CLUSTERING RATE-REVERSAL TEMPERATURE AND OTHER PRE-PRECIPITATION CHARACTERISTICS OF Al-Zn-Ag ALLOYS

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ABSTRACT

The clustering kinetics and solute-vacancy interaction in Al–4·4 at.% Zn and Al–4·4 at.% Zn alloy containing 0·01, 0·03, 0·08 and 0·1 at.% Ag have been studied by resistometry. All the Al–Zn–Ag alloys studied exhibited a characteristic Clustering Rate-Reversal Temperature, 'T_{qc}'. Depending on whether the quenching temperature is below or equal to or above the T_{qc}, the ternary alloys age faster, at equal rate or slower as compared to the binary alloy. The T_{qc} is also dependent on the ageing temperature. Some of the isothermal resistivity parameters like time to reach the maximum in resistivity and resistivity increment at peak vary regularly with the silver concentration in the Al–Zn alloy. The silver-vacancy binding energy has a mild dependency on the silver content in the alloy. A simple model has been proposed for the clustering rate-reversal in Al–Zn–Ag alloys.

INTRODUCTION

TRACE elements have a marked influence[1] on the decomposition characteristics of a binary alloy, where the solute has only a low interaction energy with vacancies. The Al-Zn-Ag alloys belong to this group. Al-Zn and Al-Ag alloys show a pronounced clustering tendency. Because of the negligible misfit, the zones formed are spherical in both the alloys. Therefore silver additions to Al-Zn alloys or zinc additions to Al-Ag alloys would provide an interesting system for studying the effect of trace elements in age-hardenable alloys. Silver additions to Al-Zn alloys were considered important as silver is a very desirable trace element[2] in Al-based alloys[3], especially, the Al-Zn-Mg alloys[4]. There is a lot of discrepancy in the reported values of silver-vacancy binding energy[5]. Also, Ohta and Hashimoto[6] reported that in Al-Zn-Ag alloys, the shapes of the isothermal resistivity curves are similar and the time to reach the peak in resistivity is unaltered by silver additions, so that it was not possible to evaluate the binding energy values from time-to-peak measurements. Since the existing theories of pre-precipitation could not satisfactorily explain these observations, which could as well be due to the ageing conditions[7], the work on Al-Zn-Ag alloys was considered to be all the more important.

Al-4·4% Zn (all compositions in the text and tables are given in atomic per cent only) and Al-4·4% Zn with 0·01, 0·03, 0·08 and 0·1% Ag alloys have been chosen for the investigation. The clustering kinetics of these alloys have been studied by following the isochronal and isothermal annealing characteristics and reversion and reageing experiments.

EXPERIMENTAL

Data concerning the purity of the metals used, alloy preparation, specimen design and treatment and measuring techniques have been discussed and given eslewhere[5,8,9]. The resistivity was measured on helical wire samples using the four-probe potentiometric technique. Fully reverted value of resistivity measured at the desired temperature was used for the reference state. Resistivity during isothermal ageing was measured at the ageing temperature, T_a, itself. Isochronal annealing was done in steps of 20° C, in the range — 80° C to 200° C; the measurements were made at the liquid air temperature.

The data have been presented in terms of resistively increments $\Delta\rho$, obtained from the relation:

$$\Delta\rho = \rho_0 (R_T - R_0)/R_0 \qquad (1)$$

where, R_0 and ρ_0 are the resistance and resistivity at the reference temperature and R_T is the resistance at the temperature T.

RESULTS AND DISCUSSION

Isochronal Annealing

This set of experiments were performed to gain a general picture of the pre-precipitation process and no quantitative interpretation was sought.

