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Nucleation of the diamond phase in aluminium-solid solutions

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Precipitation was studied from fcc solid solutions with silicon, germanium, copper and magnesium. Of all these elements only silicon and germanium form diamond cubic (dc) precipitates in fcc Al. Nucleation of the dc structure is enhanced if both types of atom are dissolved in the fcc lattice. This is interpreted as due to atomic size effects in the pre-nucleation stage. There are two modes of interference of fourth elements with nucleation of the dc phase in Al + Si, Ge. The formation of the dc phase is hardly affected if the atoms (for example, copper) are rejected from the (Si, Ge)-rich clusters. If additional types of atom are attracted by silicon and/or germanium, dc nuclei are replaced by intermetallic compounds (for example Mg_2Si).

1 Introduction

The prerequisite for nucleation of the diamond cubic (dc) phase in aluminium is the solubility of suitable elements in the metallic fcc solid solution. Of the four elements, carbon, silicon, germanium and tin, that may have the dc structure, only silicon and germanium fulfil this requirement. The complete insolubility of the carbon atoms must be due to their small atomic size, and high tendency to form covalent bonds and graphite. Tin, owing to its large atomic size, also has no solubility in aluminium and forms the dc structure only at low temperatures ($\leqslant 13\,^{\circ}C$). The formation of the diamond structure is associated with a transformation from metallic to covalent bonding and, consequently, with a change from 12 to 4 nearest neighbours.

There have been numerous studies of the Al–Si and Al–Ge binary systems and these have been recently reviewed [1]. The results may be summarized as follows: there is a fixed, $(100)_{dc} \| (100)_{fcc}$; $[100]_{dc} \| [100]_{fcc}$, orientation relationship between the fcc and dc lattices; however, there exists a wide variety of habit planes and morphologies of the dc particles. The transition to covalent bonding is associated with a reduced atomic distance, but an increased atomic volume [2]. Therefore, vacancies in the binary fcc alloys play an essential role in nucleation of the dc structure. Vacancies can affect nucleation in two ways; they can increase the diffusion rate of solute atoms at moderate temperatures and thus increase the growth rate of solute clusters, and they may become a part of the nucleus and thus reduce the barrier to precipitation. The binary alloys have an undesirable "quench sensitivity", i.e. nucleation of the dc particles is very sensitive to changes in the solution heat-treatment temperature, the quench rate, and the temperature to which the alloy is quenched before ageing [3].

2. Al + (Si, Ge) alloys

It has recently been pointed out that "successful" precipitation hardening aluminium alloys contain second and third alloying elements which are larger and smaller than the aluminium [4]. Fulfilment of this rule implies a decrease in the strain energy in the lattice, a reduction in the energy barrier and a decrease in the critical size for nucleation and, consequently, an increase in the age-hardening potential of the alloy. The validity of the "rule" was recently confirmed for the combination of the elements silicon and germanium (Table I) [2, 5, 6]. Fig. 1 shows the microstructure of a binary (silicon or germanium) and a ternary (Si + Ge) alloy with the same atomic concentrations of dc-forming atoms after an identical heat treatment. The density of the nuclei in the ternary alloy is increased by one order of magnitude and their shape is much more equiaxed compared with nuclei in the binary alloys. An interpretation of this phenomenon is given in Fig. 2 which is based on the assumption that the dc-structure forms from small (Si, Ge)-rich clusters in the fcc lattice. The growth of pre-nuclei clusters is limited by accumulation of coherency stresses in Al–Si and Al–Ge alloys. Vacancies are necessary in the binary alloys to minimize these stresses and allow the nuclei to grow to the critical size for precipitation of the dc phase. However, in the ternary alloys the stresses are almost completely cancelled by the combination of silicon and germanium which allows a much larger number of nuclei to grow to the critical size ($d_c \approx 2$–3 nm) for the fcc (Si, Ge)-rich clusters to collapse into the dc structure.

$$d_c \geqslant (\gamma_{fcc/dc}/g_{fcc} - g_{dc})C \qquad (1)$$

where $\gamma_{fcc/dc}$ is the interfacial energy.

