PRECIPITATION KINETICS AND MECHANISMS IN A BINARY Al-Sc ALLOY

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ABSTRACT

The precipitation kinetics of Al_3Sc in an Al-0.2wt%Sc alloy has been studied. Solution heat treated specimens were isothermally annealed at temperatures between 230 and 470°C, with 20°C intervals, and the progress of the precipitation reaction was followed by means of electrical conductivity measurements.

A TTT-diagram was plotted from the resistivity data and one finds that the C-curves have two noses. This indicates that there is a shift in precipitation mechanism in this temperature range. Further, JMAK-plots of each isothermal transformation curve clearly indicates that in the temperature range 370-470° there is a shift in mechanism during the isothermal transformation.

TEM and light microscopy studies indicate that at lower temperatures the Al_3Sc phase precipitates by homogenous nucleation and growth, while at higher temperatures discontinuous (also known as cellular) precipitation has occurred.

Keywords:
Al-Sc, precipitation kinetics, C-curves, nucleation and growth, discontinuous precipitation

1. INTRODUCTION

Over the last few decades, various investigations have been done on the possible advantages of adding scandium to aluminium alloys. In various wrought alloys, one can by adding a relatively small amount of Sc achieve[1-4]

- Grain refinement in casting or welding
- Strengthening from finely dispersed Al_3Sc precipitates
- Increased resistance to recrystallization of wrought material
- Enhanced superplastic properties
- Less tendency for hot-cracking during welding

In general the effects of Sc are further accentuated when combined with a Zr-addition.

The former Soviet Union had some research programmes on Sc in Al-alloys in the eighties, which lead to the development of several series of standarized Al-alloys with various Sc-content[5]. Only the last few years, commercial use of Sc-containing Al-alloys has emerged in the western world. So far, it seems like commercial use is limited to sports equipment (baseball bats, bicycle frames etc.) and filler material for arc-welding. However, several western companies are looking into the possibilities of using such alloys for structural parts in automotive and aerospace applications.

Although the precipitation process of Al_3Sc has been studied by several scientists both in binary Al-Sc alloys and in more complex alloy systems, more work is necessary in order to give a complete

description of this process. Most of the papers published concerning the nucleation and growth of Al_3Sc particles, conclude that the equilibrium $L1_2$ Al_3Sc phase forms directly from the supersaturated solid solution without any preceding formation of GP-zones or transient phases[6,7]. It has also been noted that discontinuous precipitation of the Al_3Sc phase can occur in some cases[8,9].

2. EXPERIMENTAL PROCEDURE

The Al-0.2wt.%Sc alloy used in this investigation was prepared from superpure aluminium and scandium of 98% purity. The melt was cast in thin rod-shaped moulds with 12 mm diameter. The rods were cut in disks of suitable thickness for the experiments.

Specimens were solution heat treated in molten salt furnaces at 600°C, and quenched directly from this temperature to the precipitation temperature in another molten salt furnace. Isothermal precipitation kinetics were studied in the temperature range 230-470°C, with 20°C intervals. The progress of the precipitation was followed by means of electrical conductivity measurements of water-quenched samples at room temperature. Electrical conductivity was measured by means of a Sigmascope eddy-current apparatus. Two measurements were made of each specimen, one from each side of the disc.

A selection of samples were prepared by standard techniques for studies in light and transmission electron microscope. TEM pictures are taken in a JEOL JEM 2010 at 160 kV acceleration voltage.

3. RESULTS AND DISCUSSION

During the isothermal transformation the average solute Sc content in the α aluminium phase will gradually decrease as Al_3Sc-particles nucleate and grow. The electrical conductivity of the α phase will increase accordingly. In treating the data obtained by conductivity measurements in this investigation, it is for each temperature assumed that the partial increase in electrical conductivity is proportional to the partial decrease in solute content in the α-phase, and thus

$$X(t) = \frac{\sigma(t) - \sigma_0}{\sigma_\infty^T - \sigma_0} \tag{1}$$

where $\sigma(t)$ is the conductivity at the time t, σ_0 is the conductivity at $t = 0$, and σ_∞^T is the conductivity after very long time at that particular temperature. $X(t)$ is the isothermally transformed fraction at the time t.

Three examples of transformation/time plots are shown in the upper part of Figure 1. At temperatures below 370°C, the curves are close to a sigmaoidal shape. At temperatures above 370°C the curves start to deviate from this shape in the later stage of the transformation, and at 470°C the curve is almost linear.

