

A model for two-step ageing

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Abstract. In commercial practice, two-step ageing is commonly used in Al–Zn–Mg alloys to produce a fine dispersion of h' precipitates to accentuate the mechanical properties and resistance to stress corrosion cracking. While this is true in Al–Zn–Mg alloys, two-step ageing leads to inferior properties in Al–Mg–Si alloys. This controversial behaviour in different alloys can be explained by Pashley's Kinetic model. Pashley's model addresses the stability of clusters after two-step ageing. In the development of the model, the surface energy term between cluster and matrix is taken into account while the coherency strains between the cluster and matrix are not considered. In the present work, a model is developed which takes into account the coherency strains between cluster and matrix and defines a new stability criterion, inclusive of strain energy term. Experiments were done on AA 7010 aluminium alloy by carrying out a two-step ageing treatment and the results fit the new stability criterion. Thus it is found that the new model for two-step ageing is verified in the case of Al–Zn–Mg alloy.

Keywords. Two-step ageing; delayed ageing; clusters; coherency strains.

1. Introduction

In Al–Zn–Mg alloys, preageing at a lower temperature after solutionizing, followed by a higher temperature artificial ageing is known to give a fine dispersion of h' precipitates (Lorimer and Nicholson 1966) and thus enhance the mechanical properties. While this is true in Al–Zn–Mg alloys, in Al–Mg–Si alloys, room temperature storage after solutionizing, followed by high temperature artificial ageing leads to a coarse precipitate (b') structure (Pashley *et al* 1966). This phenomenon is termed delayed ageing wherein the delay after solutionizing before ageing leads to inferior properties (Ghate *et al* 1984; Murali *et al* 1993).

Pashley *et al* have put forth a kinetic model to describe the stability of clusters after two-step ageing, which qualitatively explains the controversy between Al–Zn–Mg and Al–Mg–Si alloys. In Pashley's kinetic model, a parameter K is defined which is proportional to the surface energy between the cluster and matrix which determines the stability of distribution of clusters in two-step ageing. In the case of Al–Zn–Mg alloys, fine scale seeding takes place at a lower temperature ageing which gets stabilized at higher temperature ageing resulting in a fine dispersion of h' precipitates. However in Al–Mg–Si alloys only the coarse clusters are stabilized at the artificial ageing tem-

perature and this leads to a coarse distribution of b' precipitates.

While Pashley's kinetic model addresses the surface energy between the cluster and the matrix, the elastic coherency strains between them are not considered. Therefore it is the objective of the present work to include coherency strains between the cluster and matrix in the development of the Pashley's kinetic model (extended Pashley's model) and verify the same.

2. The model

In the present model, elastic strains between the cluster and matrix are considered. The elastic strains are introduced via the classical definition of Gibbs free energy. Thus the Gibbs–Thomson relationship is modified in that not only the curvature effect is considered in terms of the partial molar free energy but also elastic strain energy is included. The Gibbs–Thomson relationship is the one that describes the solubility as a function of curvature of an interface. Here only the surface energy and curvature have an influence on solubility. In the modified Gibbs–Thomson relationship not only the curvature and surface energy have an influence on the solubility but also the elastic strain energy. Using the modified Gibbs–Thomson relationship, the criterion for the stability of the clusters is derived for two-step ageing. Further, it is also assumed that the elastic modulus of the cluster is greater than that

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of the matrix and therefore the coherency strains are accommodated in the matrix.

It is known from classical thermodynamics (Fast 1970), that Gibbs free energy can be expressed as

$$G = U - TS + \sum XY, \quad (1)$$

where G is the Gibbs free energy, U , the internal energy, S , entropy, T , absolute temperature, $\sum XY$ the work done due to elastic strains, thus $\sum XY$ can be expressed as two terms viz. volume work (PdV) and work done due to elastic strains, thus

$$G = U - TS + PV + V_m \sigma \left(\frac{\dot{a}}{2} \right), \quad (2)$$

V_m is molar volume, σ , stress in the matrix which is elastic.

