

"Universal" Laws for the Density of Dispersoids after the Homogenisation Heat Treatment of Aluminium

Anne Lise Dons¹

¹SINTEF Metallurgi, Alfred Getz vei 2, N-7465 Trondheim

Dispersoids are small intermetallic particles that form in the aluminium matrix during the heating to the homogenisation temperature. They often form as metastable phases, but usually transform to the stable phases $Al_6(Mn,Fe)$ or $\alpha-Al(Mn,Fe,Cr)Si$, during the heat treatment [1,2,3,4]. It is possible to predict the number of dispersoids at the end of the heat treatment in different alloys as AA6063, AA6082 and AA3003 with the same set of equations and the same set of tuning constants.

The chances for nucleating a dispersoid depend on suitable sites: Dislocations, vacancy clusters, small particles of other types, and grain boundaries. Except for the small particles, the number of sites is roughly equal in the three types of alloys.

The chances for nucleating an $\alpha-Al(Mn,Fe)Si$ -particle on a given site increase with the number of suitable atoms in the vicinity. If it takes three Mn-atoms and one Si-atom to make a formulae unit of $Al_{12}Mn_3Si$, the probability of forming a nucleus with x formula units should be proportional to

$$(CMn^3*CSi)^x. \quad (1)$$

As the nucleation is heterogeneous, x will be a low number, corresponding to a small nucleus. The probability of forming a nucleus also depends on the supersaturation, which can be described as

$$(CMn^3*CSi)^y/(C_0Mn^3*C_0Si)^y - 1, \quad (2)$$

where C_0 is the equilibrium concentration at the current temperature, and y probably equals to 0.25. (The aluminium part of the solubility product is set to 1. Alstruc [5,6,7] uses a site saturation approach, starting the calculations at 400°C, which requires equations for growth, dissolution and coarsening. Wagner's coarsening law for isothermal heat treatment is used for the holding period. The paper will show the form of the equations and compare the simulations from "Alstruc" with experimental data.

Keywords: Aluminium, homogenisation, dispersoids, nucleation, coarsening

1. Introduction

DC-cast aluminium billets and slabs are cooled as fast as possible after solidification. This leaves Fe and Mn in solid solution, at severe supersaturation at room temperature. When the material is reheated for homogenisation, Mn-and Fe-rich particles, called dispersoids, nucleate, grow, coarsen, and partly dissolve. This happens in as different alloys as AA6063, AA6082 and AA3003. An example of a microstructure is shown in Fig.1. Dispersoids slow down recrystallisation after rolling or extrusion. This is sometimes a desired effect, and sometimes not. In any case it is important to keep track of the size and number of dispersoids, and preferably to be able to predict them.

Table 1 shows examples of compositions of these alloys. The dispersoids in these alloys have been investigated on diverse occasions, for instance by [1,5-9].

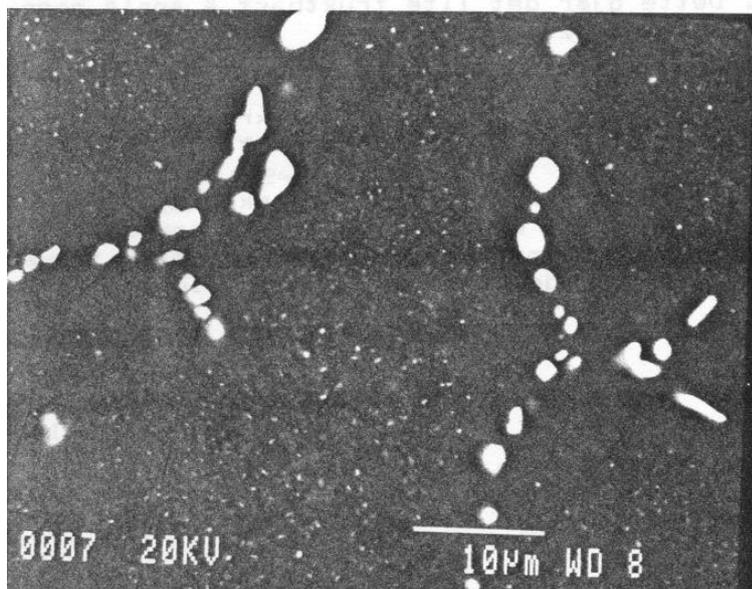


Fig. 1 Back scattered SEM-image of the microstructure in a homogenised AA6082-like alloy with Cr instead of Mn. Primary Al(FeCr)Si particles are large and white, while dispersoids are small and white. There are dispersoid free zones around the primary particles.

2. Type of Dispersoids

The dispersoids in AA6063, AA6082 and AA3xxx alloys usually end up as cubic α -Al₁₂₋₁₅(Mn,Fe,Cr)₃Si₁₋₂, or as α -AlCrSi at the end of the homogenisation. However, they usually nucleate as small, metastable icosahedral particles [1-4].

