

Lecture 4: Mechanical Alloying, Case Study

Introduction

An alloy can be created without melting, by violently deforming mixtures of different powders, Fig. 1. Inert oxides can, using this technique, be introduced uniformly into the microstructure. The dispersion-strengthened alloyed powders are then consolidated using hot-isostatic pressing and extrusion, to produce a solid with a very fine grain structure. Heat treatment then induces recrystallisation, either into a coarse columnar grain structure or into a fine, equiaxed set of grains.

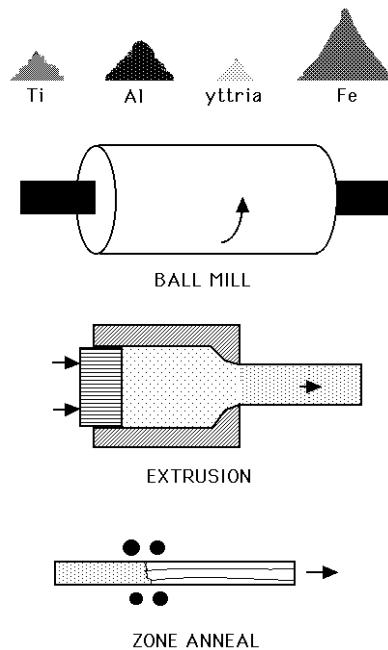


Fig. 1: The manufacture of mechanically alloyed metals for engineering applications. The elemental powders/master-alloys/oxides are milled together to produce solid solutions with uniform dispersions of oxide particles. This powder is consolidated and the resulting material heat-treated to achieve a coarse, directional grain structure.

The chemical compositions of some of the commercial alloys produced using this method are listed in Table 1. They all contain chromium and/or aluminium for corrosion and oxidation resistance, and yttrium or titanium oxides for creep strength.

Fe-base	C	Cr	Al	Mo	Ti	N		Ti ₂ O ₃	Y ₂ O ₃	Fe
MA956	0.01	20.0	4.5	–	0.5	0.045		–	0.50	Balance
PM2000	< 0.04	20.0	5.5		0.5			–	0.5	Balance
Ni-Base	C	Cr	Al	Ti	W	Fe	N	Total O	Y ₂ O ₃	Ni
MA6000	0.06	15.0	4.5	2.3	3.9	1.5	0.2	0.57	1.1	Balance
PM1000 †		20.0	0.3	0.5		3.0			0.6	Balance

Table 1: Compositions (wt%) of some typical alloys.

CHEMICAL STRUCTURE

The intense deformation associated with mechanical alloying can force atoms into positions where they may not prefer to be at equilibrium. The atomic structure of solid solutions in commercially important metals formed by the mechanical alloying process can be studied using field ion microscopy and the atom-probe.

A solution which is homogeneous will nevertheless exhibit concentration differences of increasing magnitude as the size of the region which is chemically analysed decreases. These are random fluctuations which obey the laws of stochastic processes, and represent the real distribution of atoms in the solution. These equilibrium variations cannot usually be observed directly because of the lack of spatial resolution and noise in the usual microanalytical techniques. The fluctuations only become apparent when the resolution of chemical analysis falls to less than about a thousand atoms block. The atom probe technique collects the experimental data on an atom by atom basis. The atom by atom data can be presented at any block size.

Fig. 2 illustrates the variation in the iron and chromium concentrations in fifty atom blocks, of the ferrite in *MA956*. There are real fluctuations but further analysis is needed to show whether they are beyond what is expected in homogeneous solutions

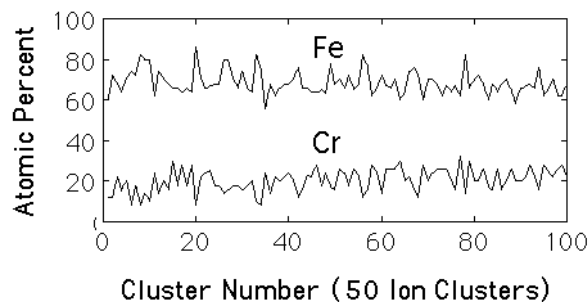


Fig. 2: The variation in the iron and chromium concentrations of 50 atom samples of MA956.

