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A study on composition and crystal structure of dispersoids in AlMgSi alloys

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Mn bearing dispersoids play a very important role in recrystallization and solution-aging process in AlMgSi alloys. Plenty of research have been made on the effect of the disperoids on recrystallization and quenching sensitivity behaviour in these alloys. But study on the nature of these dispersoids is very limited. With an idea to understand the nature of these dispersoids and hence to control their size and distribution, this study was performed. It was found that in AlMgSi alloys, the size of the dispersoids is dependent on Mn/Fe ratio, the higher the Mn/Fe ratio, the smaller the size of the dispersoids. A crystal structure transformation with Mn/Fe ratio change was also found in these dispersoids. With higher Mn/Fe ratio, these disperoids have a simple cubic crystal structure while with lower Mn/Fe ratio they have a BCC structure. A critical Mn/Fe ratio for this change was found to be 1.6 in studied alloys. Results were explained with consideration of the originating local surroundings and heat treatments.

1. Introduction

Mn bearing dispersoids in AlMgSi alloys are introduced for grain refinement during recrystallization for their pinning effect on grain boundaries. While many studies have been performed on the effect of these dispersoids on microstructures, understanding of the nature of these dispersoids themselves are quite limited. In high purity AlMgSi alloys it is said that these dispersoids are ternary phase which can be described as $Al_{12}Mn_3Si$ [1]. Recently, in 6013 alloys, Donnadieu *et al.* [2] reported that these dispersoids may contain some iron with a Mn/Fe (in atomic ratio) ratio more than 3. Since iron virtually exists in all commercial alloys, it is clear that the dispersoids in AlMgSi alloys are quaternary phase which contain Al, Mn, Fe and Si. The size and density of these dispersoids are of big importance because the pinning effect depend on size and density. As suggested in [3] the pinning force of secondary phase on boundary per unit area, F/A, is proportional to $f\gamma/r$, where γ is the boundary energy, f and r are the dispersoid volume fraction and average size respectively. Therefore, with same volume fraction, the finer the dispersoids the higher the pining force. Generally Mn dispersoids were reported to have a size range of from 0.1 to 0.5 micrometer, but there are two features that we want to mention here:

1. Different author give different sizes. This imply that the size of dispersoids depends on more complex factors.

2. Most authors found a size range instead of a uniform size [2]. One exception is that Martin [1] reported a uniform size of 0.1×0.3 rod shape dispersoids in AlMgSi alloys with high purity.

No research has ever mentioned about the reason for the non-uniform size of these dispersoids. The original idea of present study is then to characterize these dispersoids by size, chemical composition and crystal structure. And try to find the correlation between these factors.

For the crystal structure of this quaternary phase, it is suggested as isomorphous to α-AlMnSi with a Pm3 space group [4] and α-AlFeSi with an Im3 space group [5]. The formula can be written as α-Al(Mn, Fe)Si [6]. The crystal structure could be determined from the ratio of Mn and Fe. But the critical ratio has not been decided yet [6, 7]. However, in an effort to find the effect of Mn induced ordering in this phase Donnadieu *et al.* [6] imply that this ratio may fall between 1 and 3.

Thus, from the reasons described above, the size, composition as well as crystal structure of dispersoids in AlMgSi alloy need further investigation.

2. Experimental

Alloy with a composition of Al-0.50Mg-0.65Si-0.20Mn-0.12Fe-0.034Cu was made by air melting and chill cast method under commercial facilities. Specimen for research was taken from extruded plates which

was homogenized at 560 °C for 8 hours, air cooled, and then reheated to 470 °C and held for 30 min before extrusion. Extruded plates (1.5 mm in thickness, extrusion ratio 73:1) were solutionized at 470 °C for 30 min and then water quenched. The composition and crystal structure analysis of the dispersoids were performed on a transmission electron microscope (TEM) (Philips CM-30) equipped with an energy-dispersive X-ray spectrometer (EDS) (EDAX9900). Thin foils for TEM observation were made by standard chemical method.

The atomic ratio of Mn/Fe (where Mn and Fe contents are in at %) was estimated through a standardless quantification of spectra. When the dispersoids have a very small size, the spectra contains contribution from surrounding matrix. But considering the very low contents of Mn and Fe in matrix, the Mn/Fe ratio will not be affected significantly by those contribution from matrix. This was also suggested by literature [2].