The isochronal annealing behaviour of Al-4·4% Zn and Al-Zn-Ag alloys with 0·01, 0·03, 0·08 and 0·1% Ag additions have been presented in Fig. 1. This shows that there are three broad regions of change; in the range — 80° to 20° C, the resistivity increases to a peak due to clustering; the zone growth in the range 20° to 120° C leads to a decrease to a plateau and finally

a second decrease occurring due to a possible reversion at high temperatures. Comparison of the isochronal curves for the binary and ternary alloys indicate that the general pattern of the isochronal annealing behaviour is not altered by the silver additions. Complete data on the isochronal annealing characteristics of the binary and ternary alloys have been given elsewhere[8,9].

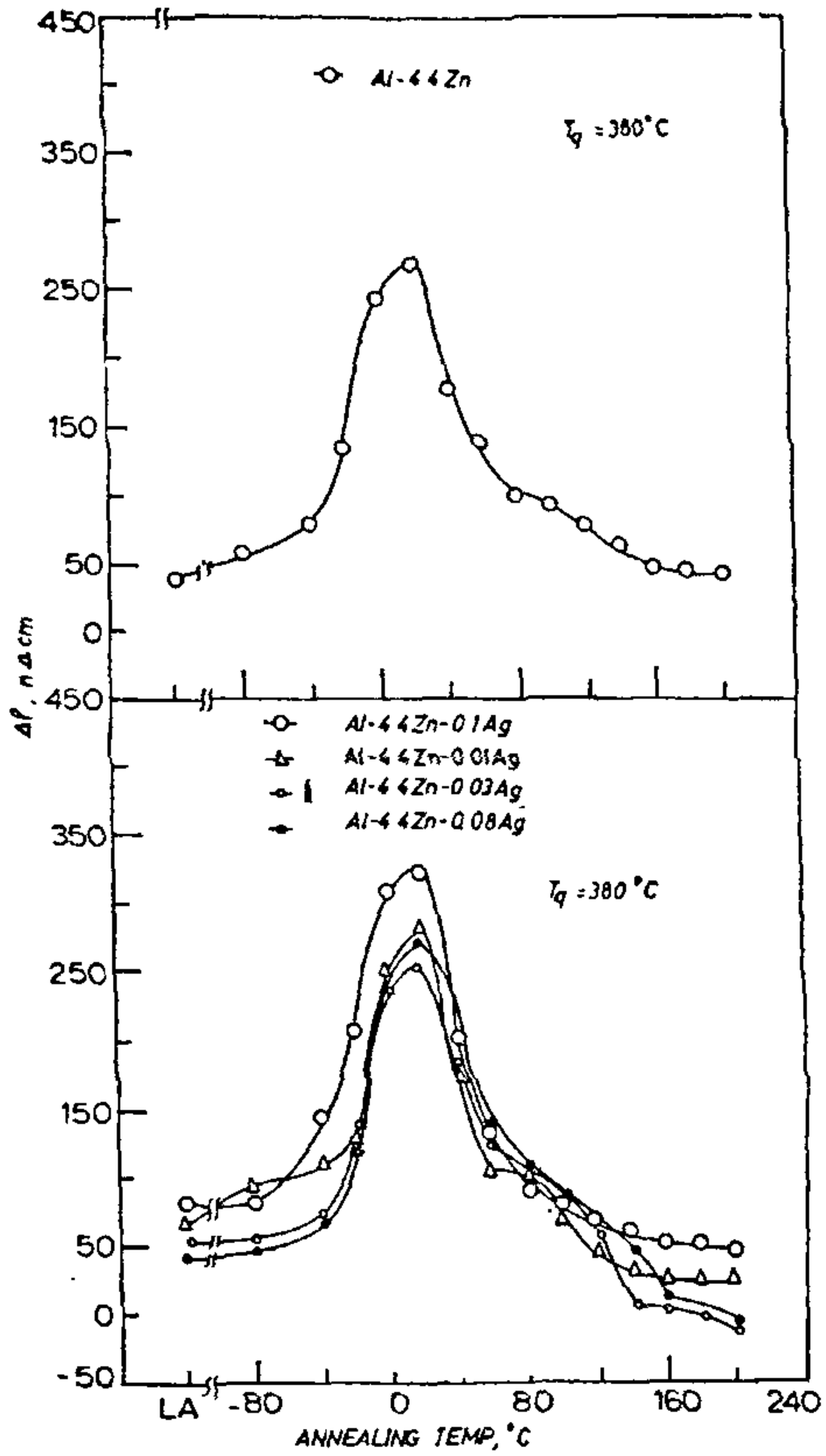

FIG. 1. Isochronal annealing behaviour of the alloys (LA : Liquid Air).