For a random solution, the distribution of concentrations should be binomial since the fluctuations are random; any significant deviations from the binomial distribution would indicate either the clustering of like-atoms or the ordering of unlike pairs.

The frequency distribution is obtained by plotting the total number of composition blocks with a given number of atoms of a specified element against the concentration. Fig. 3 shows that the experimental distributions are essentially identical to the calculated binomial distributions, indicating that the solutions are random.

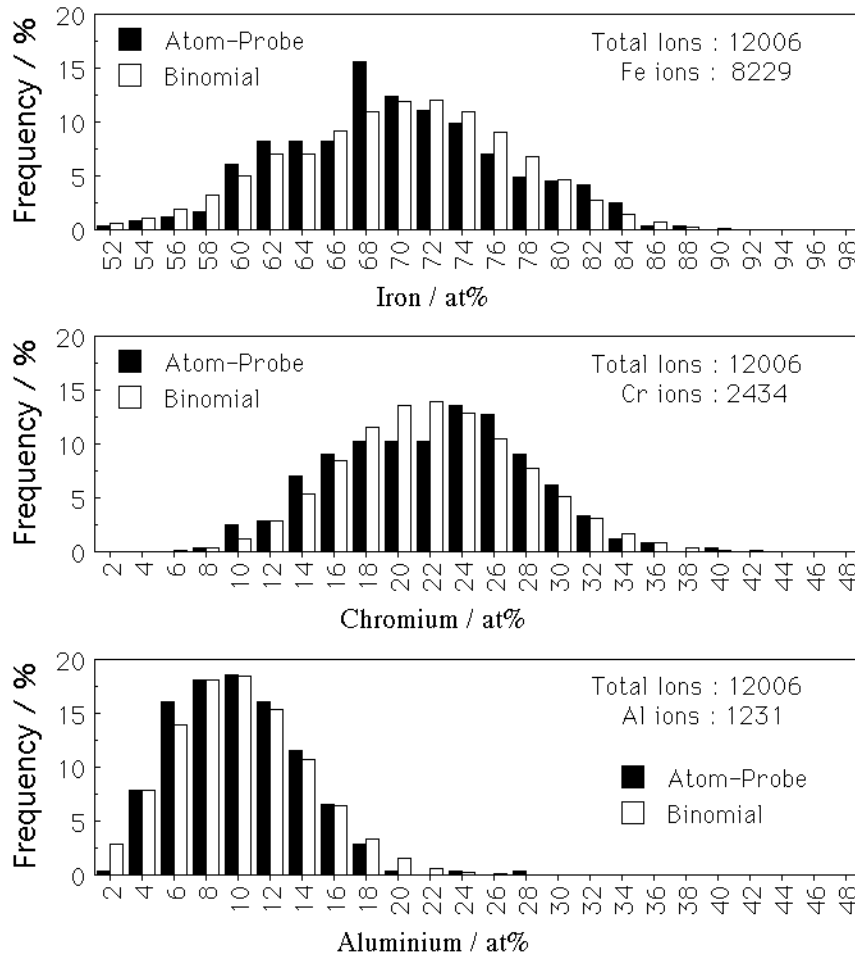


Fig. 3: Frequency distribution curves for iron, chromium and aluminium in mechanically alloyed MA956.

This does not mean that the solutions are thermodynamically ideal, but rather that the alloy preparation method which involves intense deformation forces a random dispersal of atoms. Indeed, Fe–Cr solutions are known to deviate significantly from ideality, with a tendency for like atoms to cluster. Thus, it can be concluded that the alloy is in a mechanically homogenised nonequilibrium state,

and that prolonged annealing at low temperatures should lead to, for example, the clustering of chromium atoms.

Solution Formation

Normal thermodynamic theory for solutions begins with the mixing of component atoms. In mechanical alloying, however, the solution is prepared by first mixing together lumps of the components, each of which might contain many millions of identical atoms. We examine here the way in which a solution evolves from these large lumps into an intimate mixture of different kinds of atoms without the participation of diffusion or of melting. It will be shown later that this leads to interesting outcomes which have implications on how we interpret the mechanical alloying process.