For crystal structure analysis, we used SAD (selected area diffraction) pattern together with CBED pattern for quick analyzing. By CBED (convergent beam electron diffraction) pattern, primitive cell volume can be calculated. This volume data can be used for preidentification of crystal structure without indexing the SAD patterns [8].

3. Results and discussion

3.1. Composition and size

Fig. 1 shows the typical morphology of dispersoids in studied alloys. They are mostly round as reported by Donnadieu *et al.* [2], but there are also some dispersoids which have rod shape as indicated by arrows. For comparation with other people's work, here we only discuss about the round shape dispersoids which occupy the majority of all dispersoids. The size of these dispersoids covers a range from 0.03 to 0.5 μm.

EDS data show that all dispersoids contain Al, Mn, Fe, and Si elements. Mn/Fe ratio was calculated from EDS data, but for dispersoids with size below 0.08 μm contribution from dispersoids is too weak to be analyzed. Fig. 2 shows the distribution of Mn/Fe ratio vs. size of dispersoids. Measurement results were obtained from two specimens. From this figure a trend that the size increases with the decrease of Mn/Fe ratio is quite apparent. It is reported [2, 9] that in 6013 alloys, all dispersoids (with size between 0.1 and 0.3 μm) have a Mn/Fe ratio of more than 3 regardless of the nominal composition of the alloys. And for constituent particles (their size generally bigger than 1 μm), which were also considered as alpha particles, they have a Mn/Fe ratio of a range from 0.2 to 1 depending on the nominal Mn/Fe ratio of the alloys. In our case, considering the small size of the particles studied here they should be dispersoids which were formed during homogenization. In Fig. 2 the Mn/Fe ratio is in a range of from about 0.7 to about 7 and size of dispersoids is in a range of 0.08 to 0.5 μm. So it covers a more wider range than that of the dispersoids studied by Donnadieu *et al.* [2]. The reason why dispersoid size increases with the decrease of Mn/Fe ratio is not clear now but it may be suggested that when these dispersoids were formed under different local surroundings, e.g. different local iron and manganese content, they may grow to different sizes. Detail research for this reason is needed because smaller dispersoids are of high importance to mechanical properties through grain refinement.

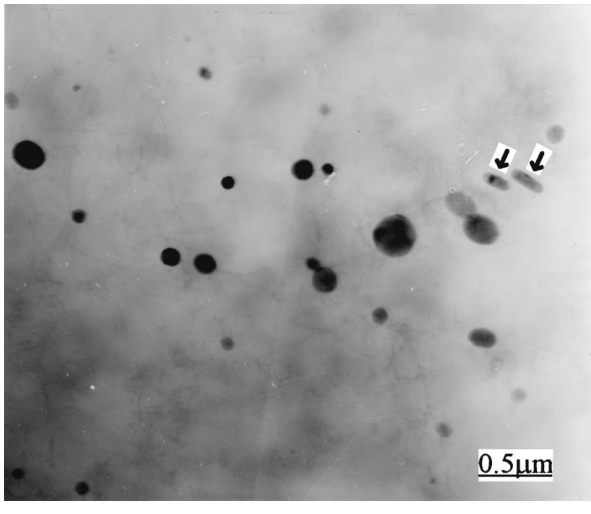

Figure 1 Morphology of dispersoids in AlMgSi alloy.

3.2. Crystal structure

SAD pattern analysis shows that the dispersoids have two kinds of crystal structures, one is B.C.C, the other is simple cubic. However, the unit cell parameters of the two crystals are the same. By SAD pattern it can be calculated to be about 1.25 nm.

Using the method developed by Kim *et al.* [8], with CBED pattern, the primitive volume of dispersoids with different Mn/Fe ratio was calculated. Two examples of SAD and CBED analysis are given in Figs 3 and 4 together with the schematic indexing of the SAD patterns. Calculated results were shown in Fig. 5. From this figure it can be seen that the dispersoids with high Mn/Fe ratio have a primitive cell volume of around 2000 Å^3, and that have lower Mn/Fe ratio have a primitive cell volume of around 1000 Å^3. A critical Mn/Fe ratio of about 1.6 can be decided by the figure. Although there are no report on the primitive cell volume of these dispersoids, according to space group and reported data [2, 7] on the unit cell parameter (from 1.25 to 1.27 nm) the primitive cell volume of Im3 and Pm3 crystal structure can be calculated to be 977–1024 Å^3 and 1953–2048 Å^3 respectively. These results are then in good agreement with present study.