A high concentration of vacancies is not required for formation of the zones of the ternary Al–Si–Ge

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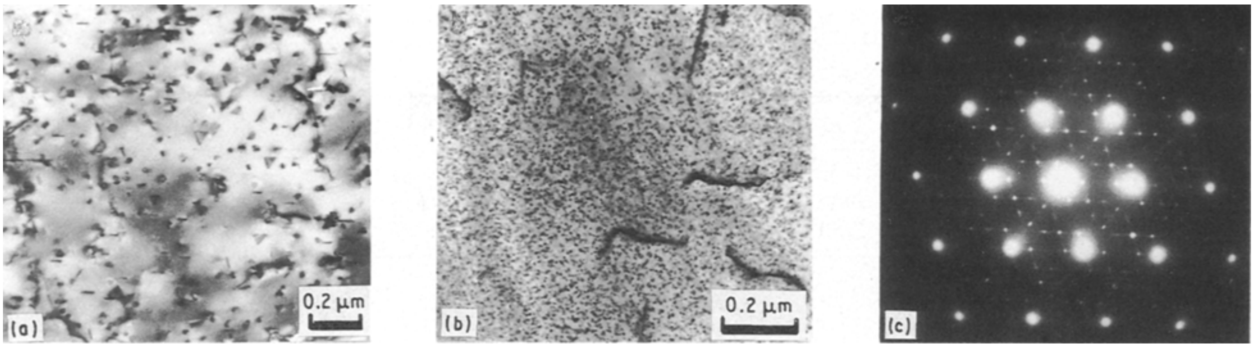

Figure 1 f c c Al + d c structure in alloys homogenized and aged at 160 °C, 10 h (chemical composition in at%). (a) Al + 1 Si, transmission electron micrograph. (b) Al + 1/2 Si + 1/2 Ge, transmission electron micrograph. (c) Al + 1/2 Si + 1/2 Ge, selected-area diffraction pattern.

TABLE I Metallic atomic diameters of alloying elements dissolved in f c c Al (d_{Al} = 0.286) and ternary combinations of larger x and smaller y atoms

Large atoms x	d_x (nm)	$\varepsilon_x = \frac{d_x - d_{Al}}{d_{Al}}$ (%)	Small atoms y	d_y (nm)	$\varepsilon_y = \frac{d_y - d_{Al}}{d_{Al}}$ (%)	$\lvert\varepsilon_x + \varepsilon_y\rvert$ (%)
Li	0.304	+ 6	Cu	0.256	− 10	4
Mg	0.320	+ 12	Si	0.278	− 3	9
Mg	0.320	+ 12	Cu	0.256	− 10	2
Mg	0.320	+ 12	Zn	0.266	− 7	5
Ge	0.292	+ 2.1	Si	0.278	− 2.7	0.6

