflection EH ²	time (h)	temp. (K)	ه \$1 ^(∞) (nm)	experiment (nm)	Eq. (20) (nm.)
LQ Alloy	8						•
		11	256	397	0.5429 (+ 2)	-2	-4
		24	256	425	0.5425 (+ 2)	-6	-5
2.3	2.8	11	256	448 (= A)	0.5428 (+ 1)	-3	-6
		27	A+1	471	$0.5426 (\pm 1)$	-5	-7
		11	256	397 (= B)	0.5429 (+ 2)	- 2	- 3
		24	256	4,25	0.5427 (+ 1)	-4	-4
10.6	12.5	24	256	448	0.5426 (+ 3)	-5	- 5
		27	B+1	471	0.5429 (+ 1)	- 2	-6
SQ Alloy	\$						
		NR	1024	450	0.54306 (+ 1)	-0.3	- 5
10.0	11.8	NR	2056	492	$0.54308 \ (\pm 1)$	-0.1	-7

<u>Table 1</u>: The Si-rich phase lattice parameter, $a(\omega)$, after completed precipitation (t = ∞). NR = Nelson-Riley extrapolation.

ageing time t, $\Delta a_{\lambda_1}^{\chi}(t)$, it is obtained from Eqs. (3) and (7):

$$\Delta a_{A1}^{V}(t) = 0.00896 y_{Si}^{prec}(t) (nm)$$
 (10)

where $y_{Si}^{prec}(t)$ is the volume fraction of the Si rich phase just precipitated. Note that $y_{Prec}^{prec}(t)$ is to be distinguished from y(t), which includes the fraction Si-rich phase already present before ageing. The relation between $y_{Si}^{prec}(t)$ and x_0 , x(0) and x(t) is complicated, but to a good approximation the volume of the alloy does not change on precipitation. Then it follows simply:

$$y_{Si}^{prec}(t) = y(t) - y(0)$$
 (11)
Si Si Si

On precipitation the silicon content of the Al-rich phase, x(t), and hence the Al-rich phase lattice paramete[§]: a(t), changes. In equilibrium, the silicon content dt the Al-rich phase at the ageing temperatures applied can be neglected. Therefore, the change of the Al-rich phase lattice parameter as a result of the precipitation-induced change of the silicon content after an ageing time t is given by

$$\Delta a_{A1}^{\text{prec}}(t) = p \left(x(t) - x(0) \right)$$
(12)
Si Si

where $p = -1.74 \times 10^{-2}$ (nm) (3). Ignoring relaxation of stresses, the Al-rich phase lattice parameter after an ageing time t, a(t), can now be written as:

$$\begin{array}{c} a(t) = a(0) + \Delta a^{\text{prec}}(t) + \Delta a^{\text{T}}(t) + \Delta a^{\text{T}}(t) + \Delta a^{\text{T}}(t) \\ Al & Al & Al \end{array}$$
 (13)

According to Eqs. (8), (10), (12) and (13) a(t)increases continuously with ageing time. Al However, if relaxation occurs the slope of a(t)versus t diminishes and even a maximum can occur (see section 2.1 and Figs. 1-6).

Cooling-induced Shift - When a_{A1} becomes stationary (see Figs. 4-6), the precipitation is

completed and the precipitation-induced stresses are fully relaxed, i.e. $a(0) + \Delta a^{PIEC}(m) = a^{eq}_{A_1}$ and $\Delta a_{A_1}(m) = 0$. Then, according Alto Eq.(13)^A the deviation of the Al-rich phase lattice parameter at the largest ageing times applied (written as t = m) can be fully ascribed to cooling-induced stresses (see Fig. 9):

$$\Delta \mathbf{a}_{\mathrm{A1}}^{\mathrm{T}}(\boldsymbol{\omega}) = \mathbf{a}(\boldsymbol{\omega}) - \mathbf{a}_{\mathrm{A1}}^{\mathrm{eq}}$$
(14)

In Fig. 8 our previous (14) and present data for $\Delta a_{A1}^{(\infty)}/\Delta T$ are plotted vs. $y(\infty)$, where $y(\infty)$ is the volume fraction of all ^{Si}si-rich phase present in the alloy after ageing. The bold line is the best fit with the experimental results (14); the dashed line represents Eq. (8). The relatively large deviations between the results for the SQ AlSi 1.4 at% and SQ AlSi 2.4 at% alloys and the bold line in Fig. 8 may be due to incomplete relaxation of precipitation stresses (see discussion about Δa_{A1} and grain size in next subsection).

Recognizing the simplicity of the model, there is a fair agreement between theory and experiment. In view of the questionable compatibility of literature elastic constants with the model applied, an experimental value for Al (see Eq. (3)), C_{A1}^{exp} , is preferred. This value can be obtained from the bold line in Fig. 8, which is described by:

$$\frac{\Delta a^{T}(\omega)}{\frac{A1}{\Delta T}} = 3.73 \times 10^{-6} \text{ y}_{S1}^{(\omega)} (nm \text{ K}^{-1})$$
(15)

This results in:

$$c_{A1}^{exp} = 0.112$$
 (16)

Preoripitation-induced Shift - In Figs. 9a and 9b the Al-rich phase lattice parameter is schematically depicted as a function of ageing

Alloy at% Si	Al-ric grain size (µm)	h phase x ^{t=0} Si x 10 ²	y ^{prec} (t _{max}) x 10 ²	ageing temp. (K)	t _{max} (h)	∆a _{Al} (t _{max}) experiment (nm)	x 10 ⁵ Eq. (18) (nm)
LQ Alloys							
2.3 10.6	3	1.3 3.5	0.2 2.4	445 445	0.5	6 25	3 L 28 13
SQ Alloys							
1.4	300	1.4	1.7	402 450 492	512 16 0.5	10 15 11	19 16 19 19
2.3	120	1.4	1.7	402 450 492	512 4 0.5	11 11 13	19 (6 19 19
10.0	20	1.4	1.5	402 450 492	2048 16 1	3 3 1	17 14 17 17

time for the LQ and SQ alloys, respectively (cf. Figs. 1-6). The maxima occurring can be interpreted as resulting from precipitation-induced stresses and their subsequent relaxation. At ageing times where Δa_{A1} effects occur, also $\Delta a_{A1}^{\text{prec}}$, Δa_{A1} and relaxation effects are present. Effective values for Δa_{A1}^{-1} , which contain the decreasing effect of relaxation, cannot be extracted in an exact way from the available experimental data. Approximate values at t_{max} , $a_{A1}(t_{max})$, where the effective value is expected to be largest (see Fig. 9), can be found in the following ways:

a. For the SQ alloys it appears reasonable that at t_{max} all silicon originally dissolved in the Al-rich phase is fully precipitated. Then, as indicated in Fig. 9b, an estimate for the effective $\Delta a_{AI}(t_{max})$ is simply obtained from:

$$\Delta a_{A1}^{V}(t_{max}) = a_{A1}(t_{max}) - (a_{A1}^{eq} + \Delta a_{A1}^{T}(t_{max}))(17)$$

To avoid uncertainties about the completeness of the relaxation at the largest ageing times applied $\Delta a_{A1}^{(1)}(t_{max})$ was not determined graphically, but from Eq. (17). Herein $\Delta a_{A1}^{(1)}(t_{max})$ was obtained from Eq. (15), where the value of $y(\infty)$ was calculated with Eq.(9) by putting $x_{Si}(t_{max}) = 0$. Results are gathered in Table 2. Theoretical estimates for $\Delta a_{A1}(t_{max})$ can be obtained from Eq. (10), based on a literature value for C_{A1} . However, the experimental value

for C_{A1} is preferred (see preceding subsection). Then Eq. 10 transforms in:

$$\Delta a_{A1}^{V(t)} = 0.0117 \text{ y}_{S1}^{\text{prec}(t)} (nm)$$
(18)

The theoretical estimates, not taking into account relaxation and calculated with Eq.