Isothermal Ageing

Isothermal resistivity changes for the binary and ternary alloys for different quenching temperatures and ageing at 0° C have been given in Fig. 2. It is apparent that the nature of isothermal resistivity variation is similar under different conditions of ageing for all the alloys : an initial increase, attainment of a peak and a final decrease. It is also clear from these results that the zone formation in these alloys takes place without any nucleation barrier. Normally the effect of trace addition is to increase the time-to-peak in the ternary alloys as compared with the corresponding binary alloy. However, in all the Al-Zn-Ag alloys studied, it was found that depending on the conditions of ageing with regard to the quenching and ageing temperatures, these alloys age at different rates with respect to the binary alloys—under certain conditions, the time-to-peak (t_m) was the same as that for the binary alloy[6,8], while under certain other conditions it was even smaller than that for the binary alloy. Also, the magnitude of the resistivity peak was independent of the quenching temperature, T_q, for a given T_a indicating that the number of zones forming at this temperature is nearly the same.

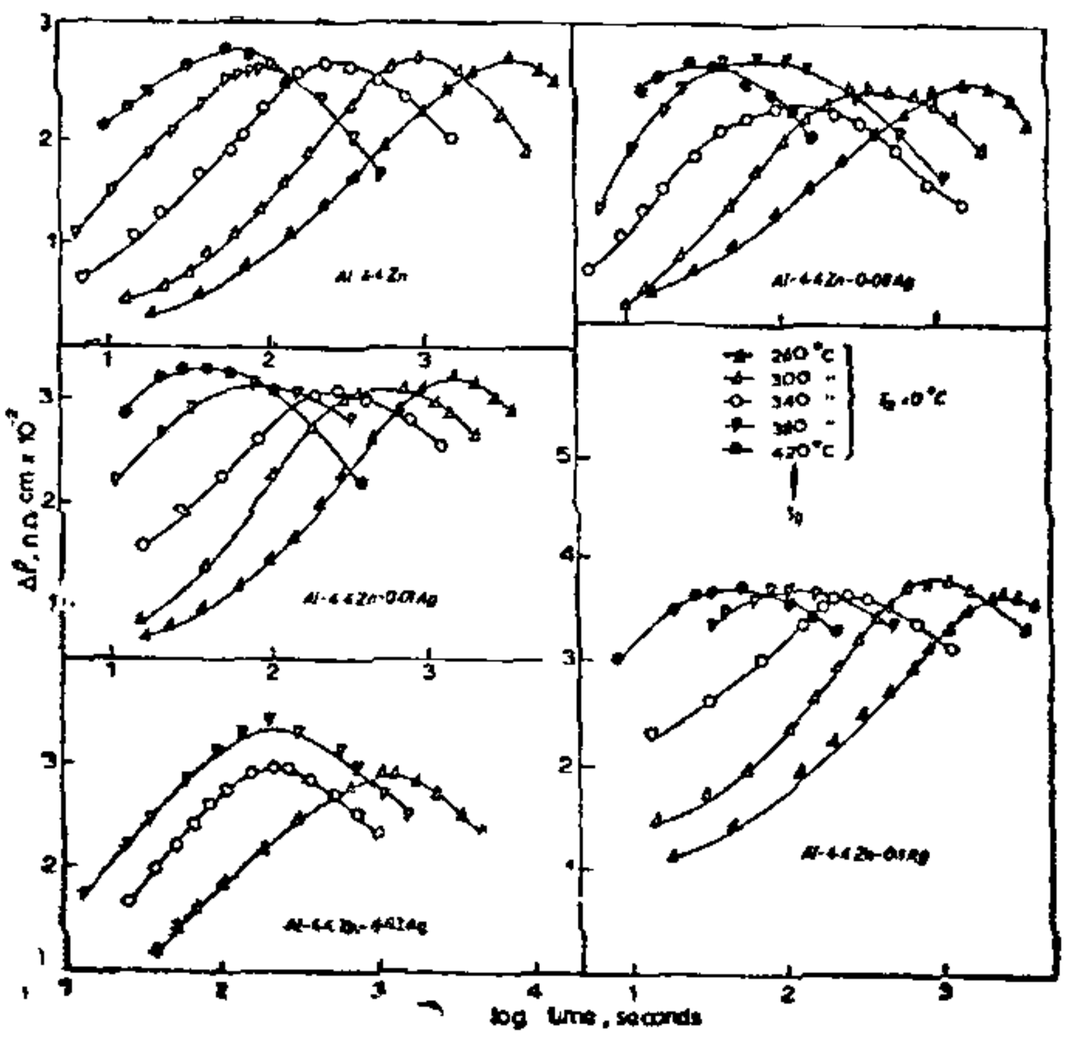

FIG. 2. Isothermal resistivity variation for the different alloys for ageing at 0° C.

If a ternary solute having considerable interaction energy with vacancies is added to a binary alloy containing a solute like zinc, having negligible interaction with vacancies, the ternary solute will act as a trap for the vacancies. If this solute-vacancy pair does not migrate to the clusters, then the concentration of excess quenched-in vacancies available for solute diffusion is considerably reduced, and as a consequence the ageing rate will be slowed down. If the time-to-peak for the ternary alloy is greater than that for the binary alloy, it is possible to evaluate the solute-vacancy binding energy by the ageing-ratio method. This has been done for Al-4·4% Zn alloy containing 0·03 and 0·08% Ag additions[5]. However, this method of evaluation is not strictly applicable to the Al-Zn-Ag alloys[8], and

