EFFECT OF TRACE SCANDIUM ADDITION ON AL-6MG ALLOY

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Abstract: *Ageing behaviour of Al-6Mg alloy doped with trace amount of scandium was investigated. Cold rolled and as cast samples were aged isochronally for 60 minutes at different temperature up to 500^oC. Some samples were aged isothermally at 300^oC for different periods ranging from 30 to 240 minutes. Hardness of the alloys was measured to study the age hardening effect due to scandium addition. Resistivity changes with annealing time and temperature were measured to understand the precipitation behaviour and recovery of strain of the alloy. Attempts were also made to understand quantitatively the grain refining effect of scandium in Al-6Mg alloy. Moreover, a kinetic analysis for precipitation in cold rolled experimental alloys has been carried out by Differential Scanning Calorimetric Technique to gain a clear understanding about the kinetics of recrystallisation and recovery in Al-Mg alloy with or without scandium additions.*

Keywords: *Al-Mg alloys, Age hardening, Resistivity, Dendrites, Second phase.*

INTRODUCTION

There is now a great interest in developing highly formable aluminium alloys and, in particular Al-Mg based alloys, for applications leading to lightweight vehicles. Aluminium alloys with magnesium as the main alloying element are widely used in industry as non-ageing, ductile, medium-strength, weldable and corrosion-resistant materials. However, their relatively low strength characteristics hinder their use as structural materials in shipbuilding and the aerospace industry. Alloying with transition metals, especially scandium looks like a promising way to solve these problems.

Significant improvement in properties of aluminium alloys can be achieved through the addition of scandium. A good number of works regarding the use of scandium in Al-Mg alloys has been reported[1-3]. The use of scandium in Al-Mg alloys is meant for taking the advantage of the unique precipitation hardening behaviour of scandium. Scandium forms a stable LI_2 phase, Al_3Sc with aluminium. The precipitation of Al_3Sc is coherent with the matrix[1]. A limited volume fraction of Al_3Sc phase produces a significant hardening[4,5]. In fact Al_3Sc is the most potential hardener on equal atomic fraction basis known in Al-based systems. Since magnesium does not enter into the precipitate structure, the strengthening effect of scandium in Al-Mg alloy is seemingly an additive to the solid solution hardening due to magnesium. Also a beneficial effect of prior deformation on the ageing characteristics has been noted[6]. It is further reported that scandium forms a supersaturated solid solution upon solidification at a rapid rate. Previous investigations into microstructures and properties of Al-Mg-Sc are documented in literature[4]. However, variation in microstructures of the alloys of different chemical and processing conditions is studied in a limited manner. It is known that scandium exerts modifying effect on the grain structure of cast alloy3. Again, it has been suggested that scandium can substitute the use of transition elements like chromium or zirconium in obtaining fine crystallites in the microstructures.

This paper discusses the results of the experiments carried out to study the above mentioned issues related to the age hardening behaviour of Al-6Mg alloy containing 0.2 wt% of scandium. Also presents the results along with the analysis on the evolution of microstructures of cast alloys. Hence, in the present investigation a detailed kinetic analysis for precipitation in cast and cold rolled experimental alloys has been carried out by Differential Scanning Calorimetric (DSC) technique. DSC study has also been used to gain a clear understanding about the kinetics of recrystallisation and recovery in Al-Mg-Sc alloy.