(18), are also collected in Table 2.

. V .

b. For the LQ alloys indications of precipitation -induced changes of the Al-rich phase lattice parameter were reported previously (1, 3). The maxima observed for LQ alloys occur, however, at times where the precipitation is not finished at all (cf. Figs. 2a and 3a). An experimental estimate of the effective $\Delta a_{A1}^{v}(t_{max})$ can be made by accounting for the change in composition by the silicon precipitation. However, this cannot be done easily and without severe assumptions. As an escape an estimate of the effective $\Delta a_{A1}^V(t_{max})$ was obtained by the simple procedure indicated in Fig. 9a. This procedure is based on the assumption that for ageing times far beyond tmax, relaxation can catch up with precipitation, i.e. $\Delta a_{A1}^{V}(t \gg t_{max}) = 0$. Results are gathered in Table 2, together with the theoretical estimates for $\Delta a_{A_1}(t_{max})$ as obtained from Eq. (18) using Eq. (11) for P^{FC} $y_{S_i}^{pree}$ (x_{Si} from Eqs. (9), (12), (13) and (15), with in Eq. (15) t_{max} for ∞).

Generally the experimental values for Δa_{A1} are smaller than the theoretical estimates, in particular for the SQ alloys. This indicates, that on continued ageing a noticeable relaxation occurs.

For the LQ alloys the supersaturation after the quench is higher than for the SQ alloys. Therefore, initially the precipitation in the LQ alloys proceeds faster than in the SQ alloys. Apparently, the relaxation cannot catch up with the precipitation and rather large values for Δa_{A1} are observed (Table 2).

For the SQ alloys the value of $\Delta a_{A_1}^{v}(t_{max})$ increases with the grain size of the Al-rich phase (see Table 2 and Fig. 10). It can be concluded that relaxation in SQ alloys proceeds more easily if the grain size is small. For the LQ alloys at the lower ageing temperature the relatively slow precipitation process and the small grain size (24) result even in an absence of these precipitation-induced maxima (see Figs. 2a and 3a).

3.5 SHIFT OF THE SI-RICH PHASE LATTICE PARAMETER DURING PRECIPITATION - Both misfit parameters discussed in section 3.3 are positive. Thus, according to Eq. (5) negative Δa_{SI} -effects are predicted. The value of C_{SI} can be obtained from data in (22) giving $C_{SI} = 0.068$. However, a semi-empirical value, C_{SI}^{exp} , can be obtained. ' From Eqs. (2) and (5) it follows that $C_{SI} = (K_{AI}/K_{SI})^{C}A_{I}$. Taking literature values for, K_{AI} and K_{SI} (22) and assuming that the ratio K_{AI}/K_{SI} is rather insensitive for the effects causing differences between C_{AI} and C_{AI}^{exp} it is obtained with Eq. (16):

$$c_{Si}^{exp} = 0.089$$
 (19)

Then, for the cooling-induced shift of the Si-rich phase lattice parameter, $\Delta a_{Si}^{T}(t)$, it is obtained from Eqs. (5) and (6):

$$\Delta a_{Si}^{T}(t) = -3.97 \times 10^{-6} \Delta T (1 - y(t)) (nm) (20)$$

For the precipitation-induced shift of the Si-rich phase lattice parameter, $\Delta a_{Si}^V(t)$, it is obtained from Eqs. (5) and (7):

$$\Delta a_{S1}^{V}(t) = -0.0124 (1 - y_{S1}^{prec}(t)) (nm)$$
 (21)

Cooling-induced Shift - The $\Delta_{a_{1}}^{T}(t)$ -values for completed precipitation, $\Delta_{a_{1}}^{T}(\phi)$, as predicted by Eq. (20), are presented in Table 1. In view of the large experimental errors inherent to the determination of the minority phase lattice parameter (see section 2.2), for the LQ alloys a reasonable agreement exists between the theoretical and experimentally determined values for $\Delta_{a_{1}}^{T}(\phi)$. For the SQ alloys the theoretical and experimental $\Delta_{a_{3}}^{T}(\phi)$ -values differ significantly. This may be a consequence of the presence of relatively large Si-particles in the SQ AlSi 10.0 at% alloy. The Si-particle size in the SQ alloy is about two orders of magnitude larger than in the LQ alloys, which may invalidate the aplication of the theory of section 3.2 for the dispersed second phase.

Precipitation-induced Shift - Because of experimental difficulties (see section 2.2) only Si-rich phase lattice parameter data as a function of ageing time are available (Fig. 7) for the SQ AlSi 10.0 at% alloy.

Referring to the Al-rich phase lattice parameter maxima, resulting from precipitation stresses and their relaxation, one expects to observe Si-rich phase lattice parameter minima at the same ageing times, also resulting from the precipitation-induced stresses and their relaxation. Figs. 6 and 7 indeed support this interpretation.

Assuming (i) at the time of the minimum all silicon has precipitated, and (ii) the

precipitation-induced misfit is accommodated fully elastically, from Eq. (21) a theoretical estimate is obtained for the SQ AlSi 10.0 at% alloy (the value of y_{Si}^{rec} (t_{min}) is calculated with Eq. (11) and $x_{Si}(t_{min}) = 0$):

$$\Delta a_{Si}^{V}(t_{min}) = -0.012 (nm)$$
(22)

The effective $\Delta s_{Si}(t_{min})$ -values were obtained in the same way as the $a_{A1}(t_{max})$ -values for the SQ alloys. From Fig. 7 it follows:

$$\Delta a_{S1}^{v}(t_{min}) \sim -0.5 \times 10^{-4} (nm)$$
(23)

Clearly, the experimental value for $\Delta a_{S_1}^{v}$ differs significantly from the theoretical estimate. To explain this difference one may refer to the large second-phase particle size in the SQ alloy (see preceding subsection).

3.6 ORIGIN OF RELAXATION - The coolinginduced misfit strains in the Al-rich and the Sirich phase, as prescribed by Eqs. (15) and (20) are at most 0.05% and 0.14%, respectively, for the alloys investigated. Apparently, the Al-rich phase accommodates this strain at room temperature in a fully elastic way (see discussion with respect to Fig. 8), while the strain prescribed for the Si-rich phase is far below the elastic limit (25).

The precipitation-induced misfit strains in the Al-rich and the Si-rich phase, as prescribed by Eqs. (18) and (21) are 0.06% and 2.2% ($yp^{rec} = 0.02$; cf. Table 2). Hence, in general⁵the predicted strains will be above the elastic limits of both phases at the ageing temperature (see above and (25)). However, for the initial stages of precipitation, i.e. small values of y^{Prec}_{Si} , according to Eq. (18) the strain in the Al-rich phase is small enough to be accommodated elastically, but the corresponding strain in the silicon particles is about 2.3%. This suggests that relaxation during precipitation is provoked because the elastic limit of the Sirich phase would be surpassed.

CONCLUS IONS

- Annihilation of excess vacancies retained after liquid quenching results in a sudden increase of the Al-rich phase lattice parameter at the start of ageing.
- The amount of quenched-in vacancies is larger for liquid-quenched AlSi alloys than for solid-quenched AlSi-alloys.
- Both the Al-rich and the Si-rich phase lattice parameters, as determined at room temperature reflect (i) the extent of the Si-precipitation, (ii) the precipitation-induced stresses and subsequent relaxation, and (iii) the coolinginduced stresses.

