

Behind structure and relation of precipitates in Al-Mg-Si and related alloys

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Investigations of precipitates in a variety of ternary Al-Mg-Si alloys by a combination of methods, such as transmission electron microscopy and first principles calculations allowed a number of the respective structures to be resolved, making possible detailed comparisons. All precipitate structures are related through a similar diamond element arrangement; which itself can be related to diamond silicon, as well as to its respective orientation in the Al. The network has been very useful for structural details in precipitates in Al-Mg-Si-(Cu) and Al-Mg-Ge. For all precipitates no matter apparent disorder or defects, their diamond element arrangement is usually perfectly ordered, in most cases with a hexagonal or near hexagonal cell $a \sim b \sim 4 \text{ \AA}$, $c = n \cdot 4.05 \text{ \AA}$ ($n \in \mathbb{Z}$). The precipitates may thus be considered as variations over this widely spaced, stable diamond element backbone within the aluminum. The network connects with aluminum through specific directions and habit planes, which can explain all the orientation relations and habit planes of the precipitates. One may therefore see the different precipitates as mere variations of a generic precipitate, the network. We show relations on the network, like sub-cell groups containing similarly decorations of atoms that can be found in most of the precipitates, ranging from Si-rich to Mg-rich precipitates.

Keywords: Al-Mg-Si, Precipitates, Silicon Network, TEM

1. The Si-network

It has recently been demonstrated, for alloys of the systems Al-Mg-Si, Al-Mg-Si-Cu, as well as in similar alloys where Ge replaces Si fully or partially, that within the structures of all the meta-stable precipitates, there exists a spacious diamond element network [1-3], called 'Si network' from here on. The meta-stable precipitates are fine needles or laths along $\langle 100 \rangle$ Al directions, along which there is full coherence. Fig. 1 shows this in one alloy, optimized for β'' [4]. Long, weak, double contrasts (as in the upper left corner) are β'' -needles along $\langle 100 \rangle$ and $\langle 010 \rangle$. In the $\langle 001 \rangle$ -viewing direction high contrast cross-sections can be seen, where dotted arrows indicate the c-axis' alignment with type $\langle 310 \rangle$ Al. Both Al and the Si-network have two planes per period 4.05 \AA . This distance prevents Si being in two neighbour planes in one column. I.e. in Fig.1 (left) Si-atoms take either white or black positions in a column. The Si-Si projected distances (columns) are mostly near hexagonally arranged, with separation 4.05 \AA . Si has not been observed between such columns in any precipitate. Figure 2a shows schematically how the network in a general precipitate aligns with Al.

The Si-network has been of good help for understanding the crystal structures of the precipitates: It soon became clear that all precipitate 2D unit cells fit almost perfectly on the projected hexagonally arranged Si-nodes [1-3]. This is shown in Figure 2b. Most precipitates contain only two hex Si planes. No Si atoms fall between network nodes, and since each Si-plane is semi-occupied, the number of Si atoms and the approximate Si projected coordinates in a precipitate unit cell may be determined. However, the height of the Si-atoms may only be determined when the space group symmetry is analysed, which must be based on electron diffraction patterns. The search for composition and total number of atoms in a precipitate unit cell can be aided by several means:

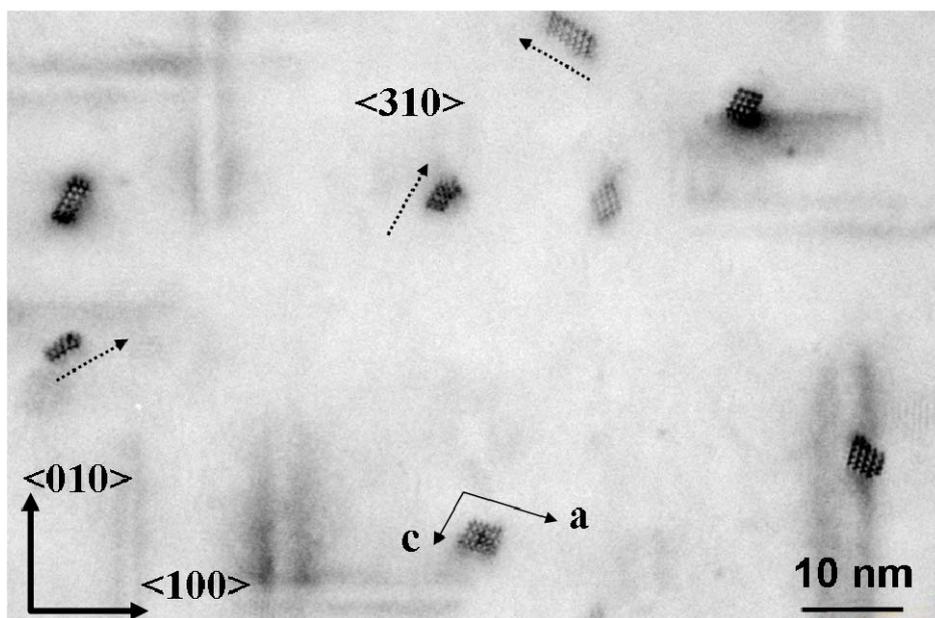


Fig. 1. Needle-shaped β'' -precipitates along the three Al $\langle 100 \rangle$ directions, which coincides with the b-axis of the β'' -phase. The needle cross-sections show how the a-axis of the precipitates aligns with $\langle 310 \rangle$ Al directions (dotted arrows), which indicates a specific rotation of the hexagonal network planes around the hexagonal axis. The c-axis of the precipitates aligns with $\langle 230 \rangle$.

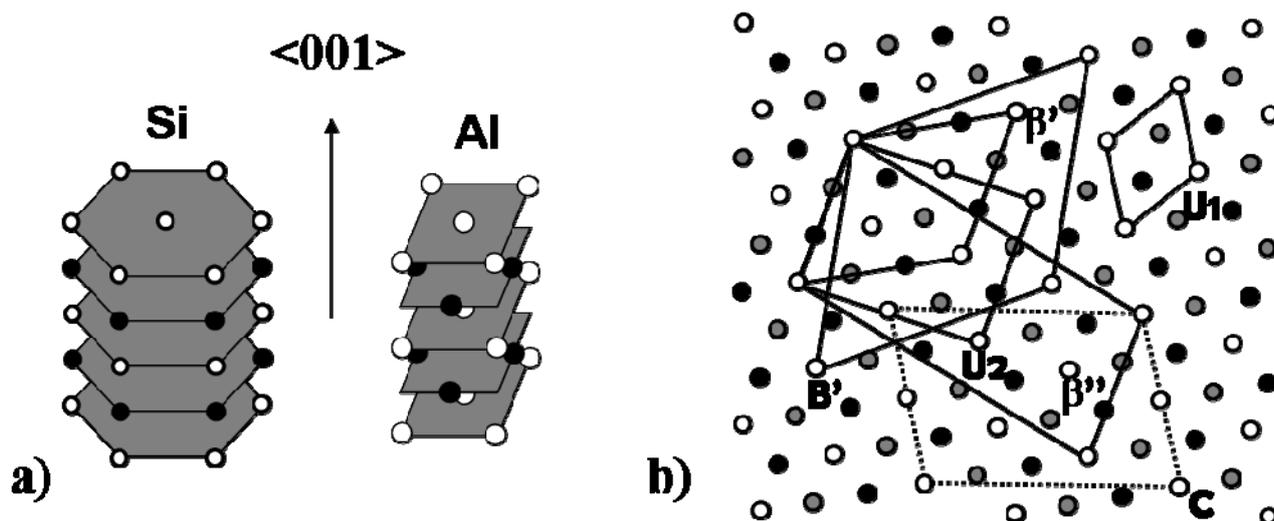


Fig. 2. a) The internal Si-network in the precipitates. Atom columns along $\langle 001 \rangle$ correspond to white disks in b), but only every second (black or white) column position is occupied. The other atoms fill in spaces between the Si network columns, and projects to positions near the grey, black disks in b). b) Projection along the $\langle 111 \rangle$ axis in diamond Si, with the A, B, and C layers as white, grey, and black is like a projection of a precipitate along the hex network axis. Precipitate 2D unit cells fit almost perfectly on the projected hexagonally arranged Si-nodes. The C and U1 phases have networks with different orientations in the aluminium [5-7].

i) The normal atomic (projected) distances can help to determine Si-heights and other atoms from extracted coordinates on HRTEM images, exit waves, or HAADF images. ii) Approximate composition of the precipitate may be determined by methods such as EDS and atom probe tomography, and the formula scaled by the known Si contents. iii) The commonly highly coherent interface between the matrix and the precipitate normally gives just two possibilities of the heights of Al-atoms. This narrows down the possibilities regarding an atom's height, real distance from interface and from Si-atoms. iv) The suggested packing may also be of help: In Table 1 is shown the composition, atomic packing in the unit cell and number of Si atoms per volume in some of the precipitates. We find in general the atom packing varies between 0.70 and 0.66 for the most coherent phases, reaching lower values in more incoherent phases like U1. Disregarding the equilibrium phase

β , the number of Si-atoms per volume varies little from Si-rich to Mg-rich phases, in spite of the crystallographic differences. This reflects the stability of the network in spite of composition and the difference in crystallography.