As extreme cases, the α-AlFeSi has a Im3 space group while α-AlMnSi has a Pm3 space group and the studied Al(Mn, Fe)Si phase has a isomorphous crystal structure with these two kinds of phases. So it is reasonable to suggest that there are a critical Mn/Fe ratio for the change of crystal structures. This was suggested by [6, 7] but the ratio was not decided. Here we found the critical Mn/Fe ratio is about 1.6, but it is worthy to note that specimens for this study were heat treated at 470 °C for only 30 min and water quenched. That means this may be not an equilibrium state and the critical ratio

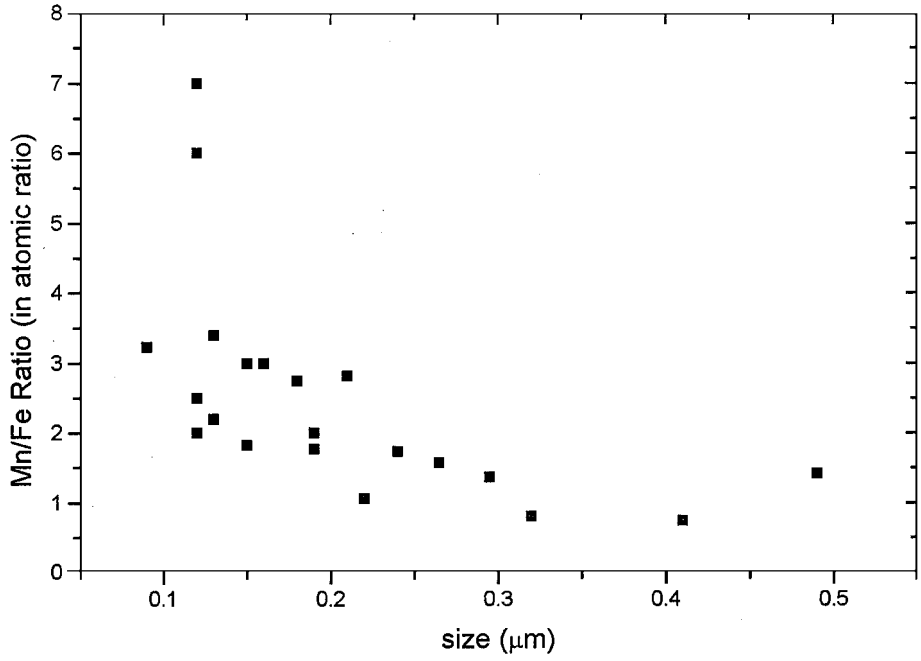

Figure 2 Mn/Fe ratio versus size of dispersoids in AlMgSi alloy.

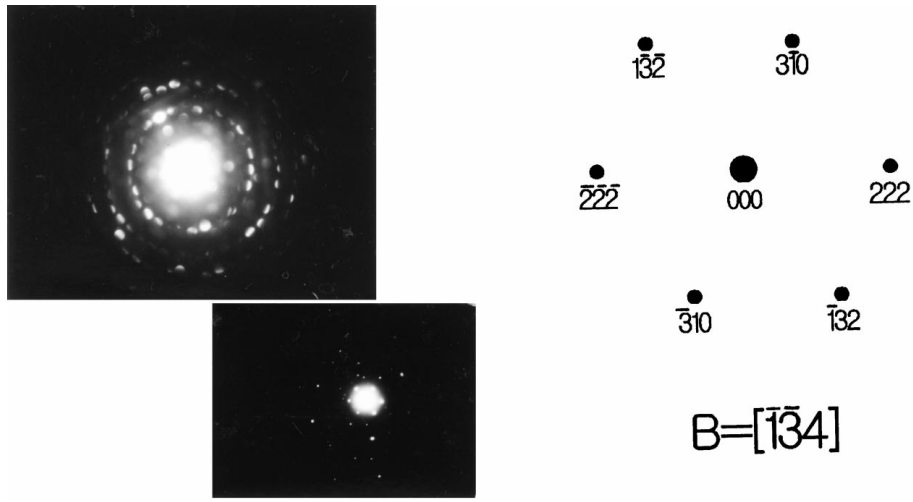

Figure 3 SAD and CBED (ring type) patterns with schematic indexing of SAD pattern. Taken from a dispersoid with Mn/Fe ration of 1.36.