3. Experiments (from the Literature)

Fig. 1 shows dispersoids in an AA6082 alloy, seen in SEM (Scanning Electron Microscope). There are also areas without dispersoids around the larger intermetallic particles. Dispersoids are often counted in TEM (Transmission Electron Microscope). The TEM operators in [5, 8, 9] have found equal number of dispersoids for the identical specimens, within a statistical uncertainty that is roughly a factor 2. Table 2 shows the dispersoid densities in $\#/\mu\text{m}^3$ at the end of the heat treatments, as measured in [5,8,9]. These numbers represent the number density of dispersoids in the areas where dispersoids are densely populated. Thus the true numbers are lower than those shown in Tab. 2.

Table 1. Typical compositions of some aluminium alloys (wt%, balance Al)

Alloy	Fe	Si	Mn	Mg	Cr	Cu	Ti
I24	0.19	0.47	0.005	0.50			0.011
I36	0.20	0.43	0.027	0.46			0.012
LMn01	0.16	0.65	0.1	0.49			0.009
IMn02	0.21	0.65	0.21	0.54			
LMn03	0.15	0.65	0.3	0.46			0.008
2018	0.20	1.04	0.56	0.60			
2018Cr	0.2	1.0	0	0.6	0.22		
3003	0.58	0.20	1.15			0.08	

Table 2. Heat treatments and number density of dispersoids

Alloy	Heat treatment		Number density, dispersoids per μm^3	
	Temperature ($^{\circ}\text{C}$)	Holding time (hours)	Measured	Calculated
I24	550	6	0.1-0.3	0.2
I36	550	6	1	0.5
LMn01	560	3	0.9	1.6
IMn02	560	4	3.5	4
LMn03	560	3	6.5	8
2018	520	4	25	38
2018	560	4?	12	18
2018	580	3	3-4	10
2018Cr	520	4	30	17
2018Cr	580	3	11	6
3003	560	1	40	40
3003	560	4	18	19
3003	560	8	13	11
3003	600	1	26	5
3003	600	4	9	1.4
3003	600	7	7	0.7
3003	630	1	0.6	0.15

4. The initial Structure

Before one can calculate the nucleation, growth, dissolution and coarsening of intermetallic particles during homogenisation, one needs a mathematical description of the microstructure after solidification. In the present case this was obtained from the Alstruc solidification program [10,11], which calculates the type and size of the primary particles, and the local variation of elements in solid solution.

5. Nucleation Theory

A potential nucleation site can be a vacancy cluster, a silicon pair, a Mg-Si-particle [1], a dislocation or a grain boundary. One would think that the nucleation on Mg-Si-particles and Si-pairs would favour dispersoids in the Mg-bearing AA6xxx alloys above those in AA3xxx alloys. However, the silicon pairs and Mg-Si-particles in their turn nucleate on vacancy clusters, dislocations and grain boundaries. So maybe they can be ignored?

With heterogeneous nucleation it is not necessarily the surface tension that limits the nucleation rate. With a surface already present, it is possible that a nucleus can consist of just one unit cell or formula unit of the dispersoid phase, which is present from the start. With a composition close to $\text{Al}_{12}\text{Mn}_3\text{Si}$, the probability of finding such a smallest unit in a given place in a randomly mixed alloy with concentrations C_{Mn} and C_{Si} is proportional to

$$(C_{\text{Mn}}^3 * C_{\text{Si}})^x, \quad (3)$$

where x is the minimum number formulae units that is required. With heterogeneous nucleation, x may be as low as 1.

Eq. 1 can be modified to include variations in the Mn:Fe:Cr-ratio of α -Al₁₂₋₁₅(Mn,Fe,Cr)₃Si₁₋₂, to

$$((C_{Mn}+C_{Fe}+C_{Cr})^{2.2} * C_{Si})^x. \quad (4)$$

This product is equal at all temperatures, regardless of whether there is supersaturation or not. The driving force for the isothermal precipitation reaction from an ideal solution in a two component system with concentration C and equilibrium concentration C_{eq} is, (disregarding surface tension):

$$dG/dC = - RT \ln (C / C_{eq}). \quad (5)$$

where G is the Gibbs energy per mole, R is the molar gas constant and T is the temperature in K. This can be approximated to

$$dG/dC = - RT \ln (1 + \Delta C / C_{eq}) \approx - RT (\Delta C / C_{eq}) \approx - RT (C / C_{eq} - 1). \quad (6)$$

The equivalent for Eq. 6 for a phase Al₉(Mn,Fe)_{2.2}Si with free miscibility between Fe and Mn (no interaction term between Mn and Fe), can be approximated to

$$dG/dC \approx - (RT/3.2) * \ln ((C_{Mn}/Mn_0 + C_{Fe}/Fe_0 + C_{Cr}/Cr_0)^{2.2} * Si/Si_0) \quad (7)$$

$$\approx - (2.2 * RT/3.2) * ((C_{Mn}/Mn_0 + C_{Fe}/Fe_0 + C_{Cr}/Cr_0) * (Si/Si_0)^{(1/2.2)} - 1). \quad (8)$$