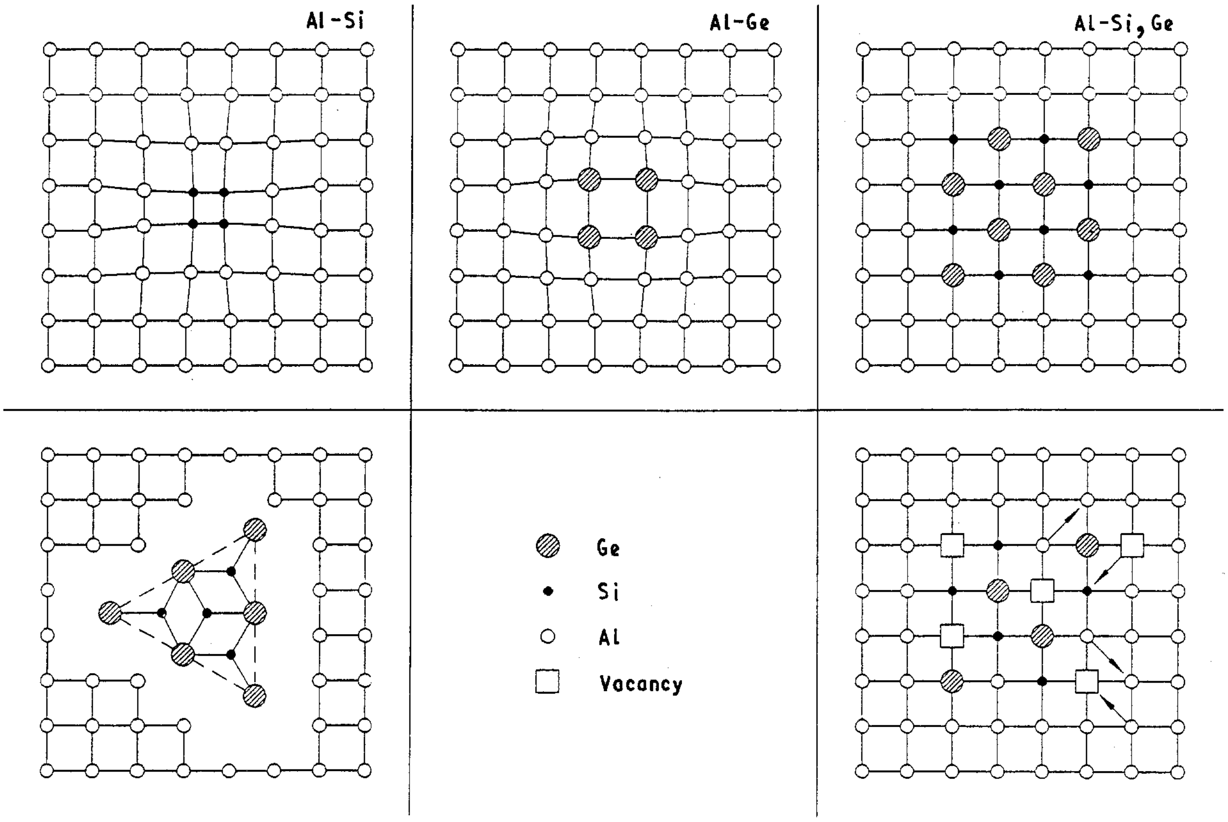

Figure 2 Schematic drawing of the nucleation of d c structure from clustered f c c states. Cancellation of misfit stresses (see Tables I and II) permits extended growth to critical size d_c (Equation 1).

alloys and pre-nucleation is affected very little by vacancy sinks, such as dislocations and grain boundaries, and by the quenching treatment [2]. Because silicon and germanium form a continuous d c solid solution, this phase should nucleate from f c c Al(Si, Ge) solid solutions. Although there are indications for size-induced ordering of the d c phase, this is neither relevant for the discussion of the nucleation

TABLE II Crystallographic data of f c c Al-base solid solutions and diamond cubic structure

	Covalent (d c)			metallic (f c c)				f c c → d c
	a(nm)	b(nm)	$V\,10^{-3}\,\mathrm{nm}^3$	a(nm)	b(nm)	$V\,10^{-3}\,\mathrm{nm}^3$	$\varepsilon_{\mathrm{AlX}}$	$\Delta V_{\mathrm{m}\rightarrow\mathrm{c}}$
Al	–	–	–	0.405	0.286	16.59	–	–
Si	0.542	0.235	19.87	0.393	0.278	15.16	– 3%	+ 19%
Ge	0.565	0.245	22.50	0.413	0.292	17.55	+ 2%	+ 21.5%

a: lattice parameters
b: smallest atomic distance
V: volume per atom
$\varepsilon_{\mathrm{AlX}}$: relative difference of atomic diameters
$V_{\mathrm{m}\rightarrow\mathrm{c}}$: relative change of atomic volume for transition metallic → covalent