Differentiating (2), we have

$$dG = dU - TdS - SdT + PdV + VdP + \frac{V_m}{2} \sigma d\dot{a} + \frac{V_m}{2} \dot{a} d\sigma. \quad (3)$$

Assuming reversibility, the term dU can be expressed as

$$dU = TdS - PdV - \frac{V_m}{2} \sigma d\dot{a}. \quad (4)$$

Substituting (4) in (3)

$$dG = VdP + \frac{V_m}{2} \dot{a} d\sigma - SdT.$$

At constant temperature ($dT = 0$),

$$dG = VdP + \frac{V_m}{2} \dot{a} d\sigma. \quad (5)$$

Assuming the elastic strains to be small, i.e. Hooke's law is valid,

$$\sigma = Ee,$$

where E is the Young's modulus,

$$d\sigma = Ede. \quad (6)$$

Substituting (6) in (5),

$$dG = VdP + \frac{V_m}{2} eEde.$$

Expressing the above relationship in terms of partial quantities,

$$d\bar{G}_i = \bar{V}_m dP + \frac{\bar{V}_m}{2} eEde. \quad (7)$$

Integrating (7) for a curved interface,

$$\bar{G}_{i,r} - \bar{G}_{i,\infty} = V_m (P_r - P_\infty) + \frac{V_m E \dot{a}^2}{4}, \quad (8)$$

$$= V_m \Delta P + \frac{V_m E e^2}{4}, \quad (8a)$$

where, $G_{i,r}$ is the partial molar free energy of a curved interface of radius 'r', $G_{i,\infty}$ the partial molar free energy of a flat interface and P_r , P_∞ are pressures across a curved interface and a flat interface respectively.

It is known from classical thermodynamics (Fast 1970) that

$$\bar{G}_{i,r} - \bar{G}_{i,\infty} = RT \ln \left(\frac{a_{i,r}}{a_{i,\infty}} \right). \quad (9)$$

Combining (9) and (8a), where $a_{i,r}$, $a_{i,\infty}$ are the activity of the solute in a curved interface and flat interface, respectively

$$RT \ln \left(\frac{a_{i,r}}{a_{i,\infty}} \right) = \bar{V}_m \dot{a} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{V_m E \dot{a}^2}{4}.$$

Since

$$\Delta P = g \left(\frac{1}{r_1} + \frac{1}{r_2} \right),$$

where, g is the surface energy and r_1 , r_2 , are the principal radii of curvature (Porter and Easterling 1992).

Assuming ideal solution behaviour,

$$a_i = X_i,$$

where X_i is the concentration,

$$RT \ln \left(\frac{X_{i,r}}{X_{i,\infty}} \right) = V_m \dot{a} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{V_m E \dot{a}^2}{4}. \quad (10)$$

Assuming spherical clusters (it is believed that the physical reasoning behind the model is not altered because of the cluster shape)

$$\ln \left(\frac{X_{i,r}}{X_{i,\infty}} \right) = \left(\frac{V_m g(2)}{RT r} + \frac{V_m E e^2}{4RT} \right)$$

$$X_{i,r} = X_{i,\infty} \left(\exp \left(\frac{V_m 2g}{RT r} + \frac{V_m E e^2}{4RT} \right) \right). \quad (11)$$

This is the modified Gibbs-Thomson relationship where not only curvature has an effect on the solubility but also strains between the cluster and matrix.

In the original Pashley's model (Pashley *et al* 1967), the stability of the clusters is dictated by the condition that the rate of arrival of solute to the cluster should be greater than the rate of departure of solute from the cluster.

Pashley *et al* (1967) have given the condition to be

$$AX_{\infty}S > BX, \tag{12}$$

where, A is the coefficient which determines the rate of arrival of solute to the clusters which is proportional to the diffusion coefficient and excess vacancies. S is the supersaturation = $W(1 - a)/X_{\infty}$, W , being the weight of the solute/unit volume, a the fraction of solute in the clusters. X_{∞} , concentration of the solute in equilibrium with a flat interface, X , concentration of the solute in equilibrium with a curved interface and B , the kinetic coefficient.

