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Precipitation Hardening Behavior of Directly Cold Rolled Al-6Mg Alloy Containing Ternary Sc and Quaternary Zi/Ti

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Abstract**—**Ageing of 75% cold rolled Al-6Mg alloy with ternary 0.4 wt% scandium and quaternary zirconium and titanium has been carried out. Alloy samples are naturally, isochronally and isothermally aged for different time and temperatures. Hardness values of the differently processed alloys have been measured to understand the ageing behavior of Al-6Mg alloy with scandium and quaternary zirconium and titanium addition. Resistivity changes with annealing time and temperature were measured to understand the precipitation behavior and recovery of strain of the alloy. Attempts were also made to understand the grain refining effect of scandium in Al-6Mg alloy. It is observed that significant hardening takes place in the aged alloys due to the precipitation of scandium aluminides and the dendrites of the Al-6Mg alloy have been refined significantly due to addition of scandium.

Keywords**—**Al-Mg alloys, age hardening, resistivity, metastable phase.

I. INTRODUCTION

BINARY Al-Mg alloys are the basis for an important class of non-heat treatable alloys commonly referred to as the 5xxx-series alloys. These alloys are widely used for applications in the automotive industry, marine and offshore constructions and in materials subjected to cryogenic conditions. Examples of use are hull plates for ships, body plates for cars, helicopter decks, buildings, containers and tanks for storing or transportation of liquid gases etc. [1]. Scandium is the most effective hardening element in aluminum alloy systems on an equal atomic basis to all other particle-forming elements alloyed with aluminum [2]. It is well known that alloying of aluminum with scandium with appropriate selection of the composition results in the increase of the recrystallization temperature above the solidus temperature [3]. 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 [4]. The use of scandium in Al-Mg alloys is meant for taking the advantage of the unique precipitation hardening behavior of scandium. Scandium forms a stable LI_2 phase, Al_3Sc with aluminum. The precipitation of Al_3Sc is coherent with matrix [3]. In a binary Al-Sc system the precipitation kinetics were studied by earlier workers [5], [6]. Any possibility of clustering before precipitate formation has been ruled out by the previous workers [7]. By employing microscopic techniques it has been conjectured that the formation of Al_3Sc is a process of nucleation and diffusional growth. Again there are reports on using kinetic analysis of hardness variation in aged Al-Mg-Sc alloys for describing the precipitation kinetics of Al_3Sc in the ternary alloy [8]. It is also reported that the maximum rate of Al_3Sc formation occurs at 300^{o}C in a decomposing Al-Mg-Sc alloy. Zirconium and titanium exploits peritectic reaction with aluminum to form metastable LI_2 aluminides phases. Al_3Zr has very similar crystal structure as that of Al_3Sc. As is to be expected, Al_3Zr and Al_3Sc are mutually soluble and $Al_3(Sc_{1-x}Zr_x)$ phase is known to be more stable in aluminum alloys containing both of them [9]. Hence it is anticipated that quaternary addition of zirconium in Al-Mg-Sc alloys may significantly influence the behavior of the ternary alloy. Titanium seems to bear similar potential as a quaternary addition.

This paper presents the results along with the analysis on the evolution of microstructures in the experimental alloys due to change in their chemistry and thermal history. Also discusses the results of the experiments carried out to study the above mentioned issues related to the age hardening behavior of Al-6Mg alloy containing 0.4 wt% of scandium. In view of the probable influence of these quaternary additions, the present age hardening studies are also extended to the quaternary alloys viz. Al-6Mg-0.4Sc-Zr and Al-6Mg-0.4Sc-Ti. Moreover Al-6Mg alloy is normally used in a work-hardened condition and will undergo softening during use. But the softening behavior of the alloy system under the influence of Al_3Sc particles pre-existing in the matrix has not been studied elaborately. Since cold working introduces huge dislocations, it is a question to resolve if the presence of dislocations has any role on the precipitation behavior of Al_3Sc during ageing of the Al-Mg-Sc alloys.