Consider the pure components A and B with molar free energies μ_A^o and μ_B^o respectively. If the components are initially in the form of powders then the average free energy of such a mixture of powders is simply:

$$G\{\text{mixture}\} = (1 - x)\mu_A^o + x\mu_B^o \quad (1)$$

where x is the mole fraction of B . It is assumed that the powder particles are so large that the A and B atoms do not “feel” each other’s presence via interatomic forces between unlike atoms. It is also assumed that the number of ways in which the mixture of powder particles can be arranged is not sufficiently different from unity to give a significant contribution to a configurational entropy of mixing. Thus, a blend of powders which obeys equation 1 is called a *mechanical mixture*. It has a free energy that is simply a weighted mean of the components, as illustrated in Fig. 4a for a mean composition x .

In contrast to a mechanical mixture, a *solution* is conventionally taken to describe a mixture of atoms or molecules. There will in general be an enthalpy change associated with the change in near neighbour bonds. Because the total number of ways in which the “particles” can arrange is now very large, there will always be a significant contribution from the entropy of mixing, even when the enthalpy of mixing is zero. The free energy of the solution is therefore different from that of the mechanical mixture, as illustrated in Fig. 4b. The difference in the free energy between these two states of the components is the free energy of mixing ΔG_M , the essential term in all thermodynamic models for solutions.

Whereas mechanical mixtures and atomic or molecular solutions are familiar in all of the natural sciences, the intermediate states have only recently been addressed. The problem is illustrated in Fig. 5 which shows the division of particles into ever smaller particles until an atomic solution is achieved. At what point in the size scale do these mixtures of particles begin to exhibit solution-like behaviour?

To answer this question we shall assume first that there is no enthalpy of mixing. The problem then reduces to one of finding the configurational entropy of mixtures of lumps as opposed to atoms. Suppose that there are m_A atoms per powder particle of A , and m_B atoms per particle of B ; the powders are then mixed in a proportion which gives an average mole fraction x of B .

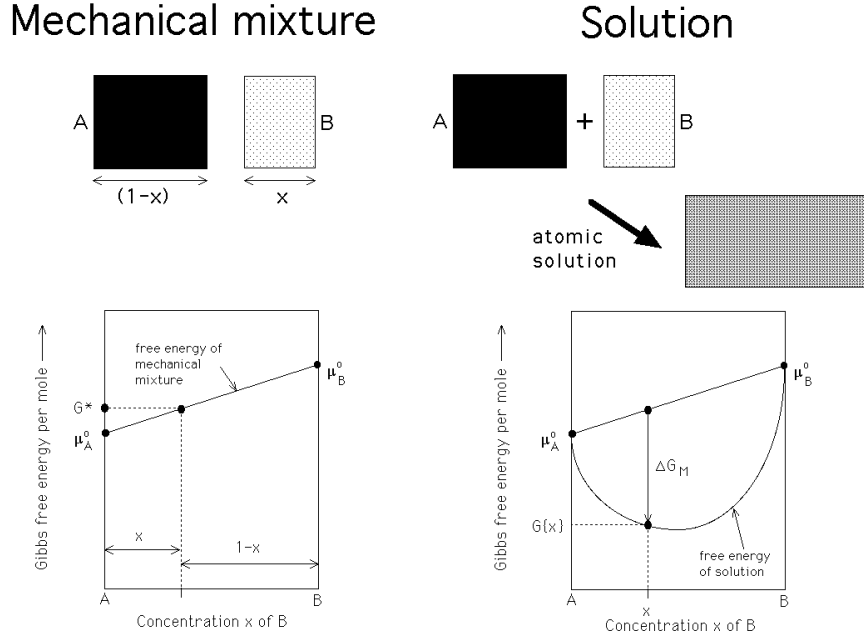


Fig. 4: (a) The free energy of a mechanical mixture, where the mean free energy is simply the weighted mean of the components. (b) The free energy of an ideal atomic solution is always lower than that of a mechanical mixture due to configurational entropy.