The Gibbs–Thomson relationship without elastic strains is

$$X_{i,r} = X_{i,\infty} \exp\left(\frac{V_m 2g}{RT r}\right). \tag{13}$$

Substituting (13) in (12) for X , Pashley arrived at the stability criterion,

$$AX_{\infty} > BX_{i,\infty} \exp\left(\frac{V_m 2g}{RT r}\right),$$

$$\text{i.e. } r \ln\left(\frac{A}{B}\right)S > \left(\frac{V_m 2g}{RT}\right). \tag{14}$$

Letting,

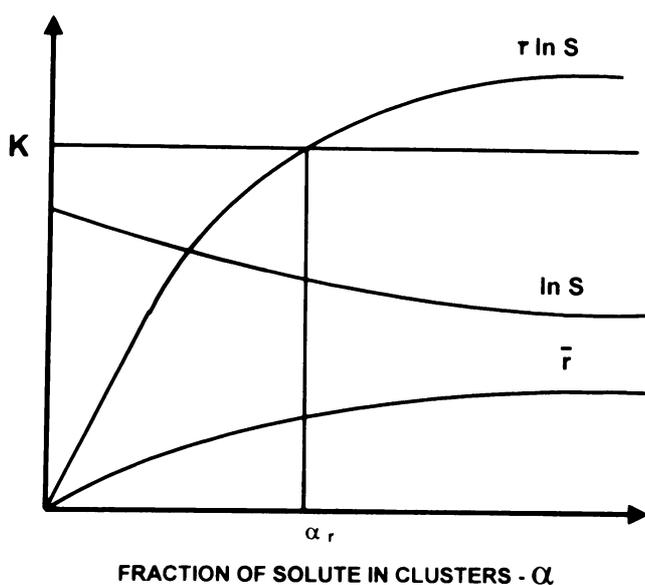


Figure 1. Schematic illustration of stability of clusters in two-step ageing.

$$K = \frac{V_m 2g}{RT},$$

(14) becomes

$$r \ln\left(\frac{A}{B}\right)S > K. \tag{15}$$

If it is assumed that no excess vacancies are present, $A = B$, (15) becomes

$$r \ln S > K. \tag{16}$$

This is the stability criterion in the original Pashley's model.

Furthermore, assuming spherical clusters, mass balance of the solute leads to the following

$$\sum \frac{4}{3} \pi r^3 n_r = aW, \tag{17}$$

where, r is the density of the cluster species, n_r , the number of cluster per unit volume.

Figure 1 shows these relationships schematically, with a delay at a lower temperature (T_1), a increases and supersaturation in the matrix decreases and when $a > a_c$, the clusters are stabilized at the artificial ageing temperature (T_2).

Figure 2 shows the effect of size distribution of clusters on the stability after two step-ageing. At a lower temperature (T_1), clustering will take place resulting in a size distribution of clusters. The size distribution can be assumed to be gaussian and accordingly the variation of r

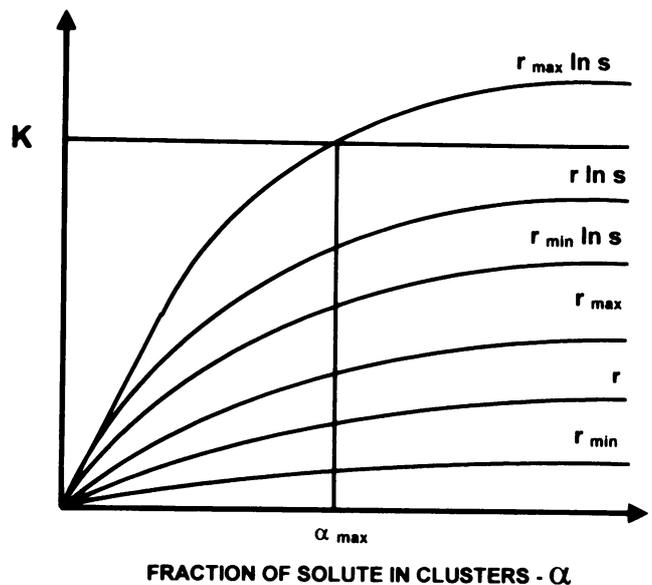


Figure 2. Schematic illustration of stability of clusters with size distribution in the original model.