II. EXPERIMENTAL

Melting was carried out in a resistance heating pot furnace under the suitable flux cover (degasser, borax etc.). Several heats were taken for developing base Aluminum-Magnesium alloy, Aluminum-Magnesium alloy containing scandium and with or without zirconium and titanium. In the process of preparation of the alloys the commercially pure aluminum (99.5% purity) was taken as the starting material. First the aluminum and aluminum-scandium master alloy (98 wt% Al + 2 wt% Sc) were melted in a clay-graphite crucible, then magnesium ribbon (99.7% purity) was added by dipping in to

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the molten metal. Zirconium and titanium were taken in the form of powder (99.98% purity) with in a cover of aluminum foil and were then added by plunging. The final temperature of the melt was always maintained at 780±15^{o}C with the help of the electronic controller. Then the melt was allowed to be homogenized under stirring at 700^{o}C. Casting was done in cast iron metal moulds preheated to 200^{o}C. Mould sizes were 12.5 x 51.0 x 200.0 in millimeter. All the alloys were analyzed by wet chemical and spectrochemical methods simultaneously. The chemical compositions of the alloys are given in Table I. Cold rolling of the cast alloys were carried out with a laboratory scale rolling mill of 10HP capacity at 75% reduction. The sample sizes were 9 x 12 x 50mm and the deformation given was about 1.25mm per pass. All cold rolled alloys were naturally aged up to 30 days. Cold rolled samples were aged isochronally for 60 minutes at different temperature up to 500^{o}C. The samples were isothermally aged at various temperatures up to 500^{o}C for different ageing times ranging from 30 to 240 minutes. Hardness of different alloys processed with different schedules and aged at different temperatures was measured in Vickers hardness testing machine with 5 kg load for assessing the age hardening effect of the alloys. Electrical conductivity of the alloys were carried out with an Electric Conductivity Meter, type 979. Finished samples of 12mm x 12mm were produced by grinding and polishing for this measurement. Electric resistivity was calculated from those conductivity data. The optical metallography of all these samples was carried out in the usual way. The specimens were polished finally with alumina and the etchant used was Keller's reagent (HNO_3 – 2.5 cc, HCl – 1.5 cc, HF – 1.0 cc and H_2O – 95.0 cc). The washed and dried samples were observed carefully in Versamet-II-Microscope at different magnifications and some selected photomicrographs were taken. Scanning electron microscopy of the selected samples was carried out by a Jeol Scanning Electron Microscope, JSM-5200.

TABLE I
CHEMICAL COMPOSITION OF THE EXPERIMENTAL ALLOYS (WT %)

Alloy	Mg	Sc	Zr	Ti	Cu	Fe	Mn	Ni	Si	Zn	Cr	Sn	Al
1	6.10	0.000	0.000	0.001	0.081	0.382	0.155	0.003	0.380	0.136	0.002	0.002	Bal
2	5.97	0.400	0.000	0.002	0.071	0.314	0.107	0.002	0.335	0.124	0.002	0.002	Bal
3	5.85	0.400	0.185	0.003	0.069	0.335	0.112	0.001	0.345	0.170	0.003	0.002	Bal
4	6.06	0.400	0.000	0.175	0.080	0.306	0.104	0.002	0.335	0.170	0.002	0.002	Bal

Remarks: Alloy 1: Al-6 wt% Mg; Alloy 2 Al-6 wt% Mg-0.4 wt% Sc; Alloy 3: Al-6 wt% Mg-0.4 wt% Sc-0.2 wt% Zr; Alloy 4: Al-6 wt% Mg-0.4 wt% Sc-0.2 wt% Ti

III. RESULTS

A. Age-Hardening Behavior of Cold-Rolled Alloys:

1. Natural Ageing*:*

The cast alloys were cold worked with 75% deformation percentage and were kept at room temperature to study the effect of natural ageing. It is seen that no significant variation of hardness has occurred during natural ageing for a period of 30 days (Fig. 1).

