

## **The thermodynamics of and strengthening due to co-clusters: general theory and application to the case of Al-Cu-Mg alloys**

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### **Abstract**

Co-clusters in ternary or higher order metallic alloys are metastable structures involving two or more distinct alloying atoms that retain the structure of the host lattice. A thermodynamic model based on a single interaction energy of dissimilar nearest neighbour interaction energy is presented, and a model for the strengthening due to these co-cluster dimers is derived. The model includes a new treatment of (short-) order strengthening relevant to these co-clusters and further encompasses modulus hardening and chemical hardening. The models are tested against data on a wide range of Al-Cu-Mg alloys treated at temperatures between 20 and 220°C. Both quantitative calorimetry data on the enthalpy change due to co-cluster formation and strengthening due to co-clusters is predicted well. It is shown that in general (short-range) order strengthening will be the main strengthening mechanism.

Keywords: Ageing; nanostructure; modelling; thermodynamics; short range ordering

### **Introduction**

#### **Clusters, co-clusters and their strengthening in metallic alloys**

The prevailing theory of strengthening of metallic alloys as developed since the 1930s recognises the contributions to the critical resolved shear stress of grains with dilute compositions as being due to the obstacles to dislocation motion in the form of solute atoms and stable or metastable second phases. These second phases often form in a precipitation process from a supersaturated solution, and several metastable structures can appear before ultimately the stable phase or phases are formed. These precipitates can be very small: precipitates as small as 10 atoms have been proposed. These small precipitates are effectively formed from a metastable solution through a solute clustering process, i.e. the clustered solute atoms are situated on position of the host lattice. If the clusters formed involve two alloying elements, the term co-clusters is employed; the simplest form of a co-cluster is a dimer (Fig. 1). In most microstructural investigation techniques, including transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) clusters of this small size can not be resolved. But atom probe experiments do allow detection of the clusters, and in the past two decades, 3D atom probe has allowed the identification of clusters as small as 10 atoms in alloys such as in maraging Fe-20Ni-1.8Mn-1.5Ti-0.59Al steel [1], Fe-C-Mn-Si steels with additions of Nb, Al and Mo [2], Al-Zn-Mg(-Cu) [3,4], Al-Mg-Ag [5], Al-Si-Mg [6]

and Al-Cu-Mg based alloys [7] (in the aluminium alloys the term Guinier-Preston (GP) zone has been associated with these clusters). The picture starting to emerge from two decades of atom probe work is that whenever the early stages of decomposition of solution treated alloys with significant alloying additions (significant in terms of influencing mechanical properties) are investigated, clusters or co-clusters are in most cases detected.

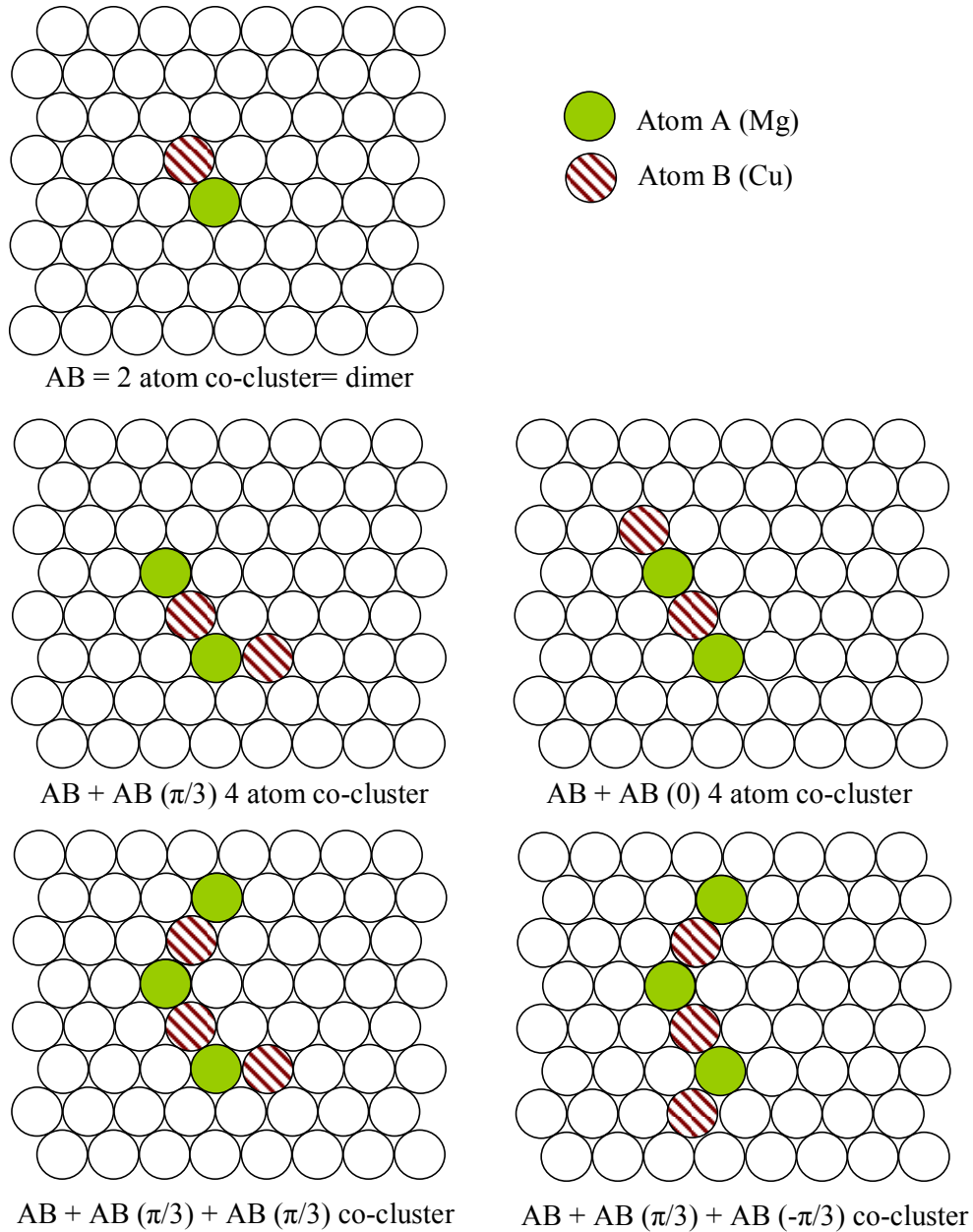


Fig. 1 A 111 plane in an FCC lattice in a ternary alloy containing co-clusters, with a notation describing the co-cluster constellation.

Hardening due to the clusters and co-clusters has been invoked as a qualitative explanation for strengthening of a range of alloys. However, attempts at providing a quantitative explanation of the strengthening effect of clusters and co-clusters have been limited and have been based on a limited physical basis. In this paper we will present a theory for the thermodynamics of and the

strengthening due to co-clusters in metallic alloys; thus providing the theoretical basis for this strengthening mode in metallic alloys. The model is applied to Al-Cu-Mg alloys and tested against an extensive amount of published and new data. This alloy system is chosen for the interlinked reasons of alloy availability, data availability, relative ease of sample preparation and analysis, and importance in engineering applications. Al-Cu-Mg alloys are extensively used for lightweight, fatigue resistant structures such as lower wing skins and fuselage of airplanes [8,9] as well as a range of other applications. The general validity of the theory is thought to not be limited to the investigated alloys: the developed theory will indicate that co-cluster formation should occur in many supersaturated alloys.

The method of choice for identifying thermodynamics of the co-clusters is calorimetry, as through calorimetry both the enthalpy changes of the system and the metastable solvi can be determined. However, calorimetry, in isolation, can not identify clusters or phases. Indications for the existence of co-clusters have mostly been obtained with 3 dimensional atom probe (3DAP) (and more recently supported by Nuclear Magnetic Resonance (NMR) [10,11], X-ray absorption spectroscopy (XAS) [12] and positron annihilation lifetime spectroscopy (PALS) studies [13]).

### **Co-clusters in Al-Cu-Mg alloys**

For solution treated Al-Cu-Mg based alloys with composition in the  $\alpha$ +S phase field, room temperature hardening occurs within several days (several weeks if the Cu content is very low) and hardening during artificial ageing is very fast, typically within minutes [14,15,16]. Whilst diverging explanations have been proposed for this phenomenon, recent experiments in combination with careful reassessment of existing evidence has indicated that the phenomenon is caused by Cu-Mg co-clusters [7]. In assessing the experimental evidence, we should note that immediately after the rapid hardening and during the room temperature hardening in these Al-Cu-Mg based alloys no distinct precipitate phase can be detected by conventional TEM [17], but differential scanning calorimetry (DSC) experiments clearly show a change in the free energy of the alloys indicating that a significant fraction of the dissolved atoms have been involved in a reaction [18,19]. There are no reports of any ordered structures at this stage. Results from several atom probe field ion microscopy (APFIM) and three-dimensional atom probe (3DAP) studies reveal Cu-Mg co-clusters of typically 1 nm diameter (10-40 atoms) [7,20,21] which by some authors are held directly responsible for the rapid hardening reaction [20,21]. Information on the composition of Cu-Mg co-clusters is limited. Ringer et al. [20,21] observed that in a high purity Al-1.7at.%Mg-1.1at.%Cu aged for 5 min at 150°C clusters with high Cu:Mg ratios existed, whilst Starink et al. [7] found that in an Al-2.78wt%Cu-0.44wt%Mg and in an Al-2.78wt%Cu-1.05wt%Mg (both alloys are commercial purity with Mn additions) the Mg/Cu ratio of the clusters varied from one cluster to another. They also contain vacancies [17].

Due to the discovery of rapid hardening Al-Cu-Mg based alloys early in the 20<sup>th</sup> century, and its subsequent extensive application, the reaction has been extensively studied and it can be considered one of the classic issues in metallurgy. But early researchers did not have the benefit of HREM and atom probe analysis, and some unsubstantiated assumptions have entered the literature. Especially

in pre-1990s work early hardening reaction in Al-Cu-Mg alloys was attributed to the formation of Cu and Mg containing structures which were termed Guinier-Preston-Bagaryatski (GPB) zones [22]. This term was coined in the 1950s and has been used for decades without evidence of what they may consist of. Consequently a range of often conflicting interpretations of these GPB zones have appeared in the literature. Only very recently a clearer picture of GPB zones using scanning transmission electron microscopy (STEM) supported by first principle modelling of the structures is starting to emerge [23]. It is the opinion of the authors that due to differing interpretation of its meaning and the lack of experimental evidence, the term ‘GPB zone’, as related to the rapid hardening in Al-Cu-Mg based alloys, has become an obstacle to the proper understanding of the mechanisms for rapid hardening. Hence we will here avoid using the term as much as possible.

## A model for the thermodynamics of and strengthening due to co-clusters

### The thermodynamics of co-clusters

For modelling the thermodynamics of the co-clusters one may consider the possibility of the co-clusters forming a range of possible constellations in the FCC lattice. From a virtually unlimited number of possible constellations, some possible constellations that are thought to be energetically favoured in Al-Cu-Mg alloys (see Discussion section) are illustrated in Fig. 1. The smallest co-cluster is a dimer of nearest neighbours of dissimilar alloying atoms Fig. 1a. In considering an approach to modelling the thermodynamics, we considered three approaches to modelling in order of increasing complexity:

- I. a regular solution model
- II. a quasi-chemical model which takes nearest neighbour interactions into account (see e.g. [24]).
- III. a first principles total energy calculation (FP-CVM) (see for instance [25]).

As described below, a dimer treated in a regular solution model (with a single bond energy), was found to fully explain all of a very extensive set of calorimetry data on Al-Cu-Mg alloys. Hence we will fully describe this treatment, and limit our consideration of more complex treatments to a brief discussion at the end of this subsection.

Within the regular solution model, the solvi of the phases and co-clusters in the ternary system can be derived as follows. Consider alloying elements A and B in a host metal M, the total number of the respective elements in the system are  $N_A$ ,  $N_B$  and  $N_M$ . The Gibbs free energy,  $G$ , of the system can be approximated as:

$$G = H_o - N_{cl}\Delta H_{A-B} - TS \quad (1)$$

where  $N_{cl}$  is the number of A-B dimers,  $H_o$  is a constant reference enthalpy and  $\Delta H_{A-B}$  is the enthalpy of formation of an A-B dimer from the random solution, i.e. the enthalpy of the reaction in which one A atom and one B atom, originally in random solution, form an A-B dimer. The entropy of the system is proportional to the logarithm of the number of states  $w$  in the system:

$$S = k_B \ln w = k_B \ln \left( \frac{N!}{(N_M!(N_A - N_{cl}))!(N_B - N_{cl})!2N_{cl}!} \right) \quad (2)$$

where  $k_B$  is Boltzmann's constant. For equilibrium it holds  $\partial G/\partial N_{cl}=0$ . Performing this derivation using the latter two equations (using the Stirling approximation  $\ln N! = N \ln N - N$ ) then provides that at equilibrium:

$$c_A c_B = \exp(-2) \exp \left[ \frac{-\Delta H_{A-B}}{RT} \right] \quad (3)$$

where  $c_A$  is the solubility (i.e. the equilibrium molar fraction) of element A in the M rich host lattice,  $c_B$  is the solubility of element B in the M rich host lattice. It can be noted that this corresponds to the more generally applied 'solubility product' equation:

$$c_A c_B = C^2 \exp \left[ \frac{-\Delta H_{A-B}}{RT} \right] \quad (4)$$

where  $C$  is a constant. In the latter form, no attempt is made to fully analyse the entropy term, and only the entropy of the atoms belonging to the Al-rich phase is considered. Thus constant  $C$ , which is related, amongst others, to the entropy of the clusters or precipitates, is considered a fittable parameter. In a more general form, the solubility limits of co-clusters according to the regular solution of any complex  $M_m A_a B_b$  is given as:

$$c_A^a c_B^b = C^2 \exp \left[ \frac{-\Delta H_{Mm Aa Bb}}{RT} \right] \quad (5)$$

where  $\Delta H_{Mm Aa Bb}$  is the enthalpy of formation of the  $M_m A_a B_b$  complex, i.e. the enthalpy of the reaction in which  $a$  atoms of type A,  $b$  atoms of type B and  $m$  atoms of type M, originally part of the M rich phase, form an  $M_m A_a B_b$  complex, which can be an ordered or disordered cluster or precipitate.

The latter two expressions can be tested through measurement of the heat evolved in the reactions of formation or dissolution of the clusters or precipitates. Particularly, when a calorimetry experiment is conducted such that the total heat evolved on completing of the co-clustering reaction is measured, exothermic heat evolved,  $\Delta Q$ , should then be given by:

$$\Delta Q = \frac{(x_A^o - x_A)}{a} \Delta H_{Mm Aa Bb} \quad (6)$$

where  $x_A^o$  is the composition of the M-rich phase at the start of the reaction, and  $x_A$  is the composition of the M-rich phase on completion of the reaction.  $x_A$  can be solved by considering that the composition during the reaction up to completion of the reaction is given by:

$$x_A^o - x_A = \frac{a}{b} (x_B^o - x_B) \quad (7)$$

whilst at completion:

$$c_A^a c_B^b = x_A^a x_B^b \quad (\text{at completion of reaction}) \quad (8)$$

Thus  $x_A$  can be solved from Eqs. 5, 7 and 8. (For particular values of the ratio  $a:b$ , the equations can be solved analytically, particularly  $a=b=1$  simplifies the equations considerably, but in general a simple iterative scheme is needed.)

An alternative treatment suggested in the literature [24] involves a quasi-chemical model which takes nearest neighbour interactions into account. Analysis of this model (see Discussion section) showed that it can not explain all the experimental observations.

Solution treated commercial alloys typically contain some small amounts of undissolved intermetallic phases or dispersoids, which reduce the amount of solute atoms available for co-cluster formation and subsequent precipitation. The composition of the supersaturated f.c.c. phase after solution treatment can generally be predicted from thermodynamic models (e.g. phase diagrams of the alloy). In commercial and commercial purity Al-Cu-Mg based alloys,  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe, S-Al<sub>2</sub>CuMg and T-Al<sub>20</sub>Cu<sub>2</sub>Mn<sub>3</sub> can be present [26,27]. A method for calculating the amounts of these phases is described in the Appendix. This method is applied for all model predictions.

### **Strengthening due to co-clusters**

Clusters and co-clusters are shearable and hence the Orowan strengthening mechanism is not applicable. Several strengthening mechanisms related to obstacle shearing need to be considered:

- a) Order strengthening (including stacking fault strengthening) or configurational strengthening
- b) Modulus hardening
- c) Chemical hardening

#### Order strengthening

The strengthening due to an ordered phase which contains short or long range order depends on the way the dislocations interact with the precipitate or clusters. If long range order is present, dislocations can travel in groups due to the anti phase boundary (APB) [28,29,30,31,32]. For the present case of co-cluster strengthening, the order can be considered to be extremely short ranged and as restoration of order by dislocations travelling in groups is not possible, dislocations will travel alone. The work done in deforming the lattice through movement of dislocations hampered by (co-)clusters equals the change in energy related to the short range order per unit area on slip planes, i.e. [33,34]:

$$\Delta\tau_{sro} = \frac{\gamma_{sro}}{b} \quad (9)$$

where  $\gamma_{sro}$  is the change in energy per unit area on slip planes (which in most cases are {111} planes) on the passing of one dislocation (a.k.a. the diffuse interphase boundary energy [33,35]). In the analysis of  $\gamma_{sro}$  we could attempt to include several orders of near neighbour interaction for

instance through considering a cluster variation approach [36]. However, we will here use a simplified approach that considers only nearest neighbour interactions. This is done for the following reasons: i) we do not have sufficient accurate data to determine all the  $k^{\text{th}}$  interaction parameters, and ii) the simpler nearest neighbour method provides a more intuitively acceptable analysis, which is a benefit as several competing analysis of strengthening due to co-clusters have been accepted. We will consider here co-clusters that consist of a single pair of atoms A and B. The amount of A atoms in the co-clusters is  $y_A$ , the amount of B atoms in the co-clusters is  $y_B$ . The amount of A atoms in the M-rich phase is  $x_A$ , the amount of B atoms in the M-rich phase is  $x_B$ . In the (M-rich) f.c.c. lattice structure each atom has 12 nearest neighbours and each atom adjacent to a slip plane will have 3 nearest neighbours on the other side of the  $\{111\}$  slip plane. The area density of A-B nearest neighbour bonds crossing the slip plane is:

$$\rho_{A-B}(n_d = 0) = \frac{(y_A + y_B)}{S_{111}} = \frac{4(y_A + y_B)}{\sqrt{3}b^2} \quad (10)$$

where  $S_{111}$  is the area on the 111 plane occupied by one atom. On passing of one dislocation through the AB co-cluster a part of the A-B bonds present before the passing will be destroyed and some will be retained (see Fig. 2).

From the geometry of the f.c.c. lattice it follows that for a single dislocation on the 111 plane, 1/3 of the A-B nearest neighbour pairs will remain nearest neighbours. The passing through of a dislocation can also create A-B nearest neighbour pairs. The area density is given by  $2/3y_Ax_B + x_Ax_B + 2/3y_Bx_A + x_Ax_B = 2/3y_Ax_B + 2/3y_Bx_A + 2x_Ax_B$ . Thus the total area density of A-B nearest neighbour bonds crossing the slip plane after passage of one dislocation is:

$$\rho_{A-B}(n_d = 1) = \frac{4}{\sqrt{3}b^2} \left[ \frac{1}{3}(y_A + y_B) + \frac{2}{3}y_Ax_B + \frac{2}{3}y_Bx_A + 2x_Ax_B \right] \quad (11)$$

The change in area density of A-B nearest neighbour bonds crossing the slip plane on passing of one dislocation is

$$\begin{aligned} \rho_{A-B}(n_d = 0) - \rho_{A-B}(n_d = 1) &= \frac{4}{\sqrt{3}b^2} \left[ \frac{2}{3}(y_A + y_B) - \left( \frac{2}{3}y_Ax_B + \frac{2}{3}y_Bx_A + 2x_Ax_B \right) \right] \\ &\cong \frac{4}{\sqrt{3}b^2} \frac{2}{3}(y_A + y_B) \end{aligned} \quad (12)$$

where the approximation is valid for dilute alloys. Passage of further dislocations will cause further changes in area density of A-B nearest neighbour bonds crossing the slip plane. As the magnitude of these changes will decrease on passing of each further dislocation, the first dislocation experiences the greatest resistance. Considering in approximation that the energy related to co-clusters is defined by the enthalpy of the nearest neighbour bond  $\Delta H_{A-B}$  we can approximate:











