hence silver-vacancy binding energy can be determined by considering the lowering of vacancy formation energy in the binary alloy by ternary additions of silver[8,9].

Dependency of v-Ag Binding Energy on Silver Concentration in the Al–Zn Alloy

TABLE I

Silver-vacancy binding energies for different Al-Zn-Ag alloys

Alloy	E_B^{v-Ag}, (± 0·02 eV)	Reference
Al–4·4 Zn–0·01 Ag	0·23	9, 10
Al–4·4 Zn–0·03 Ag	0·21	8
Al–4·4 Zn–0·08 Ag	0·21	8
Al–4·4 Zn–0·1 Ag	0·18	9, 10

Quere[11] indicated that in alloys with different solute concentrations, the solute-vacancy binding energy measured should remain practically independent of concentration at least when $12 \cdot C_i$ (C_i; solute atom fraction in the alloy) is much less than one In Al-Zn-Ag alloys, with different silver concentrations, there is a mild dependency of E_B^{v-Ag} on silver concentration (Table I). As the silver concentration is increased the silver-vacancy binding energy decreases. It can therefore be concluded that this type of behaviour, which is quite common in binary alloys[12], is observed in ternary alloys also.

Clustering Rate-reversal Temperature

The isothermal ageing curves for Al-Zn-Ag alloys for different quenching and ageing temperatures show a marked divergence from the normal behaviour of ternary additions to binary alloys. The time-to-peak for the ternary alloy, which should normally be greater than that for the binary alloy, under identical quenching and ageing conditions, is sometimes larger than, equal to, or even smaller than that in the binary alloy (all the isothermal ageing curves have not been included here)[9]. The silver additions to the Al-Zn alloy slows down the ageing rate only above a particular quenching temperature, which can be called the 'Clustering Rate-reversal Temperature', '$T_{q\cdot}$', since below this temperature the ageing rate of the ternary alloy is greater than that of the binary alloy. The magnitude of T_{qc} depends on the ageing conditions as well as the silver concentration.