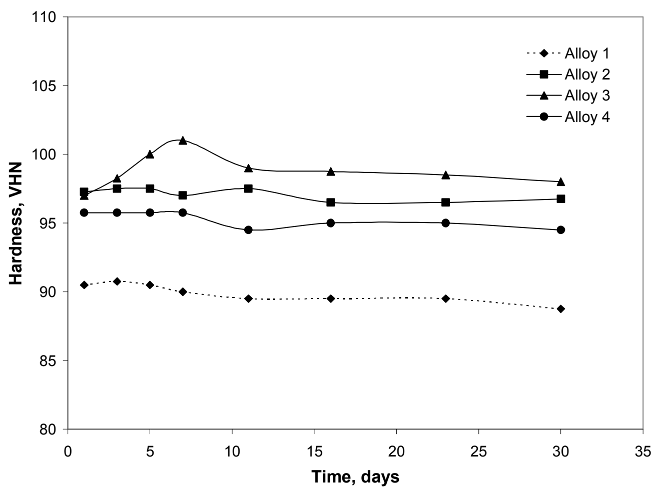

Fig. 1 Natural ageing curve of the 75% cold rolled alloys for 30 days

2. Isochronal Ageing:

The results of isochronal ageing of the cold worked alloys at different temperature for 1 hour are shown in Fig. 2. It is seen that all the alloys except base alloy (alloy 1) have shown appreciable ageing response. The base alloy (alloy 1) shows a continuous softening due to recovery and recrystallization of the strained grains. All other alloys demonstrate age hardening response with peak hardness value at 300^{o}C. An initial softening to the tune of 5 VHN is noted in almost all the alloys. The extent of age hardening varies with the composition of the alloy; however alloy 2 shows the maximum hardness. 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. 2). When the alloys are aged at higher temperature a sharp decrease in hardness is observed for all the alloys. Appreciable drop in hardness values are noted at ageing temperatures beyond 300^{o}C.

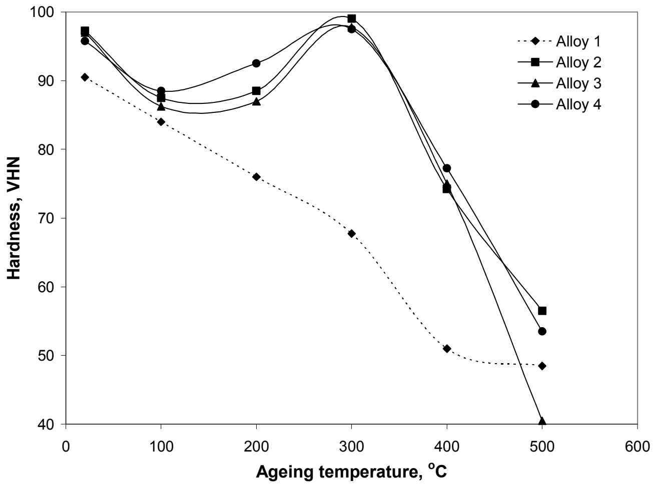

Fig. 2 Isochronal ageing curve of the 75% cold rolled alloys, aged for 1 hour

3. Isothermal Ageing:

Fig. 3 shows the isothermal ageing of the alloys at 200°C. Here small age hardening effect is visible. In these ageing curves the initial softening becomes steeper. All alloys except alloy 1 show increase in hardness (Fig. 3) after ageing for 90 min. On the other hand all the alloys except alloy 1 with 75% deformation show a trend of initial softening after certain incubation. However this incubation is not seen in titanium alloy. There are again resistivity peaks noted in most of the alloys (Fig. 4). When the alloys are aged at 300°C the base alloy shows a continuous softening due to recovery and recrystallisation (Fig. 5). All other alloys show age hardening response with the peak hardness at a time around 60 to 90 minutes of ageing before reaching a plateau. Alloy 2 and alloy 4 show maximum degree of age hardening though the peak hardness is achieved earlier in alloy 4. The resistivity curves of all the alloys show initial softening at steeper rate, then a rise to a peak followed by a near constancy value up to ageing time 240min (Fig. 6). When the alloys are isothermally aged at 400°C, the rate and degree of initial softening is same for alloys 2-4. Alloy 1 shows a very fast and steep decrease in hardness followed by a constant value. The age hardening peaks are observed in alloys 3 and 4 (Fig. 7). The resistivity curves of alloys 2-4 show an initial drop, then an increase, and finally a slow but steady decrease, when isothermally aged at 400°C. Alloy 1; however, shows a resistivity peak at higher ageing time of 120min (Fig. 8).