with a can be represented as shown in figure 2. In a similar way the term $r \ln S$ is also shown in figure 2. It is seen that when $a > a_{r,max}$, only the coarse clusters are stabilized at the artificial ageing temperature (T_2) after a delay at the lower temperature (T_1). This effect explains the behaviour of Al–Mg–Si alloys which show delayed ageing (Murali *et al* 1993) where room temperature storage (T_1) gives rise to a coarse precipitate structure after artificial ageing (T_2).

Now, considering the elastic strains between the cluster and the matrix, the modified Gibbs–Thomson relationship (11), Pashley’s criterion ($AX_\infty S > BX$ (i.e. (12)) for stability on clusters after two-step ageing can be expressed as

$$AX_\infty S > BX_{i,\infty} \exp\left(\frac{V_m 2g}{RT r} + \frac{V_m E e^2}{4RT}\right).$$

By substituting (11) in (12)

$$\ln\left(\frac{A}{B}\right) S > \left(\frac{V_m 2g}{RT r} + \frac{V_m E e^2}{4RT}\right),$$

$$r \ln\left(\frac{A}{B}\right) S > \left(\frac{V_m 2g}{RT} + r \frac{V_m E e^2}{4RT}\right).$$

Letting

$$K = \frac{V_m 2r}{RT}, \quad Q = \frac{V_m E e^2}{4RT},$$

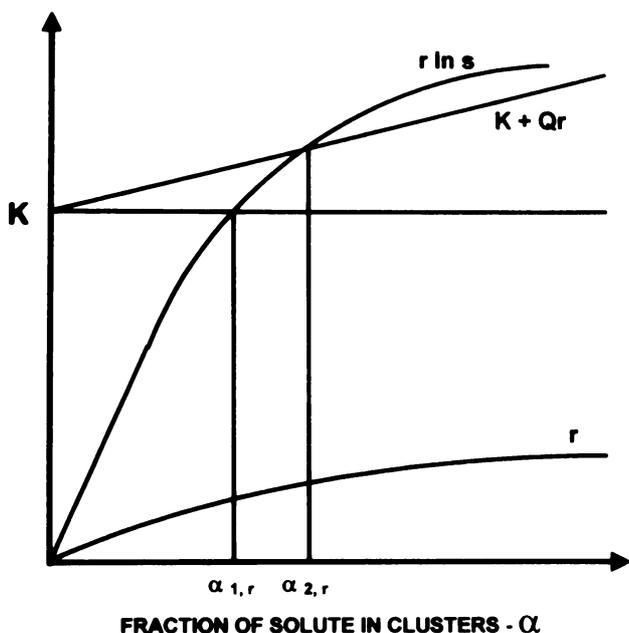


Figure 3. Schematic illustration of stability of clusters considering elastic strains.

$$r \ln\left(\frac{A}{B}\right) S > K + Qr. \tag{18}$$

Equation (18) is thus the general stability criterion for clusters which introduce elastic strains in the matrix.

If it is assumed that there are no excess vacancies, $A = B$, then (18) becomes

$$r \ln S > K + Qr. \tag{19}$$

Figure 3 shows the stability diagram for clusters after two-step ageing with K and $K + Qr$. It is clearly shown in the figure that the clusters with $a_{1,r}$ get stabilized when no strain is considered in the matrix. On the other hand, when elastic strains are considered, a much longer delay representing a situation like a_2 , (where $a_2, r \gg a_1, r$) is required for the cluster to stabilize. Thus it can be stated that clusters will find it more difficult to stabilize with the introduction of coherency strains.