The schematic diagram of log (t_m) against $1/T_q$ (Fig. 3) illustrates the Clustering Rate-reversal Temperature,

The values of T_{qc} obtained under different conditions of ageing for different Al-Zn-Ag alloys are collected in Table II. It is clear from these values that for a given silver concentration the $T_{q\cdot}$ is dependent on T_a and T_{qc} linearly decreases with T_a (Fig. 4). Further, the rate of increase of T_{qc} with decreasing T_a is seen to be independent of the silver concentration.

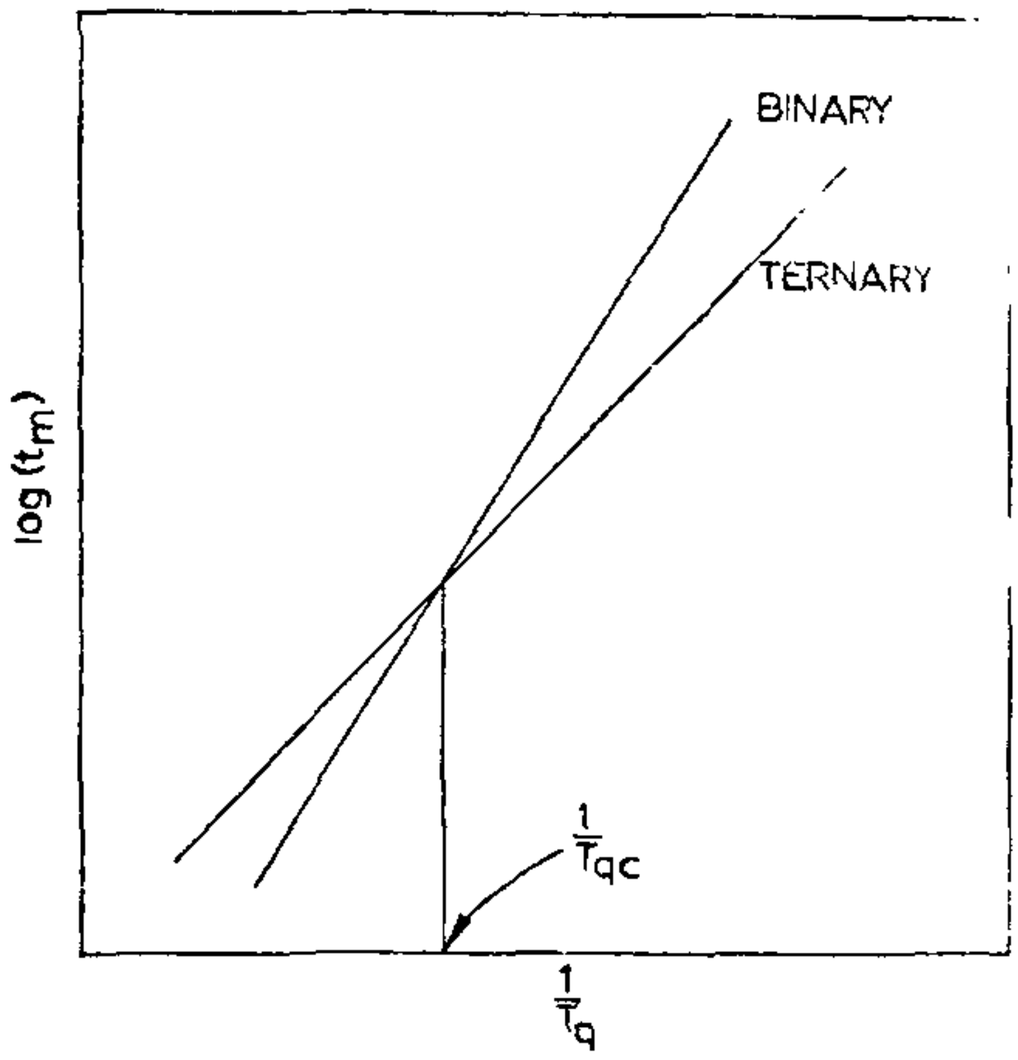

FIG. 3. Schematic diagram of log (time-to-peak) *vs.* reciprocal of quenching temperature to show the Clustering Rate-reversal Temperature.