Provided that the precipitation reaction follows the Johnson-Mehl-Avrami-Komolgorov (JMAK) relationship, $X(t)$ can be expressed as

$$X(t) = 1 - \exp\left(-k(Dt)^n\right) \tag{2}$$

where k is a constant, D is the interdiffusion constant of Sc in Al, and n is dependent on the

nucleation rate. If all the particles are nucleated at random sites at the same time $n = \frac{3}{2}$, while $n = \frac{5}{2}$ if the nucleation rate is constant during the transformation[10]. By plotting experimental data as $\log \ln \frac{1}{1-X}$ against $\log t$, one can obtain the value of n as the slope of the presumable straight line. In this paper, such plots are referred to as JMAK plots. Examples of such plots are shown in the lower part of Figure 1. Due to poor fit in the start and end of the transformation, data are plotted only for $X \approx 0.05 - 0.95$. In the temperature range 370-470°C, the data points seem to make up two rather than one straight line.
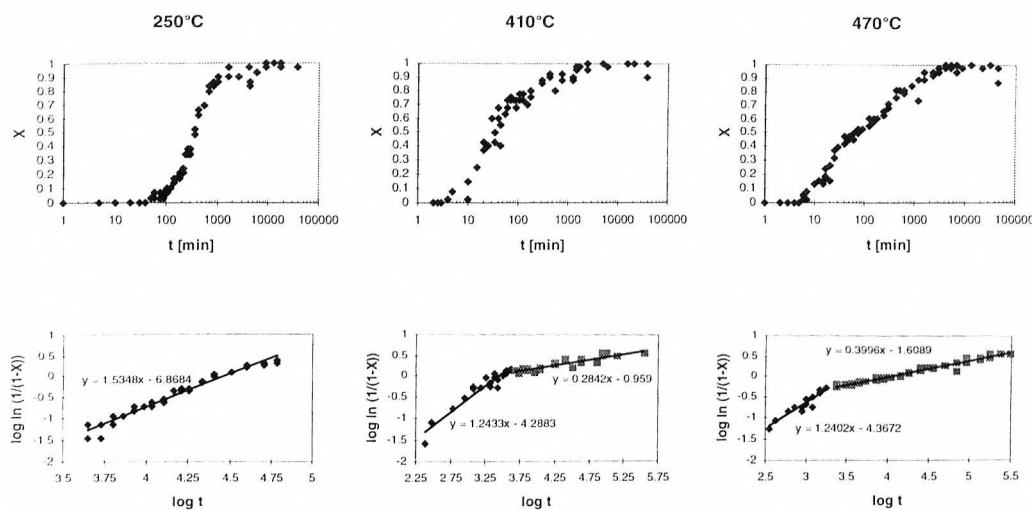

Figure 1   Three examples of transformation curves with corresponding JMAK plot
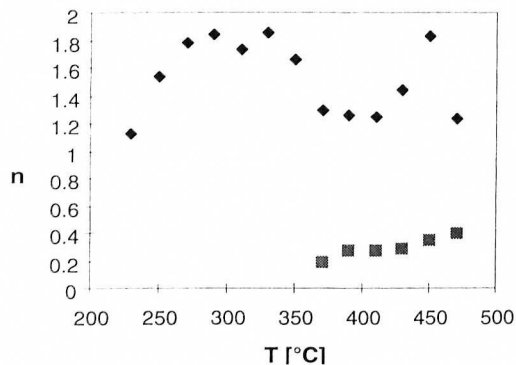

Figure 2   Dependency of n upon transformation temperature

Figure 2 shows how n varies with the precipitation temperature. At temperatures between 250 and 350°C, n is in the range 1.5 - 1.85, which according to the JMAK theory is close to a situation where all the precipitates nucleate at random sites at the same time. At temperatures higher than 350°C, where a distinct shift in the kinetics during the isothermal transformation is evident, n-values for both the early and the late stage are presented.

For each temperature the time needed to reach $X = 0.05$, 0.5 and 0.95 was estimated, and these data were used to plot C-curves in the TTT diagram shown in Figure 3. As can be seen, the C-curves have two distinct noses, one at ca. 310°C and the other at ca. 410-430°C. Double or multiple noses in TTT-diagrams are in many alloy systems attributed to the precipitation of different phases in the various temperature regions. However, for all temperature ranges in the Al-Sc system the only reported precipitated phase is the equilibrium Al_3Sc-phase. It is thus tempting to attribute the two noses to different mechanisms or conditions for

nucleation and growth in the two temperature regions. A plausible explanation seems to be found in the microstructure evolution during the isothermal transformation.
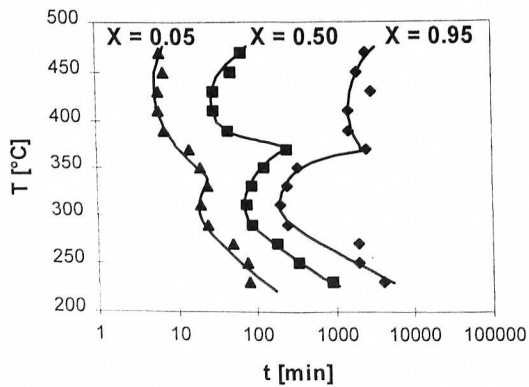