EXPERIMENTAL

Melting of alloys wase carried out in a resistance heating pot furnace under the suitable flux cover (degasser, borax etc.). Several intensities of heat were used for developing base aluminium-magnesium alloy and aluminium-magnesium alloy containing 0.2 wt% scandium. For the preparation of the alloys, the commercially pure aluminium (99.5% purity) was taken as the starting material. First the aluminium and aluminium-scandium master alloy (2%Sc) were melted in a clay-graphite crucible, then magnesium ribbon (99.7% purity) was added into solution. Casting was done in cast iron metal moulds preheated to 200^oC. Mould sizes were 12.5 x 51.0 x 200.0 in millimetre. All the alloys were analysed simultaneously by wet chemical and spectrochemical methods. The chemical compositions of the alloys are given in Table 1. Some of the samples were cold worked in a laboratory scale rolling mill. The alloys processed through different routes were aged at different temperatures for different times. Hardness of different alloys aged at different temperatures was measured in Vickers hardness testing machine at 5 kg load to assess the age hardening effect of the alloys. Electrical conductivity of the alloys in as cast and cold worked with different aged condition were carried out with an Electric Conductivity Meter, type 979. 12 mm x 12 mm finished surface samples produced by grinding and polishing were prepared for this measurement. The alloys in as cast state were subjected to metallographic studies. For the optical metallography the specimens were polished with alumina and etched by Keller's reagent. Grain size of the sample was measured using ASTM standards under a Versamet-II- Microscope.

Table 1: Chemical Composition of the Experimental Alloys (wt%)

Alloy	Mg	Sc	Cu	Fe	Mn	Ni	Si	Zn	Cr	Sn	Al
1	6.100	0.000	0.081	0.382	0.155	0.003	0.380	0.136	0.002	0.002	Bal
2	5.900	0.200	0.081	0.345	0.132	0.003	0.360	0.174	0.002	0.002	Bal

Remarks: Alloy 1 Al-6 wt% Mg and Alloy 2 Al-6 wt% Mg-0.2 wt% Sc

The cast alloys had been subjected to DSC heating run in a Du Pont 900 instruments. Inert N_2 gas atmosphere was used during DSC experiments. The samples for DSC studies were lump of 10 to 15 mg in weight. The DSC scan was conducted over a temperature range from 50°C to 650°C. A fixed heating rate of 10°C/min was used in all scans. The activation energy of transformations for the alloys in different conditions was calculated by using the method of Nagasaki-Maesono analysis[7].

RESULTS

Age-hardening behaviour: The results of isochronal ageing of the alloys are shown in Fig. 1. It is seen that alloy 2 except base alloy (alloy 1) has shown appreciable ageing response. Alloy 1 has however shown a continuous softening at increasing ageing temperatures, with a steeper hardness drop beyond 400°C. For alloy 2 the peak hardness is obtained at around 300°C. Beyond peak hardness value the usual softening due to annealing takes place. When the alloys are isothermally aged at 300°C, which is the peak isochronal ageing temperature of the alloys (Fig. 1), the ageing response of the alloy is found to be quite appreciable. The peak-aged condition is mostly reached within 60 minutes (Fig. 2). No significant softening due to over-ageing could be observed. Under such ageing condition the resistivity of alloys 2 is found to reach a plateau after an initial decrease in resistivity up to 60 minutes of ageing (Fig. 3).

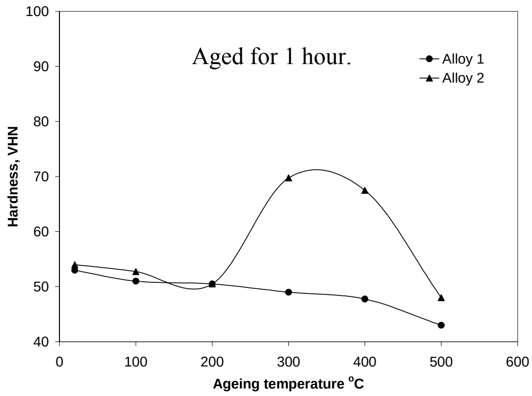

Fig. 1: Isochronal ageing curve of the cast alloys.

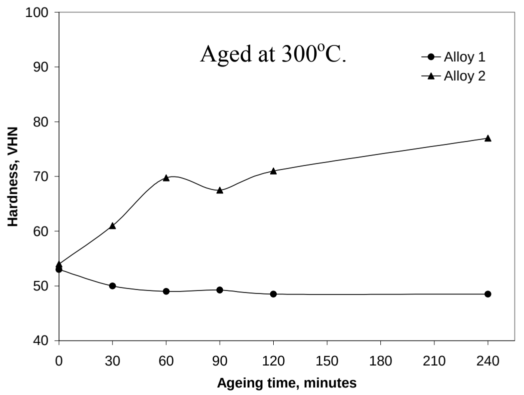

Fig. 2: Isothermal ageing curve of the cast alloys.