Figure 4 shows the effect of size distribution of clusters with increase in delay at T_1 (lower temperature) corresponding to increased a . It can be seen from figure 4 that only the large sized clusters are stabilized at $a_{r,max}$ in the original Pashley’s model whereas with coherency strains such clusters are also destabilized. In the original model, such behaviour would have led to delayed ageing wherein a coarse precipitate structure is evolved upon delay. But with large coherency strains (large Q) delayed ageing is not expected.

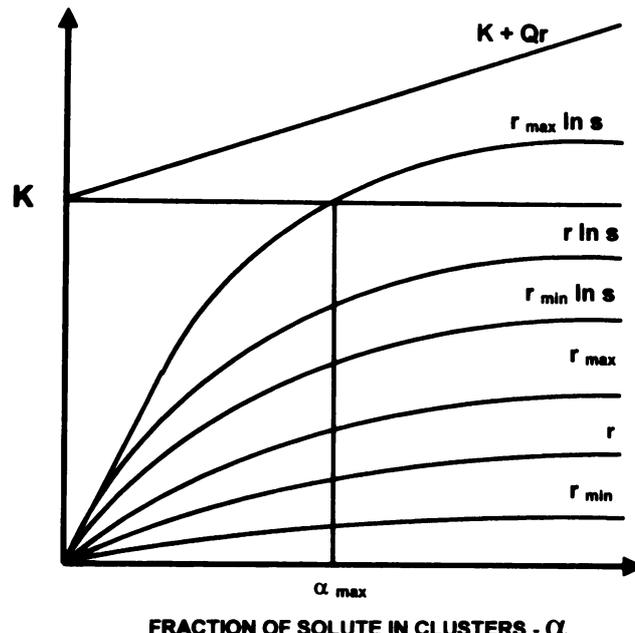


Figure 4. Schematic illustration of stability of clusters with size distribution considering elastic strains.

3. Experimental

In order to test the extended Pashley's model, alloy AA 7010 was selected for delayed ageing studies. The composition of AA7010 is given in table 1.

Samples were sectioned and heat treated AA 7010 samples were solutionized at 748 K for 50 min and water quenched. The samples were delayed for 0, 2, 4, 20 and 68 h respectively and then artificially aged at 443 K for 24 h. Samples were machined and tested for mechanical properties in an universal testing machine.

4. Results and discussion

Table 2 shows yield strength as a function of delay in artificial ageing for AA7010 alloy. There is no substantial drop in the tensile strength with delay in ageing. The percentage drop in the tensile strength is only 7.42% with 20 h delay whereas in Al-Mg-Si alloy (Murali *et al* 1993), the percentage drop in tensile strength is 15%. Thus it can be seen that delayed ageing is more severe in Al-Mg-Si alloy.

To rationalize the above results, the following analysis was carried out. The elastic strain free energy is given by Eshelby (Cahn *et al* 1991) as,

$$\Delta G_{el} = 2G \left(\frac{1+\nu}{1-\nu} \right) d^2,$$

where, G is the shear modulus, ν , the Poisson ratio.

$$d, \text{ the misfit strain parameter} = \frac{a_{ppt} - a_{matrix}}{a_{matrix}},$$

a_{ppt} is the lattice parameter of the precipitate, a_{matrix} , the lattice parameter of the matrix.

To relate elastic strain in the matrix due to coherency strains between precipitate and matrix

$$\frac{1}{2} se = \Delta G_{el} = 2G \left(\frac{1+\nu}{1-\nu} \right) d^2.$$

$$\frac{1}{2} Ee^2 = 2G \left(\frac{1+\nu}{1-\nu} \right) d^2.$$

Table 1. Compositions of AA 7010 and LM25.