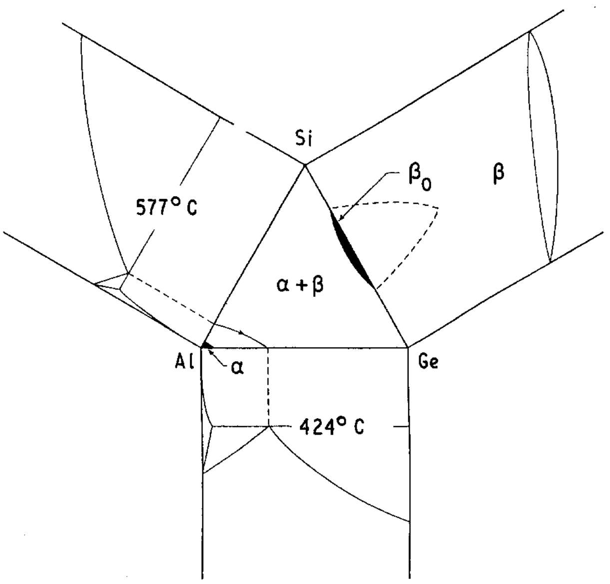

Figure 3 Phase diagram Al–Si–Ge. Silicon and germanium form solid solutions which may show size-induced order at low temperatures.

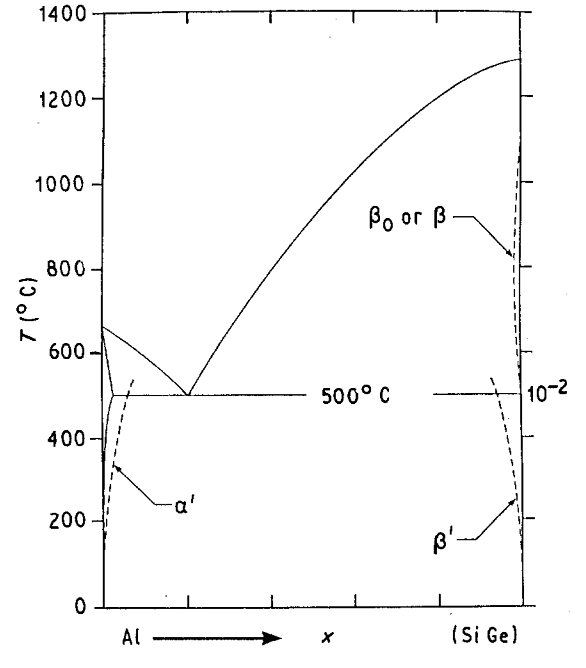

Figure 4 Quasi-binary section $\mathrm{Al}_{(1-x)}\mathrm{Si}_{0.5x}\mathrm{Ge}_{0.5x}$ (---) metastable f c c coherent equilibrium.

mechanism, the magnitude of g_{dc} (Equation 1), nor for precipitation hardening (Figs 3 and 4).

3. Al + (Si, Ge, X) alloys

Alloying elements that do not form the d c structure may either participate in the nucleation of intermetallic compounds with silicon or germanium, e.g. magnesium (Figs 5, 6), or they may have a little or no reactivity with these elements, e.g. copper (Figs 7, 8). Even small additions of magnesium (>0.2 wt% Mg) result in the formation of semi-coherent plates of $\mathrm{Mg_2(Si, Ge)}$ and a coarse of distribution of the d c particles. Evidently, the formation of $\mathrm{Mg_2(Si, Ge)}$ occurs prior to the clusters reaching the critical (Si + Ge) concentration (or d_c) for the transition from metallic to covalent. This reduces the number density of nuclei and results in a coarse distribution of the d c particles.