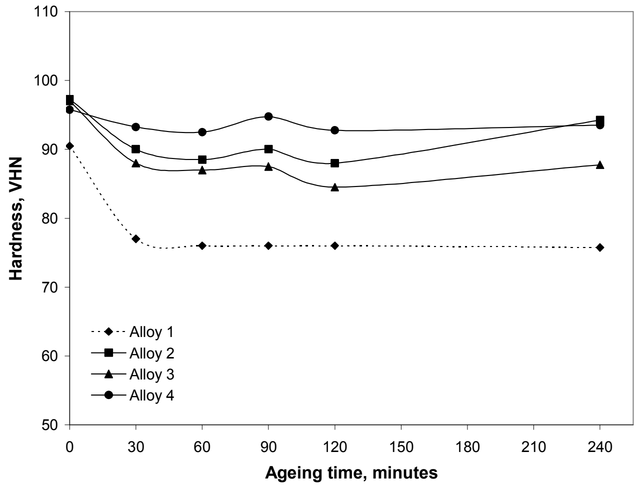

Fig. 3 Isothermal ageing curve of the 75% cold rolled alloys, aged at 200°C

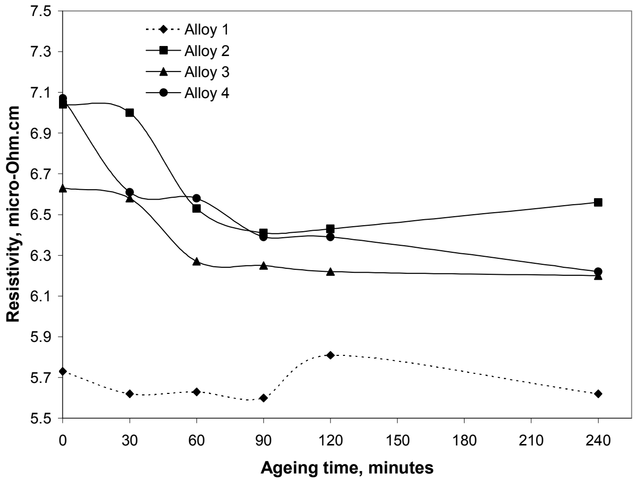

Fig. 4 Variation of resistivity due to ageing of the 75% cold rolled alloys; isothermally aged at 200°C

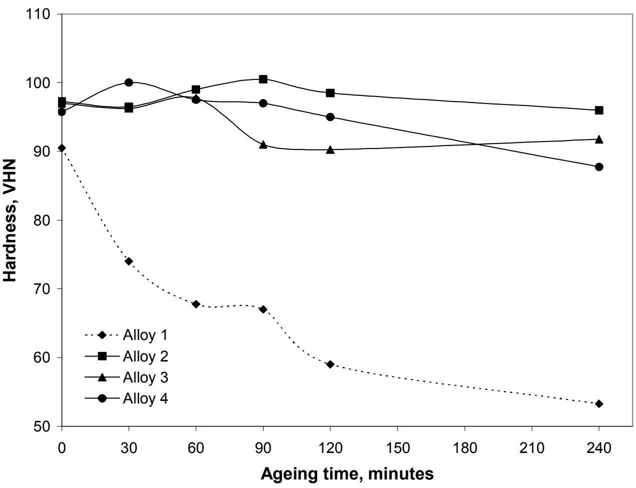

Fig. 5 Isothermal ageing curve of the 75% cold rolled alloys, aged at 300°C

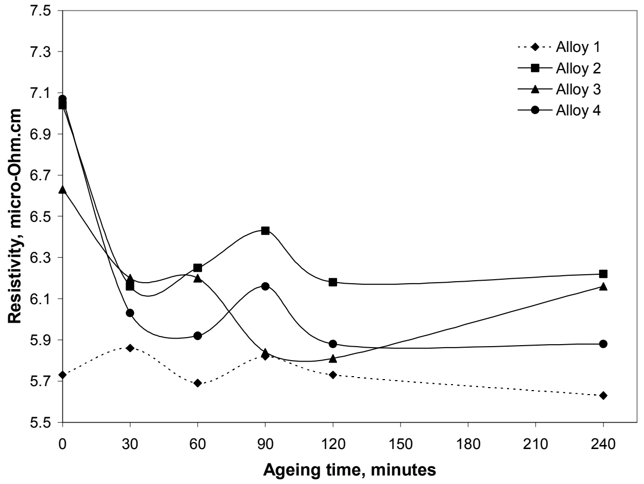

Fig. 6 Variation of resistivity due to ageing of the 75% cold rolled alloys; isothermally aged at 300^{o}C