	Element							
	Zn	Mg	Li	Cu	Zr	Si	Fe	Al
AA 7010 (wt %)	6.2	2.5	-	1.5	-	-	-	Bal
LM 25 (wt %)	-	0.3	-	-	-	7.0	0.5	Bal

Therefore,

$$e = \sqrt{\frac{4G}{E} \left(\frac{1+\nu}{1-\nu} \right)} d. \quad (20)$$

It is known that,

$$G = \frac{E}{2(1+\nu)} = 26.12 \text{ GPa for aluminium,}$$

$$E = 70 \text{ Gpa,}$$

$$\nu = 0.34.$$

Table 3 shows the misfit strain calculations for intermediate precipitate based on the orientation relationship with the matrix for several aluminium alloys. From the values of misfit strain (d), the corresponding elastic strains (e) have been evaluated using the relationship (20) and are recorded in table 3. It can be seen that the misfit strain parameter for Al-Mg-Si alloy is very small whereas in Al-Zn-Mg alloy, it is very large. Similarly elastic strain 'e' is large for Al-Zn-Mg and small for Al-Mg-Si alloy.

It should be noted from recent literature (Maloney *et al* 1999; Murayama and Hono 1999), that the chemistry of the GP zones by atom probe and field ion microscopy in Al-Zn-Mg and Al-Mg-Si alloys, respectively is determined. The composition of the GP zone in Al-Mg-Si alloys is 50 at% Mg, 50 at% Si. The composition of GP zone in Al-Zn-Mg alloy is given by 8.7 at% Zn, 6.3 at% Mg giving a ratio of Zn : Mg of 1.4 : 1.

Table 2. Effect of delay in ageing on the tensile strength of AA 7010 alloys.

Delay (h)	Alloy 7010 (Al-Zn-Mg)		LM 25 (Al-Mg-Si)	
	YS (Mpa)	% Red. (UTS)	YS (Mpa)	% Red. (UTS)
0	512	-	230	-
20	474	7.42	195	15.2

Table 3. Misfit strain values.

Alloy	Al-Zn-Mg	Al-Mg-Si	Al-Cu-Mg
Intermediate precipitate	h'	b'	S'
Orientation relationship	(001) h' (111) a	(001) b (100) α	(210) S (100) S
Misfit (d) %	-23.75	-7.4×10^{-3}	-0.1216
Elastic strain (e)	-0.4134	-0.128×10^{-3}	-2.1×10^{-3}
h' (MgZn ₂)	hexagonal	$a = 4.96 \text{ \AA}$	$c = 8.68 \text{ \AA}$
b' (Mg ₂ Si)	hexagonal	$a = 7.05 \text{ \AA}$	$c = 4.05 \text{ \AA}$
S' (Al ₂ CuMg)	orthorhombic	$a = 4.04 \text{ \AA}$ $c = 7.18 \text{ \AA}$	$b = 9.25 \text{ \AA}$

Table 4. Misfit strain values (GP zones).

Alloy	Al-Mg-Si	Al-Zn-Mg
Volume per atom	24.09 Å ³	31.136 Å ³
Volume per atom (matrix)	24.60 Å ³	29.520 Å ³
Misfit δ	0.02073	-0.0597

Taking atomic ratio of Al, Mg, Si, Zn, the volume per atom of the GP zones is calculated. Table 4 shows results of the calculation. It is seen the misfit strain (difference between volume/atom of zones and matrix) is low (0.02073) for Al-Mg-Si alloy whereas it is high for Al-Zn-Mg alloy (-0.0547). Using (20) the elastic strain is also calculated. It is also shown in table 4.

From the model, the stability criterion for clusters after two-step ageing is given by the following equation

$$r \ln S > K + Qr, \quad (19)$$

where,

$$K = \frac{2gV_m}{RT}, \quad Q = \frac{Ee^2}{4RT},$$

Q is a dimensionless quantity whereas K has units of length.