- 4. For a two-phase system misfit-induced lattice parameter shifts were estimated applying Eshelby's theory, originally developed for point imperfections in a finite crystal. These estimates agreed fairly with experimental results for AlSi alloys.
- 5. For both liquid-quenched and solid-quenched AlSi alloys the Al-rich phase lattice parameter after completed precipitation is larger than its equilibrium value, whereas the Si-rich phase lattice parameter is smaller than its equilibrium value. These shifts stem from the large difference in thermal expansion between both phases after cooling from the ageing to the room temperature. The shifts could be explained quantitatively from the model mentioned under 3.2.
- 6. For the solid quenched alloys the Al-rich phase lattice parameter is maximal at the ageing times where the Si-rich phase lattice parameter is minimal. These effects are a consequence of precipitation-induced stresses, originating from the large difference in atomic volume of silicon as dissolved and as precipitated. For both phases the shifts predicted theoretically are larger than the experimental deviations. This is ascribed to relaxation processes dissipating precipitation stresses. The relaxation in the solid-quenched alloys depends on their grain size.
- 7. In the AlSi alloys relaxation is provoked because a fully elastic accommodation of the precipitation-induced strains would result in a surpassing of the elastic limits, at first for the Si-rich phase.

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IV.5.

PRECIPITATION IN LIQUID-QUENCHED AI-Mg ALLOYS;

A STUDY BY USE OF X-RAY DIFFRACTION LINE SHIFT AND LINE BROADENING

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The precipitation process in liquid-quenched (LQ) alloys of Al with 3.2 at%, 10.5 at% and 16.7 at% Mg on ageing at 404, 450 and 492 K was investigated by X-ray diffraction analysis. It was found that only β' -phase precipitation occurred. During ageing the average Al-matrix lattice parameter was determined from line position, while a measure for the lattice spacing variations was deduced from line broadening. The β' -phase precipitation was found to occur inhomogeneously; for one alloy splitting of diffraction lines was observed. The (asymmetrical) line broadening changes observed during the β' -phase precipitation could consistently be conceived as dominated by the inhomogeneous nature of the β' -phase precipitation process. The (symmetrical) line broadening retained after completed precipitation was ascribed to the volume misfit between the precipitated β' -phase particles and the Al matrix. Analysis of the Al-matrix lattice parameter changes with ageing time revealed that the β' -phase precipitation rate is governed by the Mg volume diffusion.

1. Introduction

The initially high cooling/solidification rate inherent to liquid quenching, i.e. rapid quenching from the liquid state, can highly influence the kinetics of precipitation in Al-base alloys. Liquid quenching (LQ) as compared to solid quenching (SQ) can result in an increased amount of excess vacancies and an enhanced degree of solute supersaturation. This has been demonstrated by experiments with AlSi alloys (1).

Only a few data exist about the precipitation phenomena in LQ AIMg alloys (2), whereas the ageing phenomena in conventionally produced SQ AIMg alloys were the subject of several previous studies (3-16).

In AlSi alloys precipitation directly results in the equilibrium phase of (practically) pure silicon, whereas the precipitation in quenched AlMg alloys proceeds via intermediate metastable phases. In SQ AlMg alloys the sequence and number of these phases depend on the ageing temperatures applied (15, 16). For the precipitation below 323 K the following sequence can apply (depending on the composition of the alloys studied):

solid solution \rightarrow GP ($\rightarrow \beta$ ") $\rightarrow \beta$ ' $\rightarrow \beta$

[1]

where GP stands for Guinier-Preston zones, β'' is an intermediate phase, sometimes described as an ordered GP zone; probably having an L1₂-structure (Al₃Mg) (16), β' is a semi-coherent intermediate phase with a hexagonal unit cell (a = 1.002 nm and c = 1.636 nm (13)) and β is the equilibrium phase (about Al₃Mg₂) having an fcc unit cell (a = 2.824 nm (13)) that contains 1168 atoms.

The formation of the GP zones is associated with a large change of the enthalpy (2). Thus, the GP-zone formation in LQ AlMg alloys can be traced by applying Differential Scanning Calorimetry (DSC) (2). It was found that the GP-zone formation in an LQ AlMg 12.8 at% alloy begun after a storage of 11.5 days at room temperature, whereas in an LQ AlMg 17.2 at% alloy it started after a storage of 3 days at room temperature. On annealing with constant rates between 5-40 Kmin⁻¹ the dissolution of GP zones was completed below 400 K (2). According to Ref. 15 the dissolution temperatures of the GP and $\beta^{"}$ zones, ranging from 330-360 K(15), do not strongly depend on the Mg content of the alloys (Mg contents between 7.5 and 12.5 at%). For the same alloys the $\beta^{"}$ solvus probably lies between 500 and 550 K (15). So, on ageing of quenched AlMg alloys at temperatures between 400 and 500 K, two basically different initial conditions can be discerned:

(i) the alloy contains GP zones formed during ageing at room temperature.

(ii) the alloy does not contain GP zones, because the ageing starts immediately after the quench.

In case (ii) a direct precipitation of the β' phase occurs.

The present study concerns the β precipitation process in LQ AlMg alloys with a Mg content of 3.2 at%, 10.5 at% and 16.7 at% by ageing at 404, 450 and 492 K after a room temperature storage varying between 27 and 970 days. So, case (i) holds for the specimens investigated (see above): a partial or a full development of GP zones has occurred during the room temperature storage. However, it has been shown for case (i) that on annealing the GP zones formed are always completely dissolved before any β -phase precipitation starts(2). Hence, in case (i) and in case (ii) the β -phase precipitation begins in an essentially single-phase matrix.

As dissolution of Mg atoms in the Al matrix increases the Al-matrix lattice parameter, the precipitation of β ' phase results in a decrease of the Al-matrix lattice parameter. Therefore, in this study the precipitation phenomena in LQ AlMg alloys were traced by the determination of the Al-matrix lattice parameter and its variance as derived from the X-ray diffraction line position and line broadening.

2. Experimental procedures

Aluminium alloys with an overall magnesium content of 3.2 at%, 10.5 at% and 16.7 at% (the magnesium solid solubility at the eutectic temperature equals 18.6 at% (17)) were prepared from 99.998 wt% Al and 99.99 wt% Mg. By the melt spinning technique ribbons with a thickness varying between 20-50 μ m and a width of about 2 mm were obtained (18). As deduced from dendrite-arm-spacing measurements, the cooling rate ranged from 10⁶ to 10⁷ Ks⁻¹ (19). After the melt spinning the ribbons were stored at room temperature for at least 27 days and for at most 970 days.

The Al-matrix lattice parameter was measured at room temperature as a function of time of ageing in an oil bath maintained at 404 ± 4 , 450 ± 2 or 492 ± 2 K. Parts cut from the ribbons were placed in a specimen holder that was used for the ageing treatment and that fitted in the Debije-Scherrer (DbS) camera, enabling the investigation of the same sample throughout the whole ageing process. These specimen holders were placed in a specially designed heat treatment cylinder pervious for oil, thereby protecting the vulnerable specimens. The temperature within the cylinder reached the temperature of the oil bath within one minute. The Al-matrix lattice parameter values were obtained from DbS photographs - taken with CuK α radiation and utilizing high angle reflections - with a precision of 4 parts to 40,000. The values presented are valid at 298 K and were derived from the measured values by applying the appropriate thermal expansion coefficient (20).

The DbS photographs were also utilized to characterize the X-ray diffraction line broadening: with a densitometer the intensity on the equator of the DbS photographs was measured as a function of the diffraction angle. The A1{200} and the A1{220} line profile shapes of the LQ AlMg 10.5 at% and the LQ AlMg 16.7 at% alloys were determined, because these reflections yielded the line profiles with sufficient intensity at the highest possible diffraction angle. The background was interpolated linearly between the two extremeties of the profiles obtained. The subsequent line-profile analysis was performed using the single-line Voigt technique (21).

3. Results

3.1. The shift of the Al-matrix reflections

The A1-matrix lattice parameter is shown as a function of ageing time at the temperatures applied in Figs. 1 and 2. The increase of the A1-matrix lattice parameter occurring at the very start of ageing (see Fig. 2; note that the experimental error is about 4×10^{-5} nm) can be explained quantitatively by the annihilation of excess vacancies as discussed elsewhere (22).