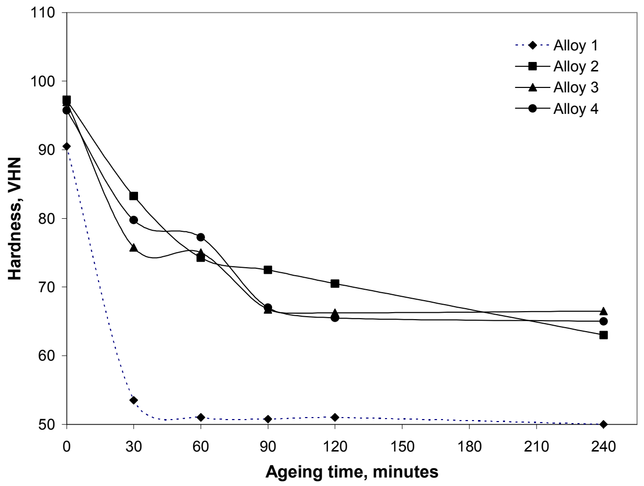

Fig. 7 Isothermal ageing curve of the 75% cold rolled alloys; aged at 400^{o}C

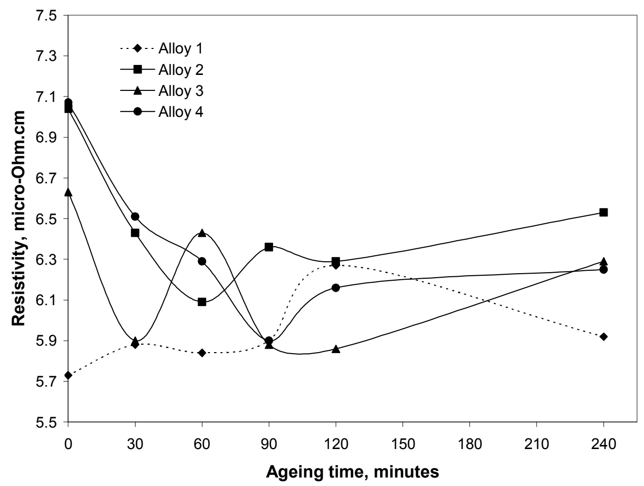

Fig. 8 Variation of resistivity due to ageing of the 75% cold rolled alloys; isothermally aged at 400^{o}C