Assuming, $V_m = 10^{-5} \text{ m}^3/\text{mole}$, $g = 0.5 \text{ J/m}^2$ (typical surface energy), $R = 8.31 \text{ J/mole}^{-1} \text{ K}^{-1}$, $T = 453 \text{ K}$ (typical artificial ageing temperature) $K = 2.65 \text{ nm}$, Q has been calculated for Al-Zn-Mg and Al-Mg-Si alloys while Q for Al-Zn-Mg alloys comes to a large value of 7.94, it is a very low value of 7.61×10^{-7} for Al-Mg-Si alloy.

Using the elastic strain from table 4, Q has been calculated for Al-Mg-Si and Al-Zn-Mg alloys. It comes to 2.9194×10^{-4} for Al-Mg-Si whereas 7.7×10^{-4} for Al-Zn-Mg.

This calculation reveals that the trend of increasing Q and Qr values from Al-Mg-Si alloy to Al-Zn-Mg alloy is consistent with the calculation of the same quantities for intermediate precipitates.

A reasonable assumption for cluster size would be $r = 10 \text{ nm}$ (100 Å). The term ' Qr ' is calculated for Al-Zn-Mg and Al-Mg-Si alloys. Qr for Al-Zn-Mg alloy comes to 7.94 nm whereas for Al-Mg-Si it is only $76.1 \times 10^{-7} \text{ nm}$.

Now the modified stability diagram is schematically shown in figure 5. It can be seen from the figure that clusters are destabilized for Al-Zn-Mg alloy after two-step ageing whereas they would be stabilized for Al-Mg-Si alloy.

This explains how the coarse clusters are stabilized at the artificial ageing temperature in Al-Mg-Si alloys and

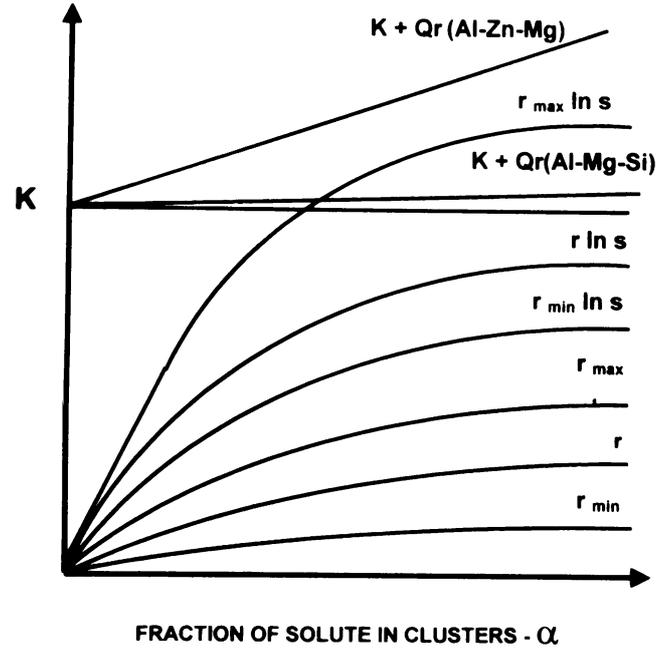


Figure 5. Schematic illustration of stability situation for Al-Mg-Si and Al-Zn-Mg alloys.

thus results in lower mechanical properties as observed. However in the case of Al-Zn-Mg alloys the clusters are destabilized however large they are because of large Qr and this results in fine and uniform precipitation of h' at the artificial ageing temperature leading to insignificant drop in mechanical properties.

5. Conclusions

- (I) A term to consider the effects of coherency strains between cluster and matrix has been successfully incorporated in the original Pashley's model.
- (II) Experimental results show an insignificant drop in mechanical properties for AA 7010.
- (III) The high coherency strain between the cluster and matrix has been shown to be responsible for the reduction of delayed ageing in AA7010 alloy. It is also argued that low coherency strain between the cluster and matrix is the reason for delayed ageing in Al-Mg-Si alloy.
- (IV) According to the extended Pashley's model developed in the present study, cluster stability definitely gets affected due to elastic coherency strains in the matrix. The prediction of the new model has been verified.

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