The precipitation-induced decrease of the Al-matrix lattice parameter occurs after an initial period with no measurable change of this lattice parameter. This period will be called the effective "incubation time". The effective incubation times for the LQ AlMg 16.7 at% alloy are shorter than those for the LQ AlMg 10.5 at% alloy. For both alloys, the incubation time decreases with increasing ageing temperature.

The Al-matrix lattice parameter of the LQ AlMg 3.2 at% alloy does not show any indication of a precipitation-induced decrease on ageing at 404 ± 4 and 450 ± 2 K. Apparently no precipitation has occurred during the ageing times applied. Because the solid solubility at 492 K corresponds with the overall composition of the alloy (17), no precipitation can be expected in this alloy at 492 K.

The DbS photographs of the LQ AlMg 16.7 at% and the LQ AlMg 10.5 at% alloys obtained after 4 h of ageing at 404 K and after 16 h of ageing at 492 K, respectively, exhibited already diffraction lines that could be

attributed to a hexagonal unit cell with an axial ratio, c/a, of about 1.68. This corresponds fairly well with the data given previously for the intermediate β '-phase (13). No indication for the presence of diffraction lines corresponding with the equilibrium β phase was obtained.

Remarkebly, at the stage of precipitation where the overall rate of transformation is largest (Figs. 1 and 2) the Al{422} and Al{333/511} line profiles from the LQ AlMg10.5 at% alloy show two maxima (see Fig. 3 (α_1 components only)). This is interpreted as caused by the simultaneous presence of regions in the Al matrix in a beginning and an advanced stage of Mg solute depletion. The behaviour of the lattice parameters calculated from the two intensity maxima is shown in Fig.1 as a function of ageing time. A corresponding microstructure is shown in Fig. 4. No such effect could be observed for the LQ AlMg 16.7 at% alloy (see discussion in section 4.1.).

The progress of the Mg depletion of a matrix can be characterized (in the absence of macrostrains) by a precipitation/transformation parameter, $1-X_t$, defined by:

$$1 - X_{t} = \frac{c(t) - c(\infty)}{c(0) - c(\infty)} \approx \frac{a_{AI}(t) - a_{AI}(\infty)}{a_{AI}(0) - a_{AI}(\infty)}$$
[2]

where c(0), c(t), $c(\infty)$ are the Mg concentrations in the Al matrix and $a_{AI}(0)$, $a_{AI}(t)$, $a_{AI}(\infty)$ are the Al-matrix lattice parameters at the start of ageing, after an ageing time t and in equilibrium, respectively. The equation $c = 4x/(a_{AI})^3$, with x as the atomic fraction of Mg in solid solution relates the Mg concentration c with the Almatrix lattice parameter a_{AI} . Literature data have been used for the relation between x and a_{AI} (23) and for the equilibrium solid solubilities (17,24). In Figs. 5 and 6, as derived from the intensity maxima observed for the Al matrix, 1-X₁ is shown as a function of ageing time at the temperatures indicated.

The equilibrium solid solubilities at the ageing temperatures applied, $x(\infty)$, correspond, within the experimental error, with the values of x as derived from the values of the Al-matrix lattice parameter measured after the largest ageing times at each temperature. This indicates a completed precipitation.

3.2. The broadening of the Al-matrix reflections

X-ray diffraction line profiles are generally broadened by instrumental aberrations, the wavelength distribution and structural imperfections. The broadening by the instrumental aberrations and by the wavelength distribution can be determined by measuring corresponding line profiles from reference specimens. The reference specimen employed consisted of pure Si powder (NBS SRM 640 (see Ref. 25); 114 h annealed at 1473 K in an argon atmosphere). The breadth parameters characterizing the broadening of Al-matrix reflections by instrumental aberrations and by the wavelength distribution were obtained by interpolation of data from, suitably chosen, measured line profiles of the reference specimen.

The line profile analysis was performed using the single-line Voigt method (21). It is often assumed that the Gaussian component of the structurally broadened profile is dominated by lattice distortions, i.e. lattice spacing variations and that the Cauchy component is mainly due to small domain sizes. It was found that the structurally broadened profile was nearly of Gaussian shape. Therefore, the total structural line broadening was interpreted as caused by lattice spacing variations.

A parameter characterizing the width of the lattice spacing distribution can be obtained from the integral breadth β^{f} of the hkl-reflection after correction for instrumental aberrations etc., as follows (21):

$$\sigma_{\rm d} = \frac{\beta f}{4 \tan \theta}$$
[3]

where θ is the Bragg angle. Values of the fractional lattice spacing variation, σ_d , are shown in Figs. 5 and 6 as a function of ageing time. Note, that the line broadening was measured for low angle Bragg reflections where the instrumental resolution was insufficient to show doubly peaked reflections discussed for the LQ AlMg 10.5 at% alloy (high-angle reflections were of too low intensity to allow accurate profile shape determination (see section 2) from DbS photographs). For the same times of ageing, the differences between σ_d values derived from the Al{200} and the Al{220} reflections are generally insignificant in view of the experimental inaccuracies. So, averaged data of σ_d will be considered only. The following observations can be made: (i) for both alloys σ_d remains constant during the effective incubation time; at the moment that the

 for both alloys od remains constant during the effective incubation time; at the moment that the precipitation parameter 1-Xt decreases, od increases.

- (ii) for the LQ AlMg 10.5 at% alloys, σ_d reaches a maximum at times where for 1-X_t a high and a low value are observed simultaneously; for the LQ AlMg 16.7 at% alloy, σ_d reaches a maximum at times where the transformation proceeds fastest, i.e. for 1-X_t U 0.5.
- (iii) the maxima of σ_d are higher for the LQ AIMg 16.7 at% alloy than for the LQ AIMg 10.5 at% alloy.
- (iv) on prolonged ageing, σ_d decreases until an approximately constant, non-zero value is reached (see in particular the data for the LQ AlMg 16.7 at% alloy).

4. Discussion

4.1. Non-uniform precipitation

The observation of a pronounced line broadening, in association with the appearance of two intensity maxima in line profiles recorded from the LQ AlMg 10.5 at% alloy, is ascribed to the occurrence of significant compositional differences in the Al-matrix during the transformation: the precipitation process takes place in a non-uniform manner (for detailed discussion of the line broadening, see section 4.2.). In the past it was suggested that discontinuous precipitation (for terminology used, see the review given by Williams and Butler (26)), initiating heterogeneously at grain boundaries, could explain the appearance of two values for the Al-matrix lattice parameter (4, 5); however, no microscopical evidence was presented. Instead, more recent transmission (10) and present transmission and scanning electron microscopy did not yield indications for the lamellar microstructure typifying the discontinuous precipitation takes place in conjunction with precipitation in the bulk of the grains (see Fig. 4). Thus, it can be suggested that the difference in kinetics of grain-boundary and bulk precipitation leads to simultaneous occurrence of *extended* Al-matrix regions adjacent to grain-boundaries poor in Mg solute and Al-matrix regions in the bulk of the grains still rich in Mg solute. Since the diffracted intensity is proportional to volume and the diffraction angle is related to composition (via the lattice spacing), the distribution of the intensity over the diffraction angle can be doubly peaked, as is seen in Fig. 3.

In a specimen the bulk and the grain-boundary precipitation processes compete. If a high supersaturation of the Al-matrix occurs, the bulk precipitation will dominate. Then a simultaneous occurrence of grain-boundary precipitation will not necessarily reveal itself by a distinct presence of a double Al-matrix reflection, i.e. a single maximum occurs in the distribution of the intensity over the diffraction angle. This description apparently applies to the LQ AlMg 16.7 at% alloy, which has an initial solute supersaturation in the Al-matrix much larger than the LQ AlMg 10.5 at% alloy.