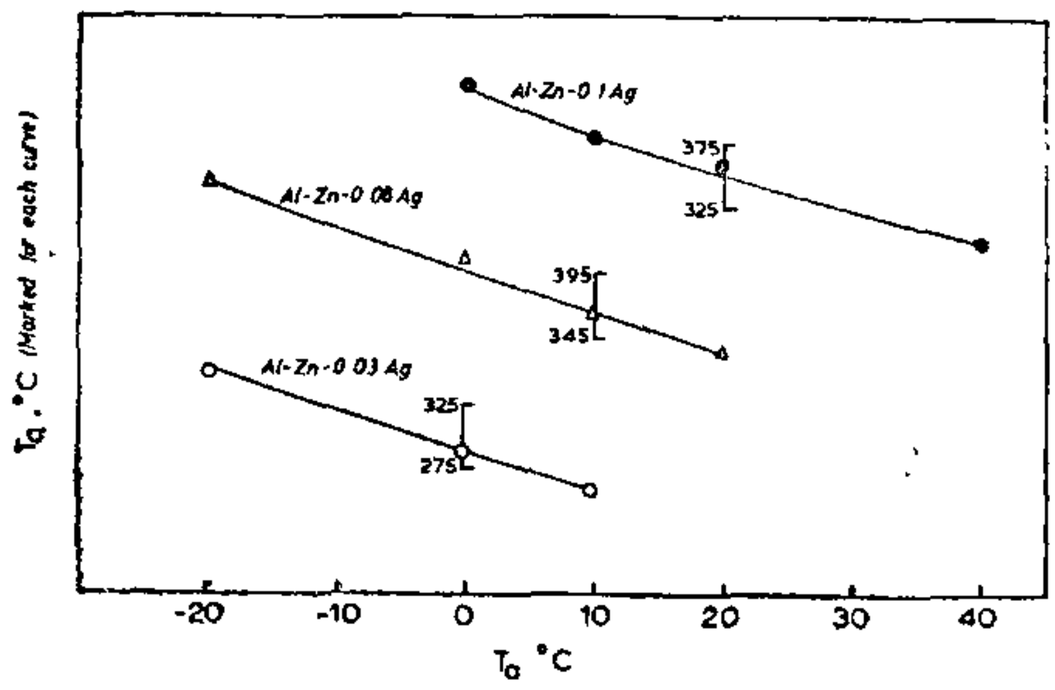

FIG. 4. Plot of Clustering Rate-reversal Temperature, *vs.* Ageing Temperature.

It is clear from the above results that for all the Al-Zn-Ag alloys studied, a Clustering Rate-reversal Temperature can be defined. The alloys behave normal above this temperature (*i.e.*, silver atoms slow down the clustering rate) and below this temperature the zone forming process is accelerated. Obviously, the binary and ternary alloys age at equal rates at the T_{qc}, and this was demonstrated by us, experimentally, in the case of Al-4·4 Zn alloy with 0·03 and 0·08% Ag additions[8],

TABLE II

Clustering Rate-reversal Temperature for Al-Zn-Ag alloys obtained under different conditions of ageing

Ageing Temperature °C	Clustering Rate-reversal Temperature, T_{qc}, °C			
	Al-Zn-0·01 Ag	Al-Zn-0·03 Ag	Al-Zn-0·08 Ag	Al-Zn-0·1 Ag
−20	..	350	420	..
0	260	290	365	420
10	..	260	320	380
20	..	..	290	360
40	..	..	..	300

Murakami *et al.*[7] observed an acceleration in the zone forming process by ternary zinc and magnesium atoms in Cu–Be alloys. Perry[13] indicated an interesting possibility in Al-Zn-Mg alloys, where the magnesium addition to the Al-Zn alloy could lead to the peak being achieved more quickly in the ternary alloy, due to its interaction with vacancies. In this investigation silver additions in different proportions to the Al-4·4% Zn alloy provide another such interesting case.