Figure 3   C-curves for Al-0.2wt%Sc

The as cast microstructure consists of large radial columnar grains. During solution heat treatment at 600°C there is some coarsening of the grains. Subsequent isothermal transformation at temperatures of 350°C and below does not seem to alter this grain structure. Many investigations have concluded that precipitation in this alloy occurs by homogeneous nucleation and growth at these temperatures. TEM studies of a specimen annealed at 350°C for 4 hours revealed finely dispersed Al_3Sc particles throughout the entire specimen volume, as shown in Figure 4. This is in accordance with what one would expect if the precipitates nucleate homogeneously
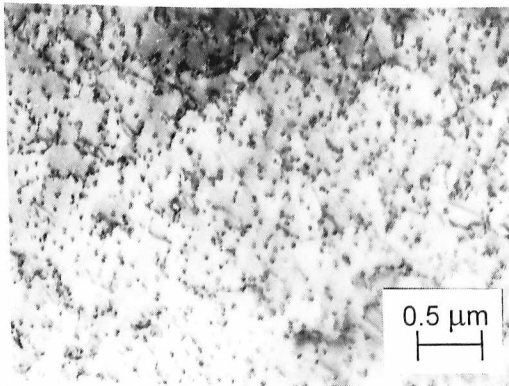
At higher temperatures though, there is substantial evidence that at least part of the transformation occurs by discontinuous precipitation. Instabilities at grain boundaries can be observed in light microscope after annealing times coinciding with the start of the precipitation process. As the reaction advances the grain boundaries get more and more ragged, and there is also some formation of new grains at grain boundaries and within old grains. An example of this evolution at 450°C is shown in Figure 5 below.

Figure 4   TEM micrograph of Al_3Sc particles in specimen annealed at 350°C for 4 h

a)   b)
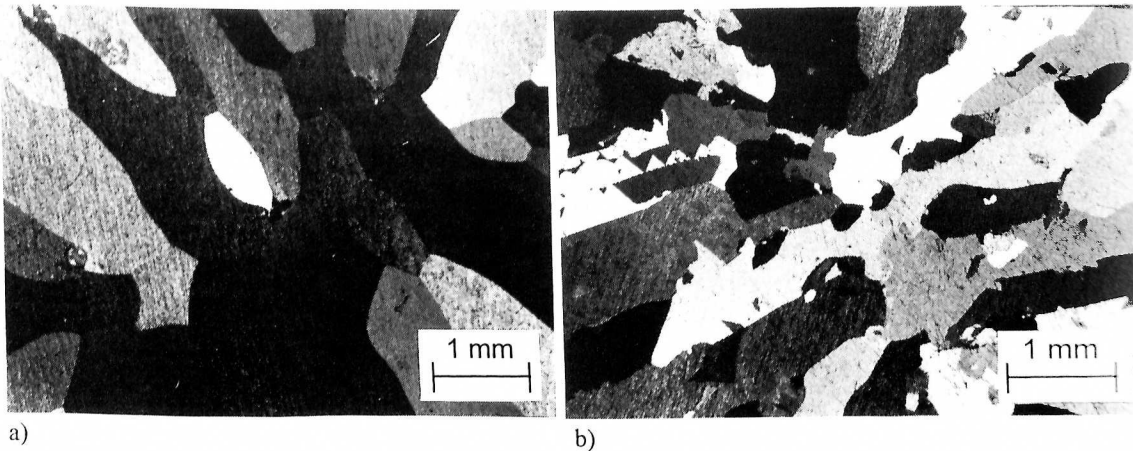
Figure 5   Grain structure after a) solution heat treatment, and b) annealing at 450°C for 10 min