Table 1. Two parameters used in evaluating precipitate structures; packing, and number of Si atoms per unit volume.

Type	Formula	Packing fraction	#Si-atoms/vol. (\AA^{-3})	Remarks
β''	$\text{Mg}_5\text{Al}_2\text{Si}_4$	0.69	0.020	See references in Hastings et al [8]
β'	$\text{Mg}_{18}\text{Si}_{10}$	0.70	0.019	Vissers et al [9]
U2	MgAlSi	0.67	0.018	Andersen et al [10]
U1	MgAl_2Si_2	0.58	0.020	Andersen et al [7]
Q	$\text{Mg}_9\text{Al}_3\text{Si}_7\text{Cu}_2$	0.69	0.019	Wolverton et al [11]
β	Mg_2Si	0.64	0.016	

1.2 The Si network compared to the diamond phase

When the network is compared with diamond Si, a surprising set of analogies is brought to light: First, and as may be seen in Fig. 2b, a single hexagonal plane (white disks) of the network is similar to one $\{111\}$ Si plane: The inter-columnar distance of a single plane (A) in this 'hexagonal' projection is $a_{\text{Si}}/\sqrt{2} = 3.84 \text{ \AA}$, as compared to $\sim 4.05 \text{ \AA}$ in the network. Secondly, in an fcc structure two identical planes (B, C) stacked onto A, are laterally displaced, so that A,B and C atoms fall between the triangles of each other. The fcc archetype is usually defined by an ABC stacking. The projections of the three atom layers - or the positions of their non-intercepting atom columns - usually fit well with the ones corresponding to the precipitate structures. In fact, except for the β'' structure, the precipitate projected positions correspond better with a hexagonal than with a square arrangement. The latter might be expected because of the high coherency observed with the matrix. Even for β'' , a reasonable correlation with a hexagonal pattern can be found (Fig. 3). In general, we can say that Si atoms correspond with columns formed by one layer, say A, the other atoms are near the B and C columns. However, as shown in Fig. 3, for the chosen super-cell for β'' , we must instead use all three layers.

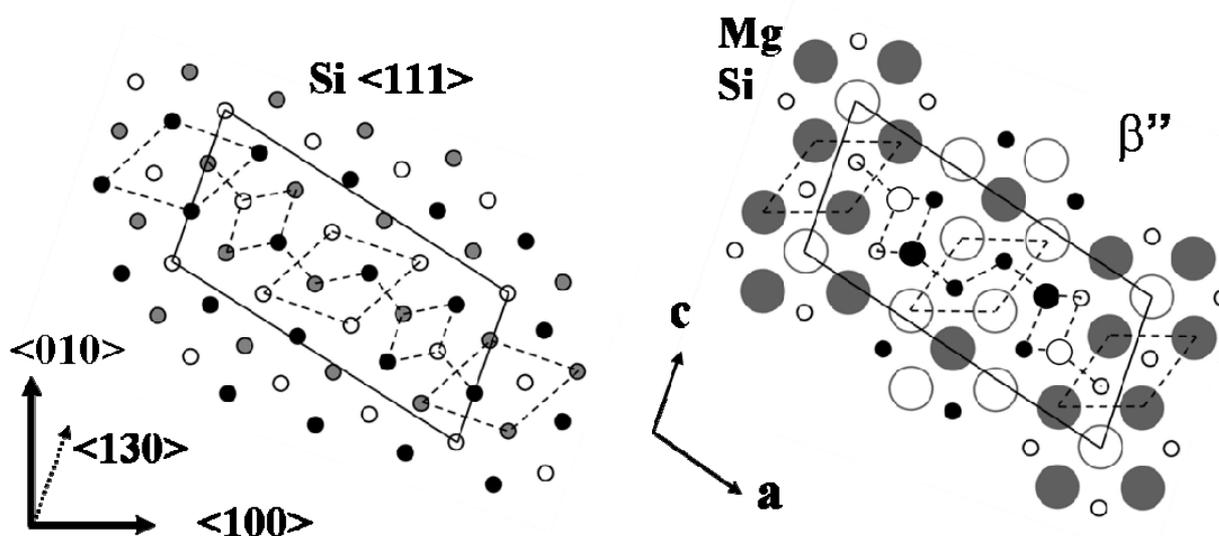


Fig. 3. Comparison between the β'' -phase (right) and one interpretation of a β'' super-cell found in a $\langle 111 \rangle$ Si projection, with a complex one-to-one correspondence between the atoms.