Here Mn₀, Fe₀, Cr₀ and Si₀ are temperature dependent constants determined from the phase diagram [12,13, 14,15,16,17], so that at equilibrium

$$(C_{Mn}/Mn_0 + C_{Fe}/Fe_0 + C_{Cr}/Cr_0) * (Si/Si_0)^{(1/2.2)} = 1. \quad (9)$$

The probability of finding a nucleus at a given site is then proportional to

$$((C_{Mn}+C_{Fe}+C_{Cr})^{2.2} * C_{Si})^x * ((C_{Mn}/Mn_0 + C_{Fe}/Fe_0 + C_{Cr}/Cr_0) * (Si/Si_0)^{(1/2.2)} - 1). \quad (10)$$

The constant of proportionality and the value of the constant x must be tuned against experiments. An equation almost like Eq.10 is used in the Alstruc homogenisation program [5,6,7]. There the constants are determined by curve fitting, for calculations that start with site saturation at 400°C.

6. Growth and Dissolution of Particles

The Alstruc homogenisation program calculates growth or shrinkage of the particles during the heating to the homogenisation temperature. The number of particles stays constant, or they all disappear in the region, until the homogenisation temperature is reached. Growth and dissolution continues during the holding part of the homogenisation. The equations that are used, are analytical diffusion equations, built on [18] and others:

$$r = ((C - C_0) / C_p * 2Dt)^{0.5}, \quad (11)$$

where C is the concentration in solid solution, C₀ is the concentration at the surface of the particle, C_p is the concentration in the particle, D is the diffusion constant and t is the time. Strictly speaking, Eq. 11 is only valid for a particle starting with radius r = 0 in a homogeneous matrix, but is approximately valid if C_p >> C and time t is long enough. Eq. 11 can be transformed to

$$r^2 := (r_1^2 + 2D(t_2 - t_1) (C - C_0) / C_p)^{0.5}, \quad (12)$$

where the radius was r_1 at time t_1 , and is r_2 at time t_2 . If more than one element is involved, it can be CPU-demanding to calculate the surface composition. It may be a good approximation to assume that some elements diffuse infinitely fast, compared to the others.

7. Coarsening

Wagner's coarsening equation [19] assumes that a family of particles starts at diameters close to zero and are almost at equilibrium with the surrounding matrix, so that the larger particles grow and the smaller ones dissolve. This gives an average increase in size d , which is given by

$$D t = a \cdot d^3 \cdot T \cdot (C_p / C_o), \quad (13)$$

where a is a constant and T temperature in K. Here $d=0$ at $t=0$. It is a useful approximation to define a nonzero starting diameter d_0 at a starting time t_0 so that

$$D t_0 = a \cdot d_0^3 \cdot T \cdot (C_p / C_o). \quad (14)$$

The diameter d then increases according to

$$d^3 = d_0^3 \cdot t / t_0. \quad (15)$$

Eq. 15 is easy to handle mathematically, but the constant t_0 has to be determined experimentally.

8. Calculations

The cases listed in Table 2 were calculated with Alstruc. The secondary dendrite arm spacing was assumed to be 20 μm . The heating time from 400°C to the holding temperature was assumed to be 0.5 h. All the homogenisation calculations were performed with the module for AA3xxx-alloys, to keep the constants identical. The resulting numbers of dispersoids per μm are listed in the last column in Table 2, and shown as a function of the measured number densities in Fig. 2.

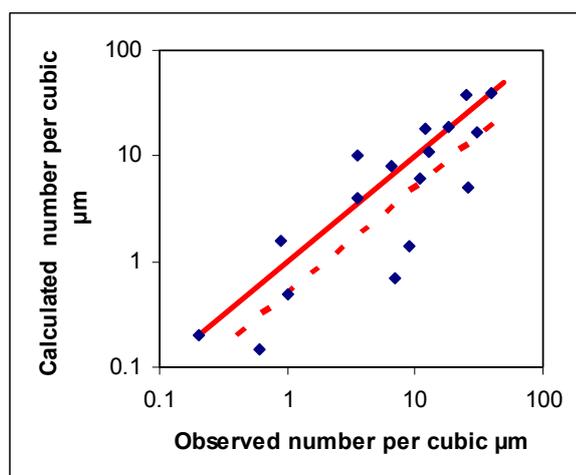


Fig. 2 Comparison of observed and calculated number of dispersoids in the alloys in Table 1 after the heat treatments in Table 2. If the fit was perfect, the symbols should fall on the red line. The dotted line takes dispersoid free zones into account.

9. Discussion and Conclusion

Dispersoid counting in TEM from 5-10 micrographs from a total of 2-3 thin foils gives a reproducibility better than a factor of 2 in the areas with dispersoids. Areas without dispersoids are usually neglected, but they constitute less than half the area, except after long times at high temperatures. Alstruc, on the other hand, tries to account for dispersoid free zones. Thus the calculated values should be between the measured ones, and half of the measured ones. In the present case 10 out of 16 calculated points fall reasonably close to the observed tendency. The errors in the fit are evenly distributed over a range from 0.1 to 40 dispersoids per μm^3 . So there is room for improvement in the equations, especially for alloys with so low silicon contents that $\text{Al}_6(\text{Mn,Fe})$ dispersoids become stable.

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