Copper is most likely rejected from the (Si, Ge) clusters, as is aluminium, Fig. 8. This has been suggested earlier for Al–(Si, Cu) alloys [7]. In Al–(Si, Ge, Cu)

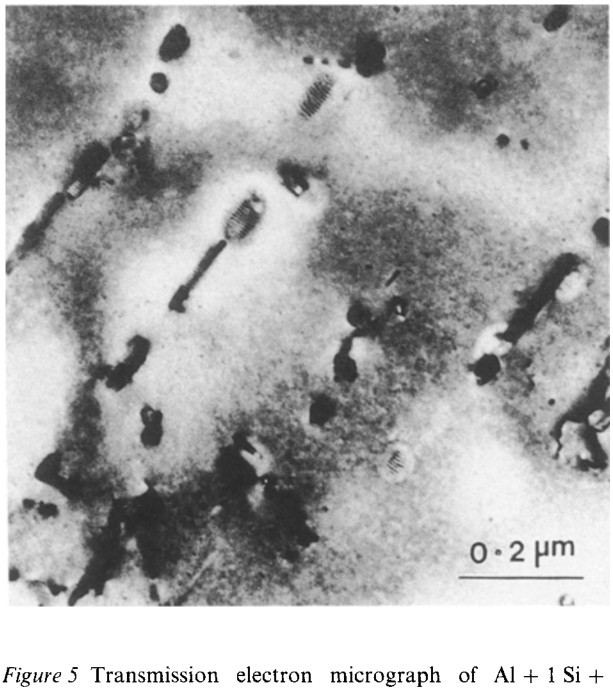

Figure 5 Transmission electron micrograph of Al + 1 Si + 1 Ge + 0.6 Mg. Homogeneous formation of d c has been replaced by $\mathrm{Mg_2(Si, Ge)}$. d c forms very coarsely at defects.

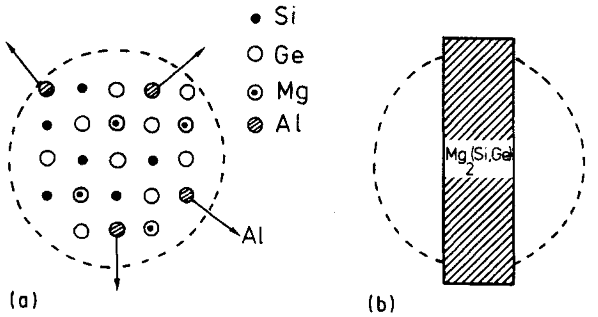

Figure 6 Effect of magnesium addition on fcc clusters and nucleation of compound; schematic representation.

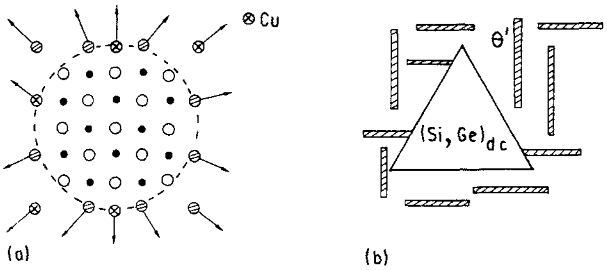

Figure 8 Schematic illustration of the role of copper addition during growth of Si, Ge-rich clusters and the nucleation of Θ' at fcc/dc interfaces.