Discontinuous precipitation is characterized by the formation of a secondary phase from supersaturated solid solution ($\alpha' \to \alpha + \beta$) behind a moving grain boundary. In many cases the grain boundary leaves behind a characteristic fan-shaped array of precipitates. Such precipitate arrangements can be seen in the two TEM images in Figure 6. These micrographs are taken of specimens annealed at 450°C for 10 and 60 min respectively. In the 10 min specimen, the only precipitates observed were the ones that were discontinuously formed. In the 60 min specimen, some coarse precipitates were also seen outside the areas of discontinuous precipitation, like the ones on the left side of Figure 6 b)

a)   b)
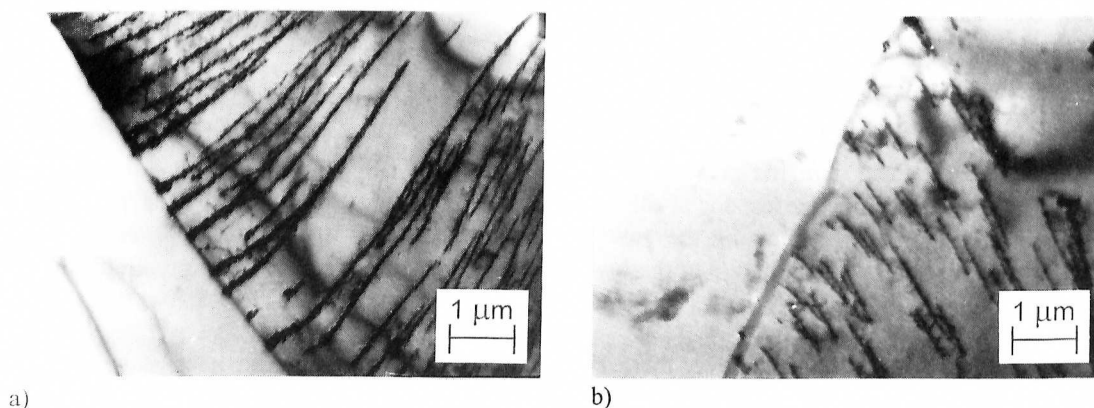
Figure 6   TEM micrographs of areas of discontinuous precipitation after annealing at 450°C for
                  a) 10 min, b) 60 min

It seems reasonable to attribute the two distinct noses of the C-curves in Figure 3 to two different precipitation mechanisms; continuous precipitation at the lower temperatures, and discontinuous precipitation at the higher temperatures. When it comes to the shift in the kinetics in the later stage of isothermal transformation at temperatures above 370°C, no satisfactory explanation has been deduced from the experimental results obtained so far. There are some indications that the discontinuous precipitation come to a halt after some time, and this might coincide with the observed shift in the transformation kinetics. However, the authors restrain from drawing any conclusions on this particular matter until further investigations have been carried out.

When comparing the present results with earlier works, a few interesting differences are noticed. In ref. [7] resistivity data for an Al-0.25wt.%Sc alloy was obtained during isothermal transformation in a wide temperature range. Up to temperatures of 300-330°C there is excellent agreement with the present investigation, both with respect to time for the start and end of transformation and to the estimated *n*-values. At higher temperatures, authors of ref. [7] measure considerably higher transformation rates, and at 460°C they reach the end of rapid growth approximately 100 times faster than what would be expected from the data in the present investigation. This difference is probably due to the fact that in [7], the specimens were water quenched between the solution heat treatment (640°C) and the precipitation. This should introduce a high number of excess vacancies, which at room temperature or during the heating to the precipitation temperature might have facilitated the formation of a high number of Al_3Sc clusters and thus ensure a rapid transformation.

Although discontinuous precipitation is not mentioned and might not have occurred in [7], the C-curves obtained in that investigation seem to have two distinct regions in the low and high temperature ranges, although not as pronounced as in the present investigation.

In [11] where among others an Al-0.23wt.%Sc alloy was investigated, there does not seem to be two distinct regions in the C-curves. Decomposition starts at earlier times than in the present investigation, especially at higher temperatures. Then again, this alloy was annealed in the as-cast condition without any preceding solution heat treatment. There is a possibility that cluster formation during cooling of the as-cast material has lead to a faster transformation in the subsequent annealing.

4. CONCLUSIONS

The C-curves obtained from the present studies of the isothermal precipitation kinetics of Al-0.2wt%Sc have two distinct noses, one at ca. 310°C and the other at ca. 410-430°C. Metallographic investigations suggest that each of the two noses are associated with different precipitation mechanisms; continuous precipitation at the lower temperatures, and discontinuous precipitation at higher temperatures.

At temperatures of 370°C and above, there is a shift in the kinetics in the later stage of the transformation.

Some of the differences noted between the present and earlier investigations are probably due to differences in heat treatments prior to the isothermal precipitation.

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