B. Optical Micrographs:

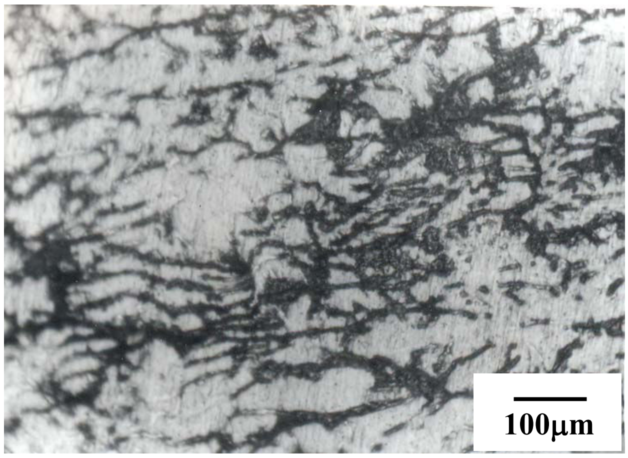

Fig. 9 Optical micrograph of 75% cold rolled alloy 1

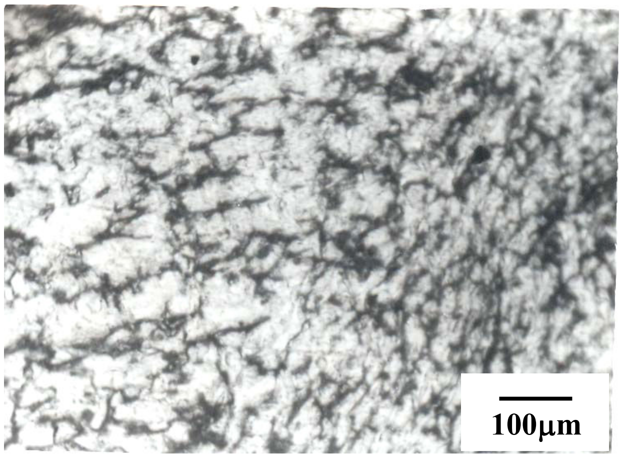

Fig. 10 Optical micrograph of 75% cold rolled alloy 3

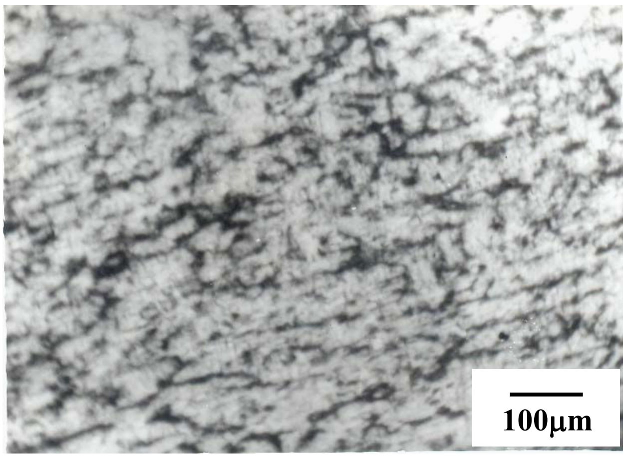

Fig. 11 Optical micrograph of 75% cold rolled alloy 4

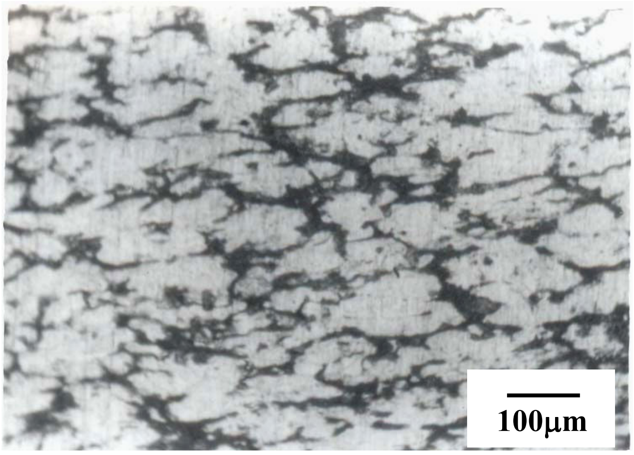

Fig. 12 Optical micrograph of 75% cold rolled alloy 3, aged at 300°C for 1 hour

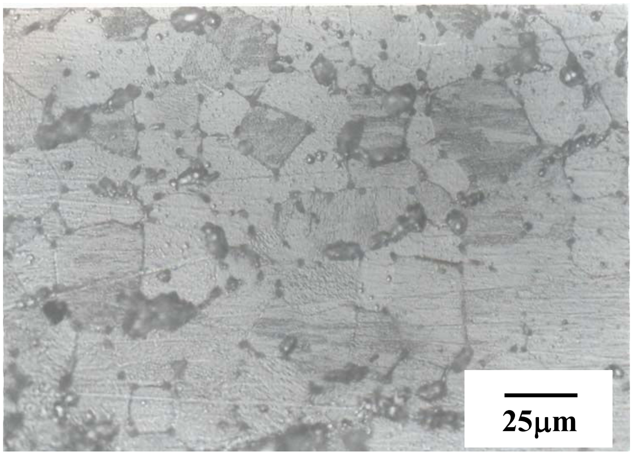

Fig. 13 Optical micrograph of 75% cold rolled alloy 1, aged at 400°C for 1 hour

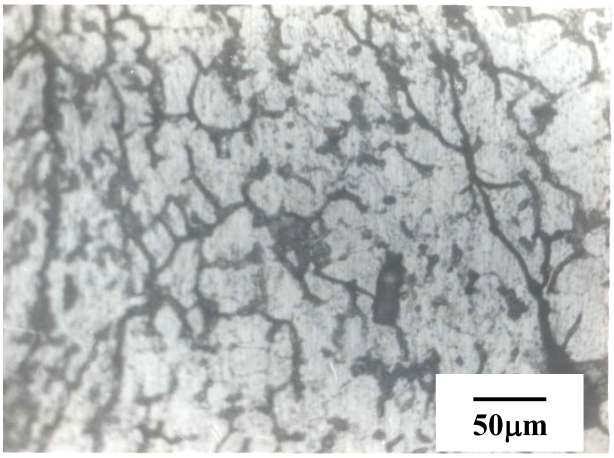

Fig. 14 Optical micrograph of 75% cold rolled alloy 3, aged at 400°C for 1 hour.

The cold worked alloy shows relatively coarse non-uniform grain structure. The overall appearance is columnar grains with second phase particles remaining aligned along the grain boundaries (Fig. 9). Fragmented dendrites, elongated along the direction of rolling, are observed in Fig. 10, showing the microstructure of cold worked alloy 3. Similar microstructures are observed in cold worked alloy 4 (Fig. 11). In case of zirconium added alloy relatively coarsen grains are noted (Fig. 14). The aspect ratio of the grains appears to be smaller than those in the alloys containing only scandium. If the alloys are annealed at 400°C, the base alloy is seen to be recrystallised almost fully (Fig. 15). However, alloy 3 is recrystallised partially at the annealing treatment 400°C (Fig. 16).