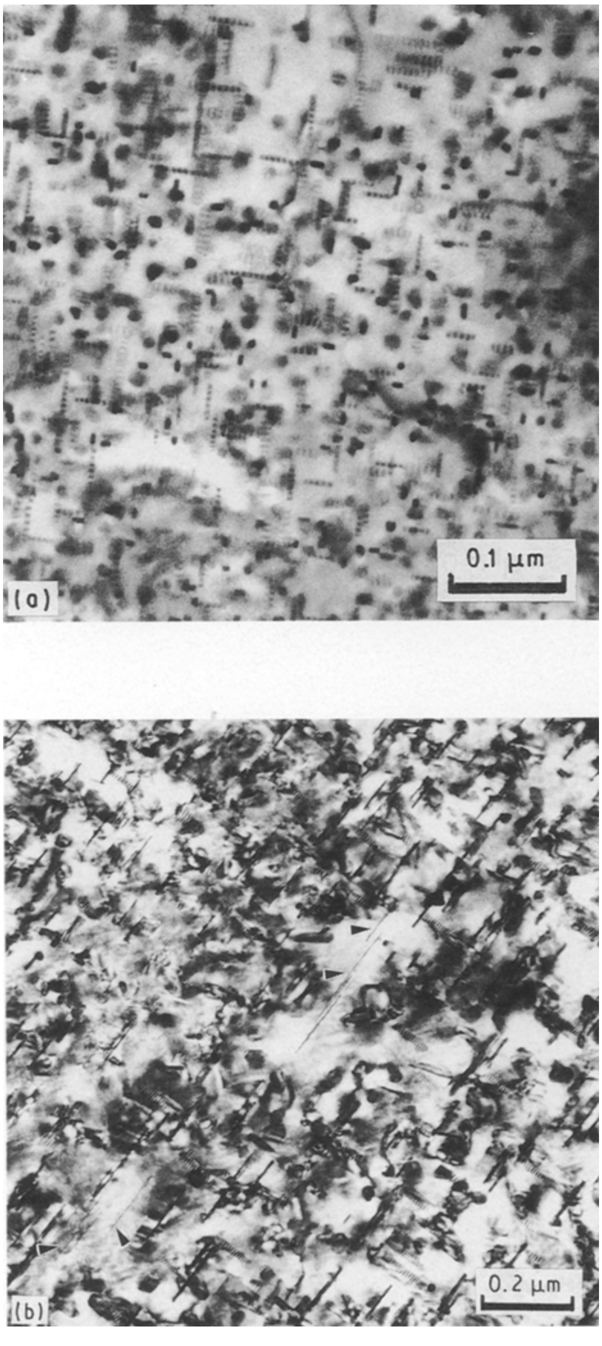

Figure 7 Transmission electron micrographs of (a) Al + 1 Si + 1 Ge + 1 Cu, nucleation of dc, hardly affected by copper addition, and (b) Al + 1 Si + 1 Ge + 1.5 Cu, nucleation of dc structure followed by Θ'-phase (Al_2Cu) partially at fcc/dc interfaces (Equation 2).

alloys the nucleation of the dc phase is hardly affected by the copper additions. However, the particles in this system are more equiaxed than those in the binary and ternary alloys. It appears that as the copper atoms are rejected they become associated with the dc/fcc interface, thereby decreasing interfacial energy, $\gamma_{fcc/dc}$ (Equations 1 and 2) as well as the strain energy associated with the volume increase of the fcc to dc transformation, and stabilize the dc particles.

In the Al(Si, Ge, Cu) alloys, the dc particle/matrix interface sometimes acts as a nucleation site for $\Theta'(Al_2Cu)$ particles [8–10], at higher copper contents (>2 wt%), or after prolonged growth of the dc particles (Equation 2, Figs 7b, 8)

$$d_c \geqslant (\gamma_{fcc/\Theta'} - \gamma_{fcc/dc}/g_{fcc} - g_{\Theta'})C \qquad (2)$$

Θ' particles also form homogeneously in the copper-enriched aluminium matrix ($g_{\Theta'}$ is the free enthalpy of the Θ-Al_2 ln-phase: unit μm^{-3}).

4. Conclusion

Several models are proposed for the transformation of clusters of germanium and silicon solute additions into precipitates with the diamond cubic structure. In binary Al–Si and Al–Ge alloys their growth is limited by misfit stresses which must be compensated for by vacancies. Additions of Ge + Si cancel the misfit distortions in the metallic solution and lead to the formation of a very high number of nuclei without the aid of vacancies. Even small additions of magnesium to the ternary Al–Si–Ge alloy inhibit the formation of (Si, Ge)-rich clusters and increase the critical particle size d_c (Equation 1) for the metallic fcc to diamond cubic transformation. Magnesium competes for silicon and germanium and nucleation of dc particles is replaced by an $Mg_2(Si, Ge)$ compound. The addition of copper hardly affects nucleation of the dc phase. However, the dc/fcc interface may subsequently act as a nucleation site for the $\Theta'(Al_2Cu)$ phase.

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