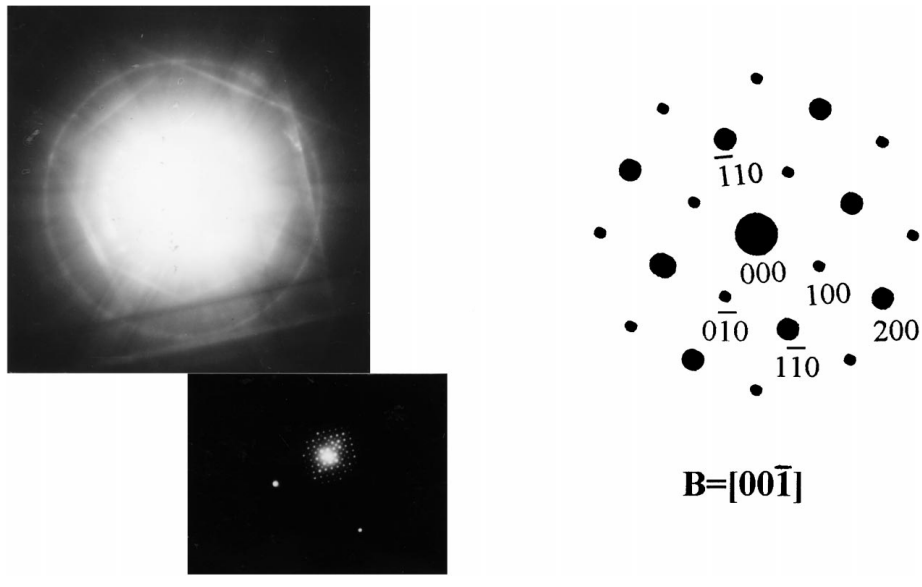

Figure 4 SAD and CBED (ring type) patterns with schematic indexing of SAD pattern. Taken from a dispersoid with Mn/Fe ration of 1.73.

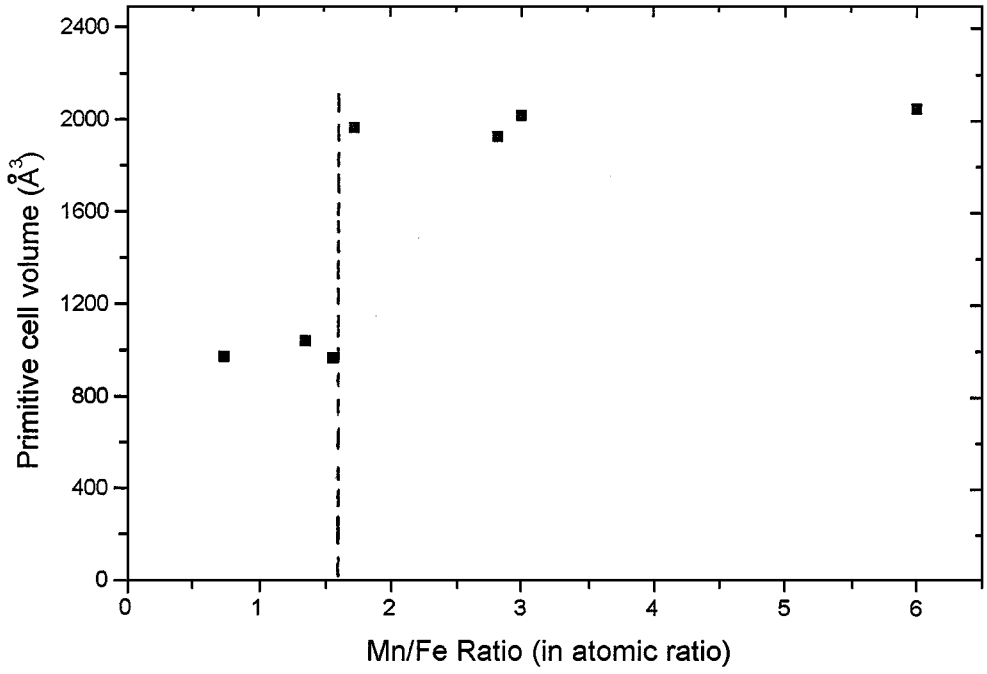

Figure 5 Primitive cell volume versus Mn/Fe ratio of dispersoids in AlMgSi alloy.