An alternative explanation for the occurrence of additional diffraction maxima, especially at high Bragg angles, has been proposed in Ref. 27: elastic strains produced by the precipitation process "weaken the regular reflections and spread out the distribution of diffuse scattering" which would lead to complicated, multiply peaked total line profiles by superposition of the weakened normal and the diffuse scattering intensity distributions. With regard to this explanation the following remarks can be made:

- In the present investigation, a doubly peaked reflection was only observed for the LQ AlMg 10.5 at% alloy
 during a very limited range of time where the overall change of 1-Xt is half-way. For all other ageing times
 applied singly peaked reflections were observed.
- For the ageing temperatures applied in Ref. 27 (comparable to those of this study) the doubly peaked reflections as observed here (the Al{422} and the Al{333/511} CuKα-profiles) can not be detected in Fig. 1 of Ref. 27, possibly due to a relatively low angular resolution pertinent to the data given in Ref. 27.
- According to Ref. 27, relaxation of the elastic strains would occur during prolonged ageing, implying a negligible remaining line broadening at the end of the ageing treatment. However, in this study a distinct line broadening is observed at the end of the ageing treatment, especially for the LQ AlMg 16.7 at% alloy (cf. Fig. 6). This remaining line broadening can be attributed to the elastic microstrains due to the misfit between the B'-phase precipitates and the Al matrix (see section 4.2.).

In this paper it is thought that non-uniform precipitation explains the double maxima for Al-matrix reflections observed during ageing of the LQ AlMg 10.5 at% alloy.

4.2. Line broadening during precipitation

Misfitting precipitates and compositional variations change lattice spacings. With respect to line broadening two types of lattice spacing variations can be distinguished:

- (i) lattice spacing variations within a coherently diffracting domain.
- (ii) lattice spacing differences between coherently diffracting domains.

Non-uniform precipitation is related with the occurrence of extended regions (domains) with different average compositions and implies line broadening from origin (ii) mainly.

The line broadening related with non-uniform precipitation would reach its maximum when in one half of the specimen the precipitation has just been completed and in the other half no precipitation has occurred at all. Indeed, the maximal line broadening is observed at about half-way the overall change of $1-X_t$.

The presence of line broadening of origin (ii) is also confirmed by the behaviour of w_1/w_2 on ageing, where w_1 and w_2 represent the low-angle and the high-angle half widths of an X-ray diffraction line profile. In early stages of the precipitation process, Mg solute-depleted regions of the matrix with a relatively small Almatrix lattice parameter are in the minority, implying for line broadening from origin (ii) a value of $w_1/w_2 < 1$, i.e. the line profile shows a high-angle tail. In later stages, a minor amount of the Al-matrix is still rich in Mg solute atoms, implying for line broadening from origin (ii) a value of $w_1/w_2 > 1$, i.e. the line profile shows a low-angle tail. Such asymmetries can be pronounced in particular in the case of non-uniform precipitation. The ratio w_1/w_2 for the Al(220) reflection is plotted in Fig. 6 as a function of ageing time. It is observed that from the moment that precipitation becomes effective, the behaviour of the ratio w_1/w_2 corresponds to the foregoing discussion.

It should be noted that line broadening due to origin (i) will also be present during precipitation because of microstrains caused by the volume misfit between the precipitated semi-coherent β' phase (13) and the Almatrix.

After liquid quenching, quenched-in stresses as well as compositional variations due to differences in solidification rates, e.g. between wheel- and upper sides of the ribbons, can occur (1, 28). Hence, during the effective incubation time the observed line broadening is ascribed to such phenomena and thus can stem from origins (i) and (ii).

The maximum line broadening for the LQ AlMg 16.7 at% alloy is larger than for the LQ AlMg 10.5 at% alloy. This can be understood by considering the amount of β' phase to be precipitated: this amount is larger in the LQ AlMg 16.7 at% alloy than in the LQ AlMg 10.5 at% alloy; the volume-averaged misfit strains and compositional variations are larger in the LQ AlMg 16.7 at% alloy than in the LQ AlMg 10.5 at% alloy. After completed precipitation all compositional variations have disappeared. Thereby, an important cause for

After completed precipitation all compositional variations have disappeared. Thereby, an important cause for asymmetry in the line profiles has been removed. The remaining line broadening is solely caused by the volume misfit between the β -phase particles and the Al matrix, which appears to be associated with symmetrical line broadening with w₁/w₂ = 1 (see Fig. 6). Obviously, this remaining line broadening will be larger for the LQ AlMg 16.7 at% alloy than for the LQ AlMg 10.5 at% alloy (Figs. 5 and 6).

4.3. β'-phase precipitation kinetics

By DSC analyses it was shown (2), that the GP/ β " zones were dissolved well below 400 K (see also section 1), amply before any β ' precipitation was detected. Since the ageing temperatures applied in this study lie between 400 and 500 K, it is assumed that a complete dissolution of the GP/ β " zones has occurred at the very start of the ageing treatment. Therefore, the effective incubaton time for the β ' precipitation, as indicated by the start of the decrease of the Al-matrix lattice parameter and by the increase of the line broadening, can not be ascribed to GP/ β " dissolution.

In early stages of phase transformations the reaction rate can be controlled by two different activation energies, one for the formation of (critical) nuclei and the other for their subsequent growth (29). In very many reactions the activation energy for nucleation decreases more than linearly with temperature, leading to a very rapid nucleation rate at large undercoolings, whereas the activation energy of growth is nearly independent of temperature (29). Therefore, at sufficiently low temperatures the nucleation rate is that large, that the nucleation sites saturate very early in the reaction. Then, the activation energy for growth controls the overall reaction rate. It is suggested that this picture applies to the precipitation experiments of this study (maximal ageing temperature equals 492 K). Consequently, the so-called effective incubation time is interpreted as a stage of such a low transformation rate that no measurable change of the Al-matrix lattice parameter occurs (for example, Avrami kinetics with an Avrami exponent larger than 1 correspond with such a situation).

The stage of the precipitation process is characterized by the state variable kt, where $t = the precipitation time and k = k_0 exp - E/k_B T_a$ with $k_0 = pre-exponential factor, k_B = Boltzmann's constant, T_a = ageing temperature and E = the effective activation energy.$

Supposing that after the effective incubation time t_i the same stage of the precipitation process has been reached, the activation energy during the time t_i can be deduced from the slope of the straight line obtained by plotting ln t_i (determined by the time until 1-X_t = 0.998) versus 1/T_a. For both alloys it is thus obtained (Fig.7):

E = 0.7 eV

Growth of the β '-phase particles can occur via the migration of the substitutionally dissolved magnesium atoms through the Al-matrix according to the vacancy mechanism. In the absence of excess vacancies, this transport of magnesium atoms will occur with an activation energy equal to about the sum of the migration and formation energies of a vacancy: ~ 1.3 eV (30). The value found for the apparent activation energy is significantly smaller than 1.3 eV. This hints at the presence of excess vacancies retained after liquid quenching which effectively reduces the contribution of the vacancy formation energy.

On liquid quenching the predominant part of the excess vacancies will be gathered into vacancy loops (31-34). At elevated temperatures (from 375 to 500 K) the excess vacancies collapsed into loops on liquid quenching are "reanimated" (34): the vacancy loops emit vacancies assisting the β ' precipitation. It is noted that the same mechanism was adopted to explain the relatively low values of the activation energies for dissolution of GP zones in AlMg alloys (2) and for the precipitation of Si in AlSi alloys (1).