C. Scanning Electron Microscopy:

Scanning electron microstructures of base alloy annealed at 300°C after 75% cold rolling shows partially recrystallised grains with ample second phase particles at the grain boundaries (Fig. 15). In case of alloy 2 (0.4 wt% Sc) there is no evidence of recrystallisation after annealing at 300°C (Fig. 16). The same alloy 2, when annealed at 400°C retains its fine grains as shown in Fig. 17.

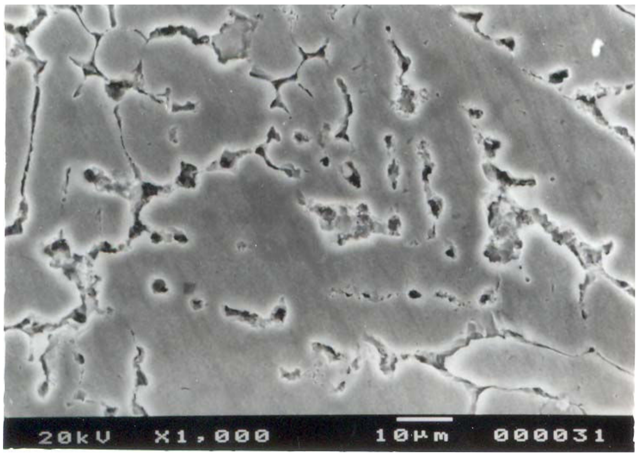

Fig. 15 SEM micrograph of 75% cold rolled alloy 1, aged at 300°C for 1 hour

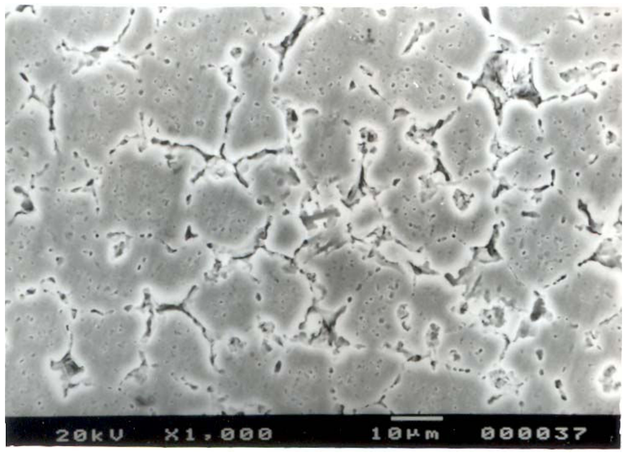

Fig. 16 SEM micrograph of 75% cold rolled alloy 2, aged at 300°C for 1 hour

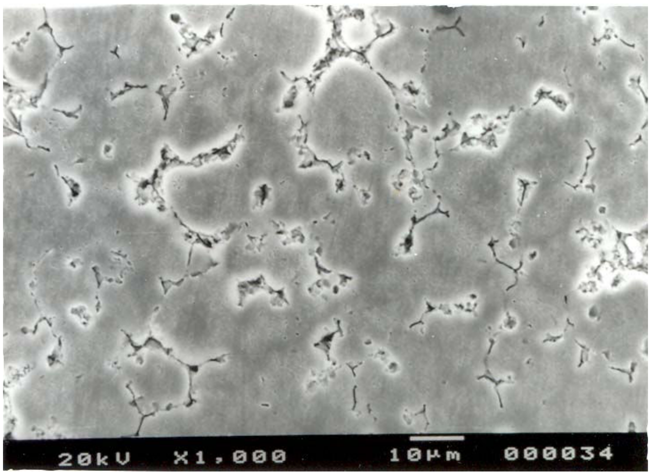

Fig. 17 SEM micrograph of 75% cold rolled alloy 2, aged at 400°C for 1 hour

IV. Discussion

It is known that aluminum-magnesium alloy is a non-age hardenable alloy and its GP zone is formed below room temperature. So response to natural ageing will not be visible in the alloy. The alloys with scandium and zirconium/titanium addition also do not show any natural ageing response since the ageing effects of these alloys are realized due to the formation of stable intermetallics. Trace addition of silver in these alloys is known to promote the formation of GP zones [10], but it is clear from the results that scandium does not exert any such effect.