In the diamond structure, to each fcc position will correspond a pair of atoms. With the pair in 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, this means the stacking is double and may be described AA BB CC, so that in a pair planes lie directly above each other with separation $a_{\text{Si}}\sqrt{3}/4 = 2.35 \text{ \AA}$. At this point it may seem almost pointless to continue a detailed comparison with the precipitates structures. However, we have shown that in the case of U1 [], a 3D super-cell may be arrived at from diamond silicon, provided we switch the height of two planes. It is also interesting to note how the fluorite structure $\beta\text{-Mg}_2\text{Si}$, with $a = 6.4 \text{ \AA}$, compares with diamond Si: Replace silicon with Mg in the position $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. Add another Mg atom at $\frac{3}{4}\frac{3}{4}\frac{3}{4}$. Now the molecule is Mg_2Si instead of Si_2 . Expand the cell from 5.4 \AA to 6.4 \AA . This 'turns' Si into β . The correspondence between precipitates and the diamond Si structure does not end with this. By studying Si-particles in a binary Al-Si alloy and in Al-Mg-Si alloys (Figure 4 is an example), a major orientation of Si-particles in the aluminium was found to be [12]:

$$(110)\text{Si} \parallel (001)\text{Al}, [1\bar{1}\bar{1}]\text{Si} \parallel [010]\text{Al}, [1\bar{1}2]\text{Si} \parallel [100]\text{Al}. \quad (1)$$

As rotation matrix it is more useful: Multiply with Si-vectors and obtain corresponding Al-vectors;

$$R = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 & -1 & 2 \\ \sqrt{2} & -\sqrt{2} & -\sqrt{2} \\ \sqrt{3} & \sqrt{3} & 0 \end{pmatrix}. \quad (2)$$