5. Conclusions

- 1. In quenched AlMg alloys non-uniform precipitation occurs: bulk and grain-boundary precipitation proceed with different rates.
- The appearance of doubly peaked X-ray diffraction line profiles in association with pronounced, distinctly asymmetrical, line broadening is largely ascribed to appreciable compositional variations inherent to the non-uniform precipitation process.
- 3. The residual line broadening observed after the precipitation in the LQ AlMg alloys has been completed is caused by the elastic accommodation of the volume misfit between the β -phase particles and the Al-matrix.
- 4. The activation energy found for the initial β'-phase precipitation suggests strongly, that the kinetics of the β'-phase precipitation are governed by the growth of the precipitate particles via excess-vacancy enhanced volume diffusion of Mg atoms.

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Figure 1 The Al-matrix lattice parameter a_{A1} as a function of ageing time t for the LQ AlMg 10.5 at% alloy at the temperatures denoted.



Figure 2 The Al-matrix lattice parameter a_{A1} as a function of ageing time t for the LQ AlMg 16.7 at% alloy at the temperatures denoted (the values of t = 0 coincide).



Figure 3 The Al(422) X-ray diffraction line profile as obtained from the LQ AlMg 10.5 at% alloy as liquid quenched (a) and from the same alloy as aged for 4h at 500 K (b). Line profiles were obtained by X-ray diffractometry using specimens prepared as described in Ref. 1 and applying CuK α radiation; smoothing was performed and the α_2 component was eliminated.



Figure 4 Optical micrograph of a cross-section of the LQ AlMg 10.5 at% alloy after 4 h of aging at 500 K, showing abundant precipitation at grain boundaries.



<u>Figure 5</u> The fractional lattice spacing variation σ_d in conjunction with the precipitation parameter 1-X_t as a function of ageing time t for the LQ AlMg 10.5 at% alloy at the temperatures denoted.



Figure 6

The fractional lattice spacing variation σ_d and the ratio of the low-angle half-width w_1 and the high-angle half-width w_2 of the Al{220} line profile, w_1/w_2 , in conjunction with the precipitation parameter 1-X₁, as a function of ageing time t for the LQ AlMg 16.7 at% alloy at the temperatures denoted.



<u>Figure 7</u> The value of the natural logarithm of the effective incubation time t_i (taken as the time until 1-X₁ = 0.998) as a function of the reciprocal ageing temperature 1/T_a for the LQ AlMg alloys denoted.

SUMMARY

This thesis deals with ageing phenomena in binary aluminium alloys rapidly quenched from a high temperature to room temperature. Quenching has been performed from temperatures at which a solid (matrix) phase possesses an increased solid solubility for the solute as compared to the one at room temperature (solid quenching \equiv SQ) and from temperatures at which the alloy investigated is in the liquid state (liquid quenching \equiv LQ). In both cases a solute supersaturated Al matrix is obtained after quenching.

Liquid quenching can provide solid alloys with special properties: (i) relatively large amounts of dissolved alloying elements and vacancies in the Al matrix and (ii) a very small grain size (see Chapter I of this thesis). In this work, the precipitation phenomena occurring on ageing after liquid quenching and after solid quenching at temperatures between 400 and 500 K have been studied.

The alloys studied were AlSi and AlMg. The choice of Si and Mg as alloying elements enabled the study of two principally different precipitation mechanisms. In quenched AlSi alloys, the precipitating phase is the equilibrium (Si) phase, whereas in quenched AlMg alloys the precipitation of magnesium proceeds via a multi-stage precipitation sequence: Guinier-Preston (GP) zones/clusters \rightarrow intermediate β ' precipitates \rightarrow equilibrium β precipitates.

In Chapter II a structural characterization of the LQ AlSi and LQ AlMg alloys has been presented. Liquid quenching was performed by melt-spinning: a molten alloy is poured onto a rapidly rotating wheel. Ribbons were obtained with the following typical dimensions: breadth of about 2 mm and thickness of about 50 μ m. The crystalline ribbons produced exhibited a layer structure: an upper (equiaxed) layer, a central (columnar) layer and a microcrystalline wheel-side layer. This layer structure has been related with the solidification history of the ribbons. The texture and the microstrains of the ribbon crystallites were dependent on the layer concerned. The ribbons showed very small overall grain sizes and possessed a surplus of (excess) vacancies. The (quenched-in) excess-vacancy concentration was estimated from the sudden change of the Al matrix lattice parameter on short-time ageing by ascribing the lattice parameter increase to excess vacancy concentration.

Adopting Eshelby's theory on elastical effects induced by point imperfections in a finite medium, it has been found (Chapter III) that the *macrostrains* derived from X-ray diffraction line shifts are proportional to a linear misfit parameter between the matrix and the dispersed phase and to the volume fraction of the dispersed phase. The *microstrains* caused by the volume misfit have been shown to be propertional to the same linear misfit parameter and to the *root* of the volume fraction of the dispersed phase.

Interpreting the observed changes of the Al matrix lattice parameter, the kinetics of silicon precipitation in LQ AlSi alloys were studied; the kinetics of silicon precipitation in SQ AlSi alloys were analysed applying "free volume" positron annihilation as well as by Al-matrix lattice parameter measurements (Chapter IV). From a comparison of the LQ AlSi alloys and the conventionally produced SQ AlSi alloys it followed that the silicon precipitation in the LQ alloys

proceeded faster than in the SQ alloys and that the activation energy for silicon precipitation for LQ AlSi alloys was smaller than for SQ AlSi alloys. The activation energy for precipitation can be considered as the sum of the formation and migration energy of a vacancy in aluminium (in a first-order approximation) as silicon precipitation proceeds via the vacancy mechanism. Therefore, it is concluded in Chapter IV that SQ AlSi alloys possess a lower vacancy concentration than LQ AlSi alloys. Further it is remarked that on quenching excess vacancies condense into loops which emit vacancies during the ageing. So, the annihilation of vacancies proceeds gradually, implying a gradual increase of the activation energy for silicon precipitation until in the end stage of the precipitation process the activation energy reaches a value corresponding to the thermal equilibrium vacancy concentration.

Since silicon as precipitated has a much larger atomic volume than as dissolved, silicon precipitation provoked stresses in the Al matrix. These stresses relaxed during precipitation at the ageing temperatures applied (400-500 K). For the LQ AlSi alloys, this relaxation process occurred more or less in line with the precipitation of silicon, but in the SQ AlSi alloys the relaxation could not catch up with the precipitation and therefore this relaxation could be studied separately. Kinetic analysis indicated dislocation climb as the process governing relaxation in SQ AlSi alloys.

On cooling after ageing *macrostrains* developed both in SQ alloys and in LQ alloys, due to difference in thermal shrinkage between the Al matrix and the silicon particles. These macrostrains could be described using the theory presented in Chapter III.

Finally, the kinetics of the precipitation in LQ AlMg alloys were studied utilizing line shift and line broadening data (Chapter IV). At the ageing temperatures between 400 and 500 K it was found that the precipitation process led to β '-phase formation. It was deduced from microscopical and diffractional analysis that the β '-phase precipitation proceeds in a non-uniform manner: differences in the kinetics of grain-boundary precipitation and precipitation in the bulk of the grains imply the development of distinct compositional differences between regions of considerable extent. The activation energy for β '-phase precipitation is smaller than that for the diffusion of Mg in Al, which hints at an increased (excess) vacancy concentration. As with AlSi alloys, on liquid quenching the excess vacancies collapse into loops, which on ageing emit vacancies assisting the β ' precipitation. The kinetics of β ' precipitation are governed by the growth of the precipitate particles.