There is only one configuration when the heaps of pure powders are separate. When the powders are mixed at random, the number of possible configurations for a mole of atoms becomes:

$$\frac{(N_a([1-x]/m_A + x/m_B))!}{(N_a[1-x]/m_A)! (N_a x/m_B)!} \quad (2)$$

where N_a is Avogadro's number. The numerator in equation 2 is the total number of particles and the denominator the product of the factorials of the A and B particles respectively. Using the Boltzmann equation and Stirling's approximation, the molar entropy of mixing becomes:

$$\begin{aligned} \frac{\Delta S_M}{kN_a} = & \frac{(1-x)m_B + xm_A}{m_A m_B} \ln \left\{ N_a \frac{(1-x)m_B + xm_A}{m_A m_B} \right\} \\ & - \frac{1-x}{m_A} \ln \left\{ \frac{N_a(1-x)}{m_A} \right\} \\ & - \frac{x}{m_B} \ln \left\{ \frac{N_a x}{m_B} \right\} \end{aligned} \quad (3)$$

subject to the condition that the number of particles remains integral and non-zero. As a check, it is easy to show that this equation reduces to the familiar

$$\Delta S_M = -kN_a[(1-x) \ln\{1-x\} + x \ln\{x\}] \quad (4)$$

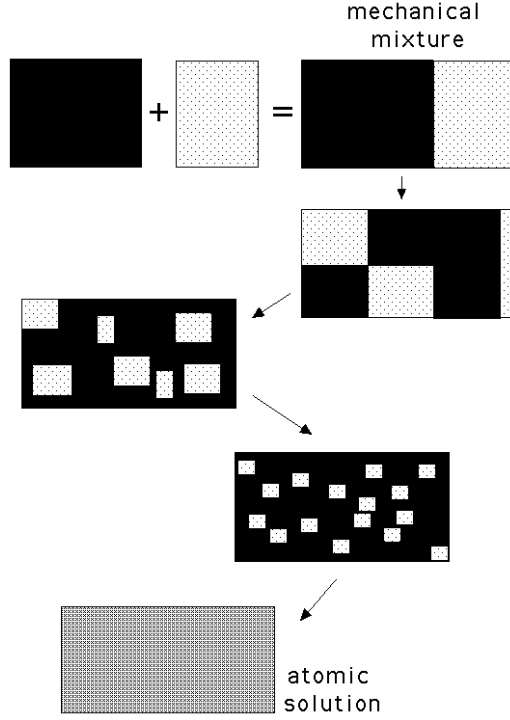


Fig. 5: Schematic illustration of the evolution of an atomic solution by the progressive reduction in the size of different particles, a process akin to mechanical alloying.

when $m_A = m_B = 1$.

Naturally, the largest reduction in free energy occurs when the particle sizes are atomic. Fig. 6 shows the molar free energy of mixing for a case where the average composition is equiatomic assuming that only configurational entropy contributes to the free energy of mixing. An equiatomic composition maximises configurational entropy. When it is considered that phase changes often occur at appreciable rates when the accompanying reduction in free energy is just 10 J mol^{-1} , Fig. 6 shows that the entropy of mixing cannot be ignored when the particle size is less than a few hundreds of atoms. In commercial practice, powder metallurgically produced particles are typically $100 \mu\text{m}$ in size, in which case the entropy of mixing can be neglected entirely, though for the case illustrated, solution-like behaviour occurs when the particle size is about 10^2 atoms.

Enthalpy and Interfacial Energy

The enthalpy of mixing will not in general be zero as was assumed above. The binding energy is the change in energy as the distance between a pair of atoms is decreased from infinity to an equilibrium separation, which for a pair of A atoms is written $-2\epsilon_{AA}$. From standard theory for atomic solutions, the molar enthalpy of mixing is given by:

$$\Delta H_M \simeq N_a z (1-x)x\omega \quad \text{where} \quad \omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} \quad (5)$$

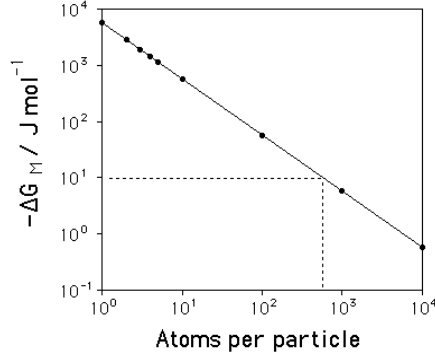


Fig. 6: The molar Gibbs free energy of mixing, $\Delta G_M = -T\Delta S_M$, for a binary alloy, as a function of the particle size when all the particles are of uniform size in a mixture whose average composition is equiatomic. $T