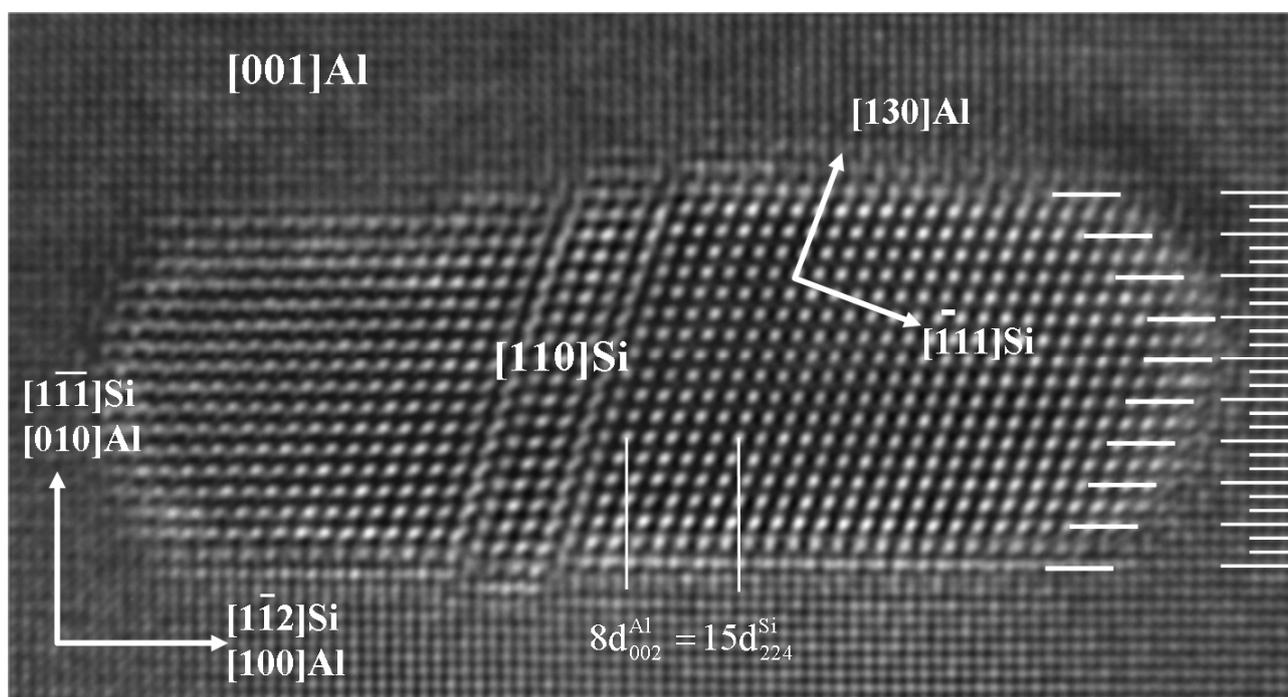


Figure 4. TEM image of a Si-particle with orientation in Al as given by Eq.1. The two $\{111\}$ Si planes with traces along $\langle 100 \rangle$ and $\langle 130 \rangle$ Al are oriented as the hexagonal Si-planes in the precipitates. There is coherency in several directions. The plane relation measured (given below the particle) indicates a 2.7% expansion in Al along $\langle 100 \rangle$. On the right hand side can be seen that $14d_{200}(\text{Al}) \sim 9d_{111}(\text{Si})$, meaning that in this direction very little strain should exist. Such particles give very little contribution to the material strength.

These relations show that the vectors $\langle 110 \rangle$ Si and $\langle 010 \rangle$ Al are parallel. The two $\langle 111 \rangle$ Si directions in the zone ($[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$) are parallel with Al $[010]$ and $[\frac{4}{\sqrt{2}}10]$. The latter is 1.04° from $[310]$. Thus, (010) and (310) planes in Al are nearly parallel with two Si $\{111\}$ planes. This is a striking result because it shows that the hexagonal planes in the diamond phase are stacked along the same direction in aluminium ($\langle 010 \rangle$), as for the hexagonal network. It is unlikely this is a coincidence. Most of the precipitate phases with a hexagonal Si arrangement in a $\{010\}$ Al plane have $\{310\}$ habit planes, unit cell parameter and coherency in $\langle 310 \rangle$ directions (see Fig. 1). In fact, the U1-phase 'uses' the second $\{111\}$ Si plane which is parallel with a $\{310\}$ Al plane, while all other precipitates adopt the $\{111\}$ Si \parallel $\{001\}$ Al pair. As an exception, the growth direction of U1 is not along this hexagonal axis, but rather along $\langle 110 \rangle$ Si. This means that U1 needles grow in the $\langle 001 \rangle$ Al directions, just as the rest of the precipitates. One may describe the arrangement of columns of the internal Si atoms of U1 in this projection as a deformed hexagonal network.

1.3 Precipitate common sub-units on the Si network and disorder

The similarity between the precipitates means that structural common sub-units may be expected. We find that units defined by the vertical zigzag Si-strings along $\langle 130 \rangle$ Al directions as shown in detail in Fig. 5, are closely connected. Here orientation in Al and the similarity with projected diamond silicon can be studied. Going from pure silicon to the Mg-rich β - Mg_2Si phase, we see that the general situation with chained cells of Si with two Mg or Al (or Si in the diamond phase) atoms between is a