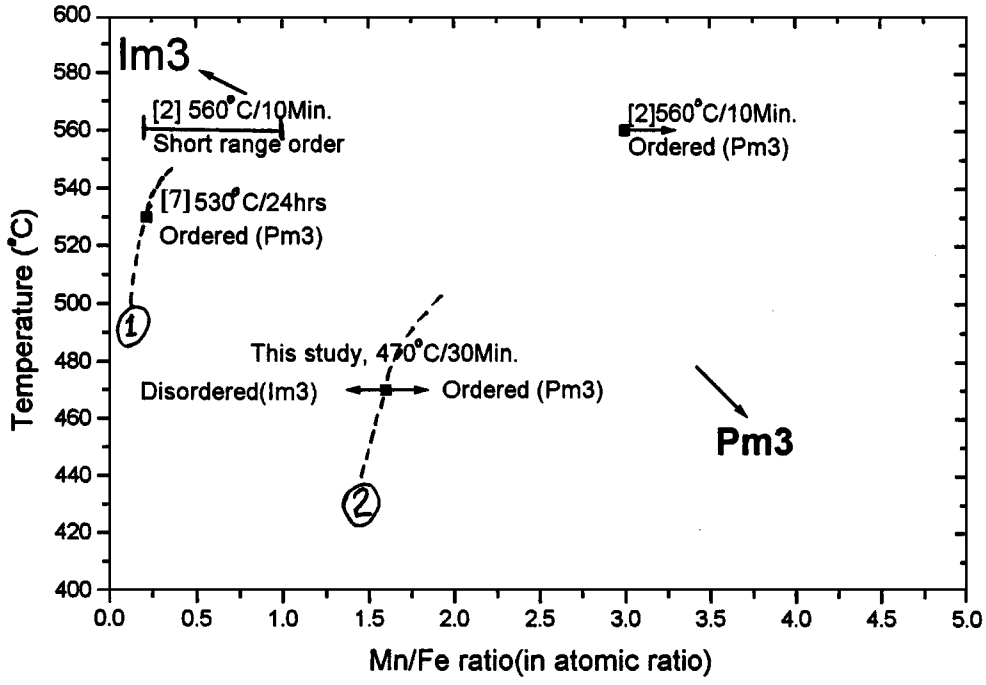

Figure 6 Schematic showing of order-disorder transformation in Al(Mn, Fe)Si dispersoids. Temperature and Mn/Fe ratio effects.

may change with heat treatment state. Now we consider the Pm3 state as an ordered state and Im3 as a disordered state as discussed by Lai and Li [7]. According to the principle of thermodynamics, the ordering state should exist at some lower temperature. In Lai *et al.*'s study the particles with Mn/Fe ratio of 0.22 have an ordered (Pm3) structure after heat treatment at 530 °C for 24 hours. And in Donnadieu *et al.* [2] research, specimens were solutionized at 560 °C, he only observed some diffused arcs in forbidden point position in particles with Mn/Fe ratio from 0.2 to 1. This means the particles are only partially ordered or in a short range order state. In our case the specimens were heat treated at 470 °C for 30 min, at this temperature the low Mn/Fe ratio particles are possible to have an ordered structure but maybe the time is too short for formation of an ordered structure. On the bases that (1) ordered structure exists at low temperature and (2) ordered structure exist at high Mn/Fe ratio, Fig. 6 was drawn to show the order-disorder transformation in these dispersoids. Two dashed lines are suggested here: line1 is suggested upon the result of literature [7] where heat treatment was conducted at 530 °C for 24 hours. Considering the long time heat treatment, this line maybe more likely near the equilibrium line. Line 2 is suggested upon this study. Compared to the equilibrium state, this line give some higher critical Mn/Fe ratio. Results in literature [2] was gotten from specimens heat treated at 560 °C for 10 min, it is almost certain that the specimens are not in equilibrium state. And the results are easy to

be explained with Fig. 6. By this figure it is clear that those α-Al(Mn, Fe)Si particles with lower Mn/Fe ratio may also show an ordered structure if they were heat treated at lower temperature and longer time. So, in researches on the order-disorder transformation in these alpha particles both Mn/Fe ratio and temperature/time effects should be taken into account.

4. Conclusions

1. The size of dispersoids in studied AlMgSi alloys is dependent on their Mn/Fe ratio, the higher the Mn/Fe ratio, the smaller the size.

2. Mn/Fe ratio decides the crystal structure of the dispersoids. With high Mn/Fe ratio, the crystal structure is a simple cubic structure and with lower Mn/Fe ratio it is a BCC structure. The critical value of Mn/Fe ratio for this change may dependent on heat treatment. Under heat treatment employed in present experiment this critical value was found to be about 1.6.

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