Entwistle *et al.*[14] reported that when the ternary atom added is a zone forming constituent (as silver is) and acquires a vacancy, as is evident from the silver-vacancy binding energy of ca. 0·2 eV, its migration will be high through the mechanism[15] involving the movement of the solute-vacancy complexes (ν-Ag) through the solvent lattice by cycles of invertion and reorientation. The ternary solute would accelerate the ageing process when both binary (zinc) and ternary (silver) solutes are rapidly transported simultaneously through the formation of clusters composing of the atoms of the two solute species and an associated vacancy. These can migrate to zones by a continual interchange of the vacancy with the clusters and the surrounding solvent atoms. It was proposed earlier[8] that since silver and zinc atoms have sizes close to that of aluminium (1·442, 1·379 and 1·429 Å respectively) the major contribution to the binding energy must be the electronic one. From isothermal resistivity data, there does not appear to be any interaction between silver and zinc atoms[16]; these merely form clusters separately and simultaneously, leading to an acceleration in the clustering rate.

Rudman *et al.*[17] observed small clusters in equilibrium at the solutionizing temperature by X-ray analysis. Walker *et al.*[18] have shown that clustering can occur at solution treatment temperatures, and from these embryonic clusters, larger clusters are developed during ageing. Also, the clusters formed during quenching may have different stabilities depending on the conditions of formation, such as quenching temperature used, quenching medium and quenching rate[7]. The clusters forming during quenching will not have any marked effect on the ageing process, if these are of the same kind as those formed during ageing[16].

In Al-Zn-Ag alloys, quenched from below the T_{qc}, the zone forming process is accelerated. This is favoured by the like-neighbour interaction at lower quenching temperatures, which promotes the formation of two types of zones (silver and zinc rich), separately and simultaneously. For alloys quenched from above the T_{qc}, solute atoms approach more and more towards singular distribution and consequently the alloy tends to behave normal, *i.e.*, the ternary solute atoms decrease the clustering rate due to the vacancy trapping.

Relationship between Isothermal Resistivity Data and Silver Concentration

In addition to the effect of T_a and T_q, the time-to-peak, t_m, and the magnitude of the resistivity peak, $\Delta\rho_m$, are both dependent on silver concentration in the Al-Zn alloy (Fig. 5). The variation is however similar, in all the cases. An increase upto a concentration of 0·03% Ag, followed by a decrease for higher concentrations and a final increase beyond 0·08% Ag in the alloy. The peak resistivity for isochronal annealing (also plotted in Fig. 5) is also dependent on the silver concentration.

The $\Delta\rho_m$ can be taken to be an index of the zone concentration[13]. This clearly shows that the number of zones forming under identical conditions of quenching and ageing is strongly dependent on the silver concentration in the alloy. In the case of Al-Zn-Ag alloys, which exhibit the Clustering Rate-reversal Temperature, T_{qc}, the time-to-peak will be a complicated function of the quenching

and ageing temperatures, and even this is seen to depend on the silver concentration, as in the case of the peak value of resistivity.