The initial softening of the cold worked alloys during isochronal ageing is thought be due to rearrangement of dislocations at the ageing temperature. The age hardening of the alloys containing scandium is attributable to the formation of Al_3Sc precipitates. The maximum attainable hardness due to ageing the cold worked alloy has not exceeded the hardness values obtained due to cold working alone. This implies that the precipitation of Al_3Sc is not dislocation induced [3]. However peak temperature in zirconium bearing alloy is responsive to cold working. It is conjectured that Al_3Zr is formed at dislocations. The Al_3Zr being isomorphous with and soluble in Al_3Sc, the nucleation of Al_3Sc is facilitated indirectly by the presence of higher dislocation density. 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 G P 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. In respect of resisting softening due to overageing titanium is found to be more effective than zirconium.

When the alloys are aged isothermally no significant ageing effect is observed at low temperature, as Al_3Sc formation is favored at around 300°C. This observation is similar to what is reported by previous workers [11]. So isothermal ageing at 300°C, has depicted a good deal of precipitation hardening effect. Both alloys 2 and 4 have shown maximum hardness. However alloy 4 containing titanium has age hardened to a significant extent even at lower ageing temperature. The experimental alloys have not demonstrated any strengthening effect when aged isothermally at higher temperature 400°C. 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 zirconium and titanium added alloys behave differently owing to the fact that these elements form their aluminides onto dislocations and hence dislocation pinning is possible. Thus the softening due to ageing is resisted if it is carried out at a temperature where the formation of fine precipitates of Al_3Zr or Al_3Ti is feasible. The rise in resistivity in alloy 1 when aged at low temperature is due to the formation of magnesium rich precipitate viz. G P zones at 100°C and β'-metastable phase at 200°C 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 alloys 2-4. The final steady decreases in resistivity stems from particle coarsening which reduces the number of scattering centers. 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 $\alpha + \beta$ eutectic within the primary dendrites of α. Here 'α' is the aluminum 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 aluminum 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 [11]. However, scandium forms an anomalous supersaturated solid solution which decomposes to form Al_3Sc [8]. Though general observations under optical microscopy have not provided much information, the overall appearance of the microstructure resembles what are normally observed in cast aluminum alloy ingot [3]. The cold worked structures are comprised of elongated grains. When annealed at 300^{o}C no alloy except base alloy shows the sign of recrystallisation. The base alloy however has started recrystallising as it is known that recrystallisation of Al-6Mg alloy becomes completed at about 400^{o}C. However alloys 2-4 have dispersion of fine precipitates of Al_3Sc. These precipitates are coherent with the matrix. It is reported that recrystallisation is almost impossible in aluminum alloys when such particles are already present [10]. Higher becomes the volume fraction of precipitates higher would be the recrystallisation start temperature. The precipitates hinder the movement of sub-boundaries and grain boundaries. On increasing the temperature to 400^{o}C, the second phase constituent is almost dissolved in base alloy and there is nothing to hinder dislocation movement. As a result recrystallisation becomes complete. In alloys containing scandium the supersaturated solution decomposes to form Al_3Sc at around 300^{o}C. These precipitates are known to be resistant to coarsening. There are reports saying that increasing the annealing temperature of Al-Mg-Sc alloy from 300^{o}C to 400^{o}C increases the size of Al_3Sc precipitates from 4 nm to 13 nm. The precipitates of Al_3Sc remain coherent with the matrix even when their size increases to 100 nm due to higher temperature of annealing [12]. In the present case however the precipitate size is around 15 nm when annealed at 400^{o}C. Therefore dislocation pinning force is very large. As a result recrystallisation is not possible. On the contrary alloy 3 with zirconium has shown onset of recrystallisation at 400^{o}C. In fact it has been reported earlier that kinetics of $Al_3(Sc_xZr_{1-x})$ coarsening is faster. Moreover Al_3Zr precipitation is dislocation induced. Since Al_3Sc forms isomorphously with Al_3Zr, the precipitates grow pretty faster due to solute transfer by pipe diffusion. Thus loss in coherency of these precipitates occurs earlier. This is why alloy 3 shows sign of feeble recrystallisation in its microstructures when annealed at 400^{o}C.

V. Conclusion

The age hardening effect shown by the alloys is due to the addition of scandium. Availability of dislocations facilitates the formation of the $\beta^/$-metastable phase in Al-Mg alloys. Precipitation onto the dislocations hinders the process of recrystallization. The precipitates grow faster in the alloys containing zirconium and shows sign of feeble recrystallisation in its microstructures when annealed at 400^{o}C.

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