VEROUDEREN VAN VLOEIBAAR-AFGESCHRIKTE EN VAST-AFGESCHRIKTE ALUMINIUM BASISLEGERINGEN; ANALYSE VAN ROOSTERPARAMETERVARIATIES

SAMENVATTING

Dit proefschrift behandelt verouderingsverschijnselen in binaire aluminiumlegeringen die snel afgeschrikt zijn vanaf een hoge temperatuur naar kamertemperatuur. Er is afgeschrikt vanaf temperaturen waarbij een vaste (matrix) fase een verhoogde vaste oplosbaarheid voor het opgeloste element in vergelijking met de oplosbaarheid bij kamertemperatuur bezit. Dit wordt vast afschrikken (Engels: solid quenching \equiv SQ) genoemd. In hoofdzaak is er afgeschrikt vanaf temperaturen waarbij de onderzochte legering vloeibaar was, wat vloeibaar afschrikken (Engels: liquid quenching \equiv LQ) genoemd wordt. In beide gevallen wordt na afschrikken een oververzadigde Al-matrix verkregen.

Vloeibaar afschrikken kan vaste legeringen met speciale eigenschappen opleveren: (i) vrij grote hoeveelheden opgeloste legeringselementen en vacatures in de Al-matrix, en (ii) een zeer kleine korrelgrootte (zie Hoofdstuk I van dit proefschrift). In dit onderzoek zijn de precipitatieverschijnselen tijdens het verouderen na vast èn vloeibaar afschrikken bij temperaturen tussen 400 en 500 K bestudeerd.

De bestudeerde legeringen zijn AlSi en AlMg. De keuze van Si en Mg als legeringselementen maakte het bestuderen van twee principieel verschillende precipitatiemechanismen mogelijk. In afgeschrikte AlSi legeringen is de precipiterende fase de evenwichtsfase (Si), terwijl in afgeschrikte AlMg legeringen de precipitatie van magnesium via een proces van verschillende stadia verloopt: Guinier-Preston (GP) zones/clusters \rightarrow intermediaire β '-precipitaten \rightarrow evenwicht β -precipitaten.

In Hoofdstuk II wordt een structurele karakterisering van de LQ AlSi en LQ AlMg legeringen gepresenteerd. Vloeibaar afschrikken werd uitgevoerd door spingieten: een gesmolten legering wordt in een dunne straal op een snel draaiend koperen wiel gegoten. Men krijgt linten met als typische afmetingen: een breedte van ongeveer 2 mm en een dikte van ongeveer 50 µm. Deze kristallijne linten vertonen een lagenstructuur: een bovenlaag (equiaxiaal), een middellaag (kolornnair) en een microkristallijne laag aan de wielzijde. Deze lagenstructuur is gerelateerd met de stolgeschiedenis van de linten. De textuur van de lintkristallieten en de microrekken hangen af van de betrokken laag. De linten vertonen zeer kleine korrelgrootten en bezitten een overschot aan vacatures. De concentratie van de (ingevroren) overschotvacatures werd geschat uit de plotselinge stijging van de Al-matrix roosterparameter na een korte-duur gloeibehandeling door deze stijging toe te schrijven aan annihilatie van (overschot)-vacatures.

Door een toepassing van Eshelby's theorie over elastische effecten door puntfouten in een eindig medium bleek (Hoofdstuk III) dat de *macrovervormingen* afgeleid uit verschuivingen van de röntgendiffractielijnverschuivingen evenredig zijn met een lineaire mispassingsparameter, die de misfit tussen de matrix en de gedispergeerde fase beschrijft, en de volumefractie van die gedispergeerde fase. De *microvervormingen* veroorzaakt door de volumemispassing bleken evenredig te zijn met dezelfde mispassingsparameter en met de *wortel* van de volumefractie van de gedispergeerde fase.

Via een interpretatie van de waargenomen veranderingen van de Al-matrix roosterparameter werd de kinetiek van de siliciumprecipitatie in LQ AlSi legeringen bestudeerd. De kinetiek van siliciumprecipitatie in SQ AlSi legeringen werd onderzocht zowel door meting van het "vrije volume" in deze legeringen met positronannihilatie als via de bepaling van de Al-matrix roosterparameter (Hoofdstuk IV). Uit een vergelijking van de resultaten van de LQ AlSi legeringen met die van de conventioneel geproduceerde SQ AlSi legeringen volgde, dat de siliciumprecipitatie in de LQ legeringen sneller verliep dan in de SQ legeringen en dat de activeringsenergie voor siliciumprecipitatie in LQ AlSi legeringen kleiner was dan die in SQ AlSi legeringen. De activeringsenergie voor precipitatie kan opgevat worden als de som van de vormings- en de migratie-energie van een vacature in aluminium (in een eerste-orde benadering), aangezien siliciumprecipitatie verloopt via het vacaturemechanisme. Daarom wordt in Hoofdstuk IV geconcludeerd dat SQ AlSi legeringen een lagere vacatureconcentratie hebben dan LQ AlSi legeringen. Verder wordt opgemerkt dat tijdens en juist na het afschrikken overschotvacatures condenseren in zgn. vacatureloops die tijdens het verouderen vacatures uitzenden. Dus wordt de

annihilatie van vacatures opgevat als een geleidelijk verlopend proces, implicerend een geleidelijke toeneming van de activeringsenergie voor siliciumprecipitatie totdat in een eindstadium van het precipitatieproces een waarde bereikt wordt overeenkomend met de thermische evenwichtsconcentratie van vacatures.

Doordat geprecipiteerd silicium een veel groter atomair volume heeft dan opgelost silicium, roept siliciumprecipitatie spanningen op in de Al-matrix. Deze spanningen relaxeren tijdens de precipitatie bij de toegepaste veroudertemperaturen (400-500 K). Voor de LQ AlSi legeringen verloopt dit relaxatieproces min of meer in lijn met de siliciumprecipitatie, maar in de SQ AlSi legeringen verloopt de relaxatie vertraagd ten opzichte van de precipitatie en daarom kan deze relaxatie afzonderlijk bestudeerd worden. Een kinetische analyse wees op het klimmen van dislocaties als het snelheidsbepalende proces voor relaxatie in SQ AlSi legeringen.

Tijdens het afkoelen na het verouderen ontwikkelen zich *macrovervormingen* zowel in de SQ als in de LQ legeringen door een verschil in thermische krimp tussen de Al-matrix en de siliciumdeeljes. Deze macrovervormingen zijn beschreven met de theorie uit Hoofdstuk III.

Tenslotte werd de precipitatiekinetiek in LQ AlMg legeringen bestudeerd door gebruik te maken van gegevens over röntgendiffractielijnverschuiving en -verbreding (Hoofdstuk IV). Bij verouderingstemperaturen tussen 400 en 500 K bleek, dat het precipitatieproces leidt tot de vorming van β '-fase. Uit optische microscopie en röntgendiffractie bleek dat de precipitatie van β '-fase op non-uniforme wijze verloopt: verschillen tussen de kinetiek van korrelgrensprecipitatie en de kinetiek van precipitatie in de bulk van de korrel impliceren de ontwikkeling van bepaalde samenstellingsverschillen tussen gebieden van een behoorlijke uitgestrektheid. De activeringsenergie voor β '-precipitatie is kleiner dan die voor de Mg-diffusie in aluminium, wat wijst op een verhoogde vacatureconcentratie. Zoals bij de AlSi legeringen, condenseren tijdens en 96 juist na het afschrikken de overschotvacatures in zgn. vacatureloops, die bij het verouderen vacatures uitzenden die de β '-precipitatie vergemakkelijken. Het voorgaande suggereert sterk dat de kinetiek van de β '-precipitatie beheerst wordt door de groei van precipitaatdeeltjes.

LE VIEILLISSEMENT DES ALLIAGES BINAIRES DE L'ALUMINIUM TREMPÉS DE L'ÉTAT LIQUIDE ET DE L'ÉTAT SOLIDE; UNE ANALYSE DES VARIATIONS DU PARAMÈTRE DU RESEAU

RÉSUMÉ

Les phénomènes du vieillissement dans les alliages binaires de l'aluminium trempés rapidement d'une haute température vers l'ambiante sont étudiés dans cette thèse. Les trempes sont effectuées depuis une température où les alliages d'aluminium sont liquides: la trempe liquide (en Anglais: Liquid Quenching \equiv LQ) et depuis une température où les alliages concernés sont solides et ils ont une phase avec une solubilité augmentée pour l'élement binaire (en comparaison avec la solubilité à l'ambiante). Cette dernière trempe est nommée la trempe solide (en Anglais: Solid Quenching \equiv SQ). Dans ces deux cas on obtient toujours une matrice sursaturée d'atomes de l'élement d'alliage.