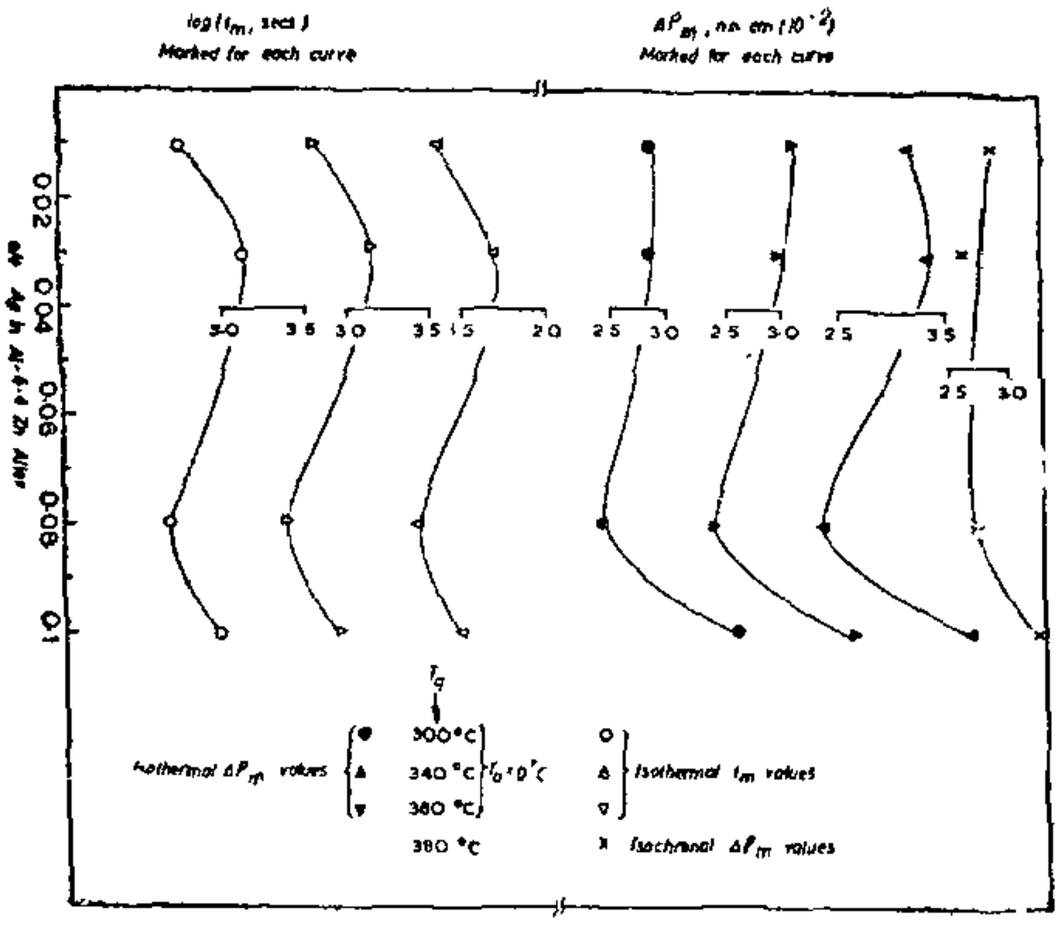

FIG. 5. Isothermal and isochronal ageing data against the silver concentration in the Al-Zn alloy.

CONCLUSIONS

The influence of silver on the clustering process in Al-Zn alloys is dependent on both T_q and T_a and also on the silver concentration. Al-Zn-Ag alloys provide an interesting case for studying the pre-precipitation processes in quenched alloys.

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USE OF LINEATION IN THE DETERMINATION OF FOLDS

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ABSTRACT

Lineation, as represented by the parallel arrangement of elongate quartz grains in quartzite, has been relied upon to interpret the folded nature of the rocks of Closepet-Satnur area in Bangalore District, South India. The maximum elongation of quartz grains is due to rotation around the fold axis *b* of the fold. Since the lineation is N-S, the rocks of Closepet-Satnur area must have undergone folding with fold axis striking N-S. The folded nature is confirmed by Petrofabric analyses.

THE AREA INVESTIGATED

FOLDS in rock formations are identified in the field if they are on a mesoscopic scale. If they are on a megascopic scale, that is, when folds are regional with limbs thrown apart for several miles, reliance is placed on converging and diverging dips of the beds and on the orderly repetition of the beds as revealed after mapping. The difficulty of identifying the folded structure of a regional kind arises when the beds dip in the same direction, as in an overfold or an isoclinal fold, and when the repetition of the beds is inconstant, because of the variation in composition within a single sedimentary