The results of isochronal ageing of the cold worked alloys at different temperature for 1 hour show identical nature of age hardening at cast state (Fig. 4). The initial

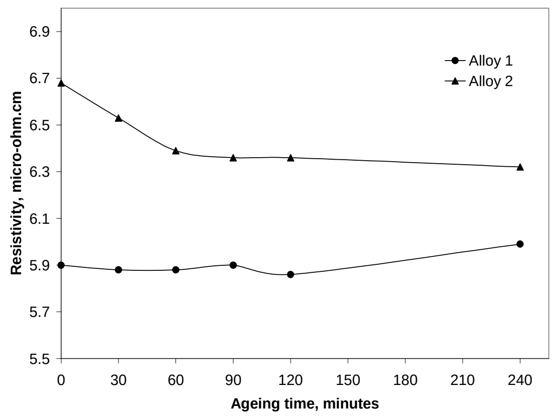

Fig. 3: Variation of resistivity due to ageing of the cast alloys. Isothermally aged at 300°C.

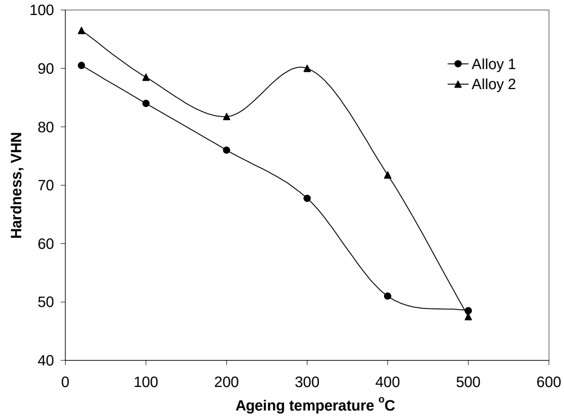

Fig. 4: Isochronal ageing curve of the 75% cold rolled alloys. Aged for 1 hour.

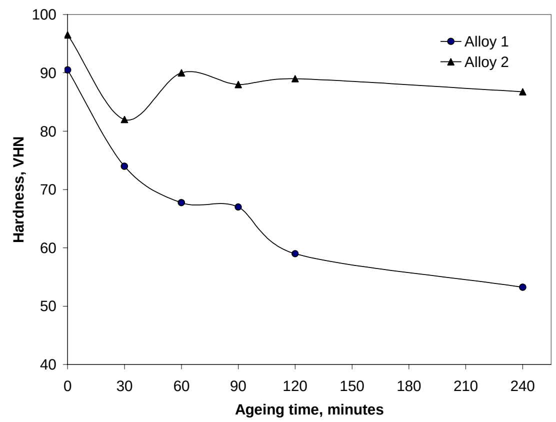

Fig. 5 cold rolled: Isothermal ageing curve of the 75% alloys. Aged at 300°C

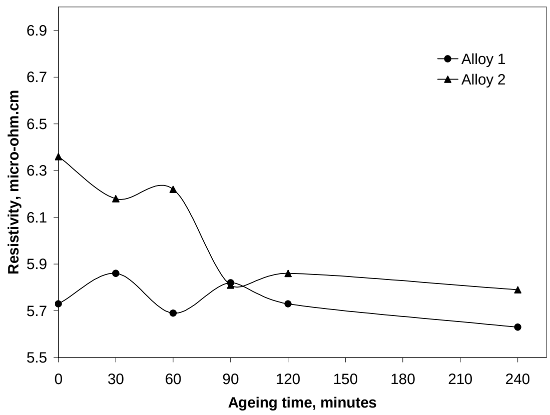

Fig. 6: Variation of resistivity due to ageing of the 75% cold rolled alloys. Isothermally aged at 300°C.

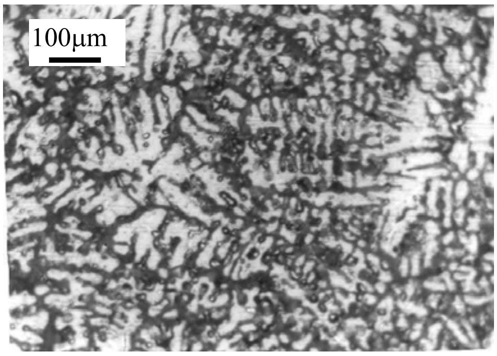

Fig. 7: Optical micrograph of cast alloy 1.

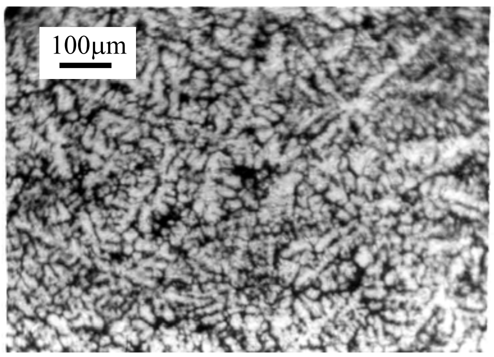

Fig. 8: Optical micrograph of cast alloy 2.

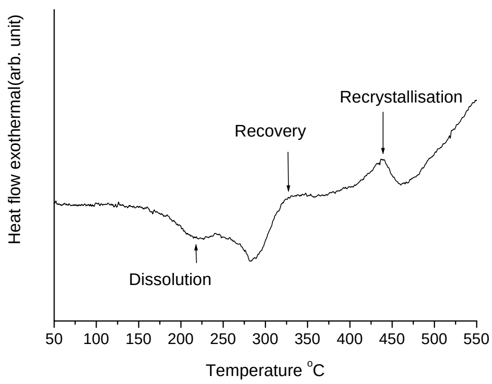

Fig. 9: DSC heating curve of alloy 1 with 35% cold deformation.

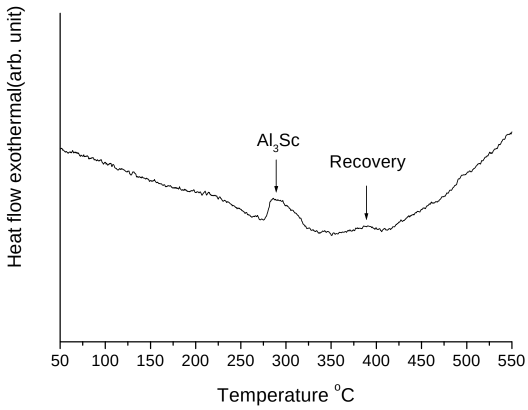

Fig. 10: DSC heating curve of alloy 2 with 35% cold deformation.

Table 2: Results of DSC heating run

Alloy	History	Transformation	Peak temp. (°C)	Actv. energy (kJ/mol)
1	35% cold deformation	Dissolution of some phases	215	137
		Recovery	325	118
		Recrystallisation	435	214
2	35% cold deformation	Precipitation of Al_3Sc	290	190
		Recovery	390	120

hardness is higher for higher amount of deformation for all the alloys. The base alloy (alloy 1) shows a continuous softening due to recovery and recrystallisation of the strained grains. All other alloys demonstrate age hardening response with peak hardness value at 300°C. An initial softening to the tune of 10 VHN is noted in the scandium added alloy. The extent of age hardening does not change with varying deformation percent. At high deformation no extra benefit in maximum value of hardness could be noted. Most of the alloys show softening during initial period of ageing and increase in hardness after ageing finally enables the maximum hardness to reach a magnitude which is comparable to the initial hardness of cold worked alloys (Fig. 4). When the alloys are aged at higher temperature a sharp decrease in hardness is observed for all the alloys. Thus appreciable drop in hardness values are noted at ageing temperatures beyond 300°C. When the alloys are aged at 300°C the base alloy shows a continuous softening due to recovery and recrystallisation (Fig. 5). Alloy 2 with 75% deformation shows age hardening response with the peak hardness at a time around 60 to 90 minutes of ageing before reaching a plateau. For 75% deformed alloy however, an initial softening is noted in case of alloys 1 and 2 (Fig. 5). The resistivity curves of all the alloys after 75% deformation show initial softening at steeper rate, then a rise to a peak followed by a near constancy value up to ageing time 240 min. (Fig. 6).

Optical Microscopy: The optical microstructure of alloy 1 shows dendrites with black second phase particles within inter-dendritic spaces (Fig. 7). Addition of scandium to the base alloy by 0.2 wt% shows a diminution in the amount of second phase particles. It further appears that dendrite arm spacing is decreased in Alloy 2 with the consequent refinement of dendrites (Fig. 8).

Differential Scanning Calorimetry: The base Al-6Mg alloy when cold rolled by 35% has given rise to the DSC heating curve as shown in the Fig. 9. In the figure it is noted that a broad endothermic peak occurs at 215°C. This is indicative of dissolution of some phase already present in the cast alloy. Following the method described elsewhere[7], the activation energy concerning dissolution reaction was calculated to be 137 kJ/mol. A broad exothermic has appeared at a temperature 325°C. This is followed by another sharper exothermic peak at 435°C. The lower temperature broad peak is due to recovery process taking place during DSC heating. The activation energy for the process of recovery was found to be 118kJ/mol. The sharp exothermic at 435°C corresponds to recrystallisation. The recrystallisation process in the cold worked alloy has almost overlapped the recovery process. The activation energy for recrystallisation is found to be 214 kJ/mol.

The DSC heating curve of cold rolled by 35% alloy 2 containing 0.2 wt% Sc is shown in Fig. 10. An exothermic at 290°C corresponds to the precipitation of Al_3Sc taking place during the DSC heating run. The activation energy for this precipitation reaction is calculated to be 190 kJ/mol. Following this, a broad exothermic peak is seen to appear at 390°C in the heating curve. This signifies the recovery process taking place at a higher temperature.

DISCUSSION

The results of the present experiments clearly indicate that the age hardening effect shown by the alloys are purely due to addition of scandium. Scandium when added in small concentrations is known to refine the grain structure of cast metal and to form a supersaturated solid solution upon solidification[3]. The effect of grain refinement of the cast structure is clearly evident from the resistivity curves, which show a significant difference of resistivity values of the scandium added alloy with that of the base alloy. The initial high resistivity of scandium treated alloy is indicative of high electron scattering sites viz. grain boundary area to mean that grains in all those alloys are finer. Formation of supersaturated solid solution assures a high precipitation hardening effect upon decomposition of this solid solution with the formation of fine coherent equilibrium Al_3Sc precipitates[4,8]. No ageing response is visible for the base alloy. In the cast condition the β-phase being already present in the microstructure of the matrix of alloy 1, precipitation hardening due to the formation of aluminides of magnesium is not envisaged. Moreover Al-Mg alloys are known to be incapable of producing significant age hardening even though the binary phase diagram contains a sloping solvus[9].

From the isochronal ageing curves it is seen that Al_3Sc precipitates form most rapidly at around 300°C, where the peak-ageing hardness values are obtained. The softening of the alloys at higher temperature may be due to particle coarsening effect. The initial softening shown in the isochronal ageing curve (Fig. 1) is thought to be due to internal stress relieving of the rapidly solidified castings. Because the addition of scandium in Al-Mg alloys leads to the formation of sufficient amount of dispersoids in the microstructure.

The initial drop in resistivity is due to stress relieving in the alloy during ageing. Transition metals are known to bind vacancies strongly[10]. For this reason, the number density of scattering centres is reduced. This causes a sharp fall in resistivity. The subsequent increase in resistivity is due to the appearance of fine precipitates.

The initial softening of the cast and cold worked alloys during isochronal ageing is thought be due to rearrangement of dislocations at the ageing temperature. From the resistivity curve it is seen that alloy 1 shows a peak following an initial drop. The initial drop is recorded for other alloy too. In the alloy 2 there is resistivity peak. The age hardening of the alloys containing scandium is attributable to the formation of Al_3Sc precipitates. The strengthening is found to be greater for alloys with higher deformation because a higher degree of strain hardening resulted from higher dislocation density. But the extent of age hardening has not improved. This means that extra advantage is not accruable by working scandium treated alloys. Moreover there has not been any change in the peak hardness temperature due to cold working. This signifies that scandium precipitation is not dislocation induced. Moreover extensive cold working also generates large number of vacancies, which form vacancy-scandium atom complexes of high binding energy. The vacancy-solute atom complexes reduce the mobility and availability of solute atoms at low temperature to form GP zones. Hence hardening takes place only at a temperature high enough to decompose the complexes thereby making solute scandium atoms available for precipitate formation. Beyond peak hardness, over ageing effect due to coarsening of the precipitates is seen to have taken place. At higher ageing temperature there is ample scope for dislocation annihilation and this softens the material.

When the alloys are aged isothermally no significant ageing effect is observed at low temperature, as Al_3Sc formation is favoured at around 300°C. This observation is similar to what is reported by previous workers [8]. So isothermal ageing at 300°C has depicted a good deal of precipitation hardening effect. This is consistent with the observation made in case of isochronal ageing, which exhibited softening beyond 300°C.

The initial drop in resistivity during isothermal ageing of the experimental alloys is indicative of dislocation rearrangement taking place within the cold worked alloys. The decrease in resistivity is found to be much higher in Alloy 1 than all other alloys. Thus it appears that the base alloy undergoes softening more than the trace added alloys. The precipitates formed by trace element hinder dislocation movement and thus limit the softening. The major drawback of Al-6Mg alloy in respect of undergoing softening during use is overcome by scandium addition. It is found from hardness plots that pinning of dislocation by formation of Al_3Sc onto them is unlikely. Nevertheless once formed, the precipitates hinder the motion of dislocations and hence lessen softening.

The rise in resistivity in alloy 1 when aged at low temperature is due to the formation of magnesium rich precipitate viz. GP zones at 100°C and β'-metastable phase at 200^0C onwards. Thus fine zones scatter the free electrons incoherently and thus resistivity increases till the time particle coarsening becomes so prominent as to diminish the incoherent scattering of electrons. For the same reasons all the alloys show resistivity peaks for isothermal ageing temperatures up to 200°C. Beyond this temperature, it is the precipitation of Al_3Sc, which is responsible for resistivity peaks in alloy 2.

The final steady decrease in resistivity stems from particle coarsening which reduces the number of scattering centres. Since precipitate coarsening is appreciable at high temperatures, the resistivity drop is also noticeable. At lower temperature ageing, drop in resistivity due to recovery is counteracted by its increase due to ongoing precipitation process. As a result, depending upon the dominance of particular event, the resistivity either remains constant or marginally increases when the alloys are aged at lower temperature for longer times.

From the phase diagram of the alloy it is found that the present alloys would contain α + β eutectic within the primary dendrites of α. Here 'α' is the aluminium rich solid solution and β is composed of intermetallics, primarily Al_8Mg_5 along with aluminides of other metals like iron, chromium, zirconium, manganese, which are present in small quantities in the aluminium used for the present experimentation. The number of non-equilibrium segregation is dependent on the magnesium content and the concentration of other potential aluminide formers[8]. However scandium forms an anomalous supersaturated solid solution, which decomposes to form Al_3Sc[11].

Though general observations under optical microscopy have not provided much information, the overall appearance of the microstructure resembles what are normally observed in cast aluminium alloy ingot[12]. The dendrites of the cast base alloy are seen to have refined significantly with the addition of scandium. Reportedly alloy with 0.2% Sc does not provide much grain refinement, but refines the primary dendrites of α with consequent diminution of dendrite arm spacing. The arm spacing in scandium treated alloys were found to lie within a range of 20 µm to 40 µm against a value of around 45 µm in case of base alloy. This is ascribed to the modification of solidification speed by scandium during the growth of the dendrite structure[3]. Also scandium-containing alloy is seen to have contained fewer amounts of intermetallic compounds. Due to increase in solidification speed the gap between liquids and solidus becomes narrower in the Al-Mg-Sc phase diagram. As a result, the super-cooling effect is weakened. This leads to faster solidification phase transition. The decrement in the amount and size of the second phase constituents with scandium addition is suggestive of suppression of the growth of these phases. This is possible under a faster solidification rate, which aids in the retention of more solutes in solution. Since dendrites are refined with scandium addition the size of individual second phase region becomes smaller as these phases are formed within the inter-dendritic spaces.

Alloy 1 with 35% cold deformation contains some metastable phase. It is reported that metastable $\beta^{/}$ phase in Al-Mg alloy gives way to the formation of β-phase[9]. Two separate DSC peaks noted for the alloy is suggestive of the probable dissolution of $\beta^{/}$ phase for subsequent formation of β-phase. Thus the endothermic peak noted at 215°C in the base alloy seems to correspond to the dissolution of $\beta^{/}$-phase. The activation energy of the process, 137 kJ/mol, is close to the activation energy for diffusion of magnesium in aluminium, which has been reported to be 130 kJ/mol[13]. Thus the dissolution kinetics is dependent upon the diffusion of magnesium in the alloy.

The broad exothermic peak at 325°C gives an activation energy 118 kJ/mol. This value is quite close to the activation energy of 120 kJ/mol for recovery in Al-Mg alloy as reported elsewhere[13]. So the peak is thought to be concerned with the recovery process taking place in the deformed sample. The following exothermic peak is relatively sharp and occurs at 435°C. Recrystallisation temperature is found similar to what has been reported earlier[13]. However, its activation energy is found to be somewhat higher (214 kJ/mol) than the previously reported value of 190 kJ/mol. This may be due to hindrance to dislocation movement by certain iron-aluminides, which might have been present due to relatively higher iron content of the alloy (~0.38 wt%)

In Fig. 10, the exothermic peak at 290°C corresponds to the formation of Al_3Sc. It may be mentioned that activation energy for diffusion scandium in aluminium is reported to be 175 kJ/mol. Also activation energy for the formation of Al_3Sc in scandium bearing aluminium alloy has been found elsewhere to be 169 kJ/mole[14]. This implies that precipitation kinetics of Al_3Sc is decided by the diffusion of scandium in aluminium. In the present case the activation energy for the aforesaid exothermic is found to be close to the previously reported value (190 kJ/mole). The higher temperature exothermic peak at 390°C refers to recovery process taking place in the deformed alloy. This implies that with the greater volume fraction of finely distributed Al_3Sc precipitates, the dislocation movement is restricted. Hence substructural stability is increased.

CONCLUSIONS

- The age hardening effect shown by the alloy is due to addition of scandium.
- No change in the peak hardness temperature due to cold working signifies that scandium precipitation is not dislocation induced.
- The dendrites of the cast base alloy are refined significantly with the addition of scandium.
- Availability of dislocations facilitates the formation of $\beta^{/}$-metastable phase in Al-Mg alloys. These precipitations onto the dislocations hinder the process of recrystallisation.
- Presence of low amount of dislocations does not appreciably influence the kinetics of precipitation of Al_3Sc. A high dislocation density affects the kinetics of Al_3Sc precipitation.
- Presence of fine coherent precipitates of Al_3Sc impedes the migration of dislocations and increase the recovery temperature. The kinetics of recrystallisation is also delayed.

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