La trempe de liquide donne des alliages solides avec des propriétés spéciales: (i) des quantités de l'élement d'alliage en solution solide relativement grandes et également un assez grand nombre de lacunes, (ii) une très petite taille des grains de l'Al-matrice (Chapitre I de cette thèse). Les phénomènes de précipitation pendant le vieillissement aux températures entre 400 et 500 K après le trempes liquide et solide sont étudiées dans ce travail.

Les alliages étudiés sont AlSi et AlMg. Ces systèmes rendaient possible la recherche de deux méchanismes fondamentalement differents. Dans les alliages AlSi trempés, la phase précipitante est la phase d'équilibre (Si), alors que dans les alliages AlMg trempés la précipitation du magnésium se déroule en plusieurs étappes: apparition des zones Guinier-Preston (GP) \rightarrow formation de précipités intermediaires $\beta' \rightarrow$ formation de précipités d'équilibre β .

Le Chapitre II contient une caractérisation structurale des alliages LQ AlSi et LQ AlMg. La trempe liquide fut effectuée par la filature en fusion (en Anglais: melt-spinning): l'alliage en fusion coule sur une roue de cuivre tournant très vite. Cette technique permet d'obtenir des rubans avec des dimensions caractéristiques suivantes: une largeur d'environ 2 mm et un épaisseur d'environ 50 μ m. Les rubans cristallins obtenus montrent une structure en couche: une couche supérieure avec des cristaux equiaxiales, une couche centrale avec des cristaux en forme aux colonnes et une couche de base microcrystalline (du coté de la roue). Cette structure en couche est reliée à l'histoire de la solidification du ruban. La texture des cristaux du ruban et les élongations à l'échelle du réseau dependent de la couche concernée. Les rubans montrent une très petite taille de grains et ils présentent un excès de lacunes. La concentration de ces lacunes est estimée à partir de l'augmentation soudaine du paramètre de l'Al-matrice qui se passe pendant un vieillissement (très courte) à une temperature élevée. Cette augmentation est attribuée à l'annihilation des lacunes en excès.

En appliquant la théorie d'Eshelby sur des effets élastiques aux défauts ponctuels dans une matière finie, il s'est trouvé (Chapitre III) que les élongations à l'échelle de l'échantillon (nommées: les macro-élongations) sont proportionelles à deux paramètres: (i) la paramètre linéaire ε qui répresente la différence des dimensions entre la phase dispersée et les trous dans la matrice qui lui correspondent, et (ii) la fraction en volume de cette phase dispersée (les macro-élongations sont déduites du déplacement des profils obtenus par la diffraction des rayons X). Les élongations à l'échelle du réseau (nommés: les micro-élongations) sont proportionelles au même paramètre ε et à la *racine carrée* de la fraction en volume de la phase dispersée.

En interprétant les changements du paramètre de matrice, la cinétique de la précipitation du silicium dans les alliages LQ AlSi à été étudiée. La cinétique de la précipitation du silicium dans les alliages SO AlSi a été étudié par l'application de l'annihilation des positrons et la détermination du paramètre de matrice (Chapitre IV). En comparant les résultats obtenus pour les alliages SO AlSi et les alliages LQ AlSi, il est apparu que la précipitation du silicium dans les alliages LQ se passait plus vite que dans les alliages SQ et que l'énergie d'activation pour cette précipitation était plus petite pour les alliages LQ AlSi que pour les alliages SQ AlSi. Cette énergie d'activation peut être considirée (en première approximation) comme le total des énergies de formation et de migration des lacunes en aluminium, parce que la précipitation du silicium se passe via un méchanisme de lacune. On a donc conclu dans le Chapitre IV, que les alliages SQ AlSi possèdent une concentration de lacunes plus petite que les alliages LQ AlSi. En outre, on remarque que pendant et juste après la trempe, des lacunes en excès se condensent en boucles qui émettent des lacunes pendant le vieillissement à une température élevée. Ainsi, l'annihilation des lacunes est un processus graduel impliquant une augmentation graduelle de l'énergie d'activation pour la précipitation du silicium. A la fin de cette précipitation, cette énergie d'activation atteint la valeur correspondant à l'équilibre thermique.

Parce que le silicium précipité a un volume atomique plus grand que le silicium dissous dans la matrice, la Si-précipitation provoque des tensions dans l'Al-matrice. Ces tensions diminuent pendant la précipitation aux températures de vieillissement choisies (entre 400 et 500 K). Pour les alliages LQ AlSi cette relaxation se passe plus ou moins avec la même vitesse que la Si-précipitation, mais dans les alliages SQ AlSi cette relaxation est en retard par rapport à la précipitation du silicium. Dans ce dernier cas on peut étudier cette relaxation séparément. Une analyse cinétique a indiqué que le processus qui gouverne cette relaxation est la montée des dislocations.

Après le vieillissement aux températures élevées, lors du refroidissement, des *macro-élongations* se développent dans les alliages SQ et LQ AlSi, à cause de la différence de contraction thermique entre la matrice d'aluminium et les particles de silicium. Ces *macro-élongations* ont été décrites en appliquant la théorie présentée dans le Chapitre III.

Finalement, la cinétique de la précipitation dans les alliages LQ AlMg a été étudiée en appliquant les données déduites des deplacements et des élargissements des profils obtenus par la diffraction des rayons X (Chapitre IV). Aux températures de vieillissement entre 400 et 500 K il s'est trouvé que la précipitation mène à la formation d'une phase β '. On a déduit d'une analyse microscopique et d'une analyse des profils de la diffractions des rayons X que la phase β ' précipite suivant une mode non-uniforme: la cinétique de la précipitation le long des frontières de grain diffère de la cinétique de la précipitation au milieu des grains, impliquant le développement des certaines différences de la composition entre des régions d'une extension considerable. L'énergie d'activation pour la précipitation de la phase β ' dans les alliages LQ AlMg est plus petite que l'energie d'activation pour la diffusion du magnésium dans l'aluminium cequi indique une concentration élevée des lacunes (en excès). Pendant et juste après la trempe liquide, des lacunes (en excès) condensent en boucles qui émettent des lacunes pendant la vieillissement à une température élevée; ce sont ces lacunes qui aident la précipitation de la phase β ' est gouvernée par la croissance des précipités β '.

(Ce texte est écrit en coopération avec Dr. M.P. Leguen).

CURRICULUM VITAE

"Zo ik iets ben, ben ik Nederlander".

De verdediger van dit proefschrift werd in 1945 te Utrecht geboren. Hij voltooide in 1966 de opleiding aan de Gemeentelijke Hogere Technische School afdeling Metaalkunde te Utrecht. Hij trad 1 januari 1968 in dienst van het Laboratorium voor Metaalkunde van de toenmalige Technische Hogeschool te Delft. Zijn studie aan de Hogeschool voor metaalkundig ingenieur werd voltooid in 1981. Met ingang van 1 januari 1986 werd hij benoemd tot universitair docent bij de vakgroep Produktietechnologie van het Laboratorium voor Metaalkunde. In een samenwerking van de Sectie Thermische Verwerkingstechnologie onder leiding van prof.dr.ir. B.M. Korevaar en de Sectie Fysische Chemie van de Vaste Stof onder leiding van prof.dr.ir. E.J. Mittemeijer verrichtte hij onderzoek naar precipitatieverschijnselen in snel vanuit de vloeibare fase afgeschrikte binaire aluminiumlegeringen.

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