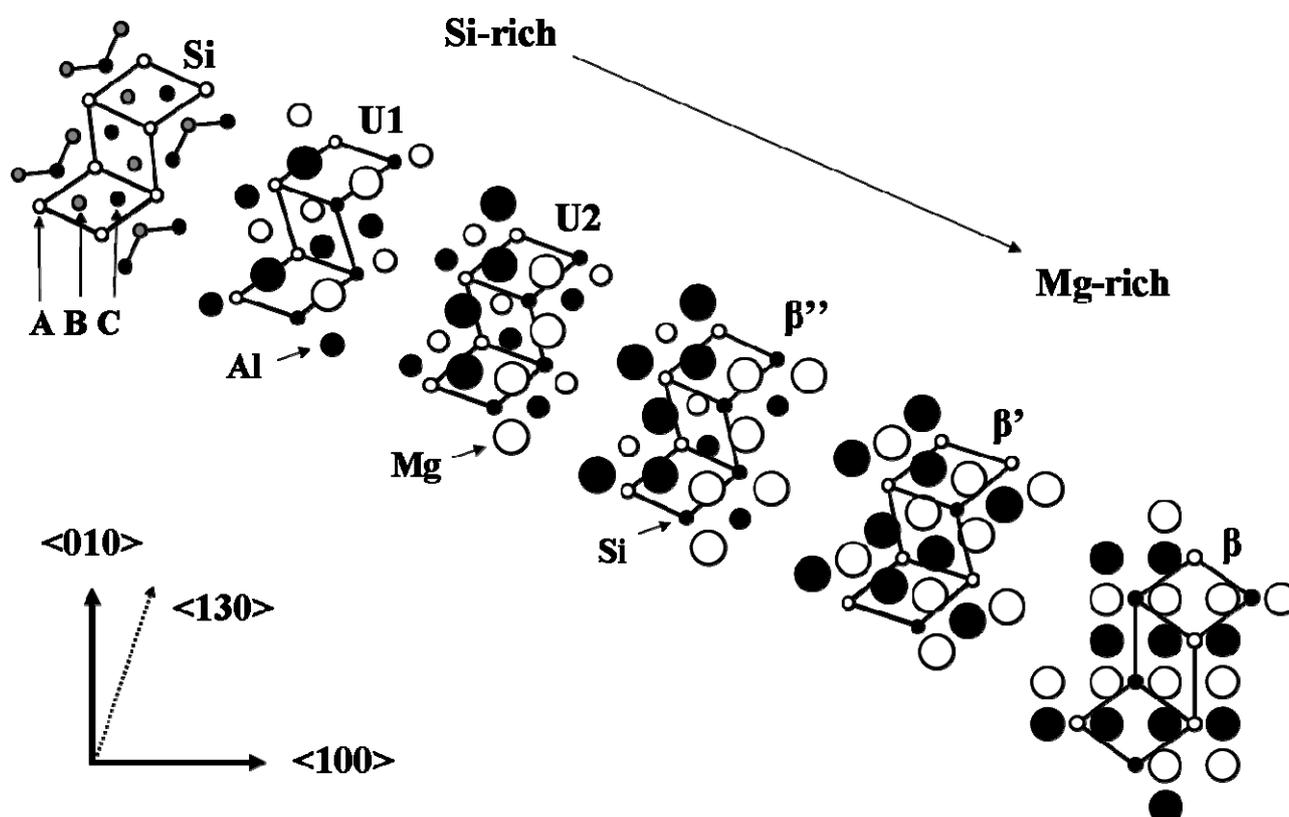


Fig. 5 Projected parts of the precipitate structures along the hexagonal Si-network axis, compared with $\langle 111 \rangle$ diamond silicon (upper left), correctly oriented in the aluminium. White/dark disks are atoms in neighbour planes in viewing direction. In Si projections are from the three different Si pairs A, B, C. Here one Si (111) layer (A) corresponds with Si network (solid lines) in the precipitates.

general situation. This merely restates what is said above, that the whereabouts of atoms within the Si cell (or atom column between the Si-columns) in the precipitate structures are of less importance than the network columns themselves. I.e. the existence of the precipitates shows that there exist a number of arrangements on the network with comparable or lower energy as compared with a disordered arrangement. This is strongly suggested also by experiments showing a high degree of disorder in the precipitates for some conditions, whereas the Si- network appears ordered and geometrically unaffected [13]. The fact that the diamond phase in binary Al-Si is intimately related to all the precipitates, strongly suggests that the initial ordering of Si in solid solution in Al-Si alloys that leads to precipitation of diamond Si, must be similar to the initial ordering of the nuclei that leads to the formation of the precipitates. A solute ordering of Si prior to the formation of Mg-containing clusters is therefore likely.

2. Experimental

The image in Fig. 1 is from the alloy designated A3 in [4], with composition Al - 0.52 Si - 0.58 Mg (wt %). The final ageing time at 175° C was 17 h. The heat-treatment and all experimental procedures may be found here [12]. The image was taken using a Philips CM30UT/FEG instrument, operated at 300 kV. The image in Fig. 4 is from a study of the alloy Al - 1.3 Si (at. %) [4], where additional information can be found.

3. Conclusions

The near hexagonal diamond network shown to exist in all precipitates in the Al-Mg-Si (Ge) and related alloy systems is a very useful concept relating to the understanding of precipitation, precipitates and their structures.

4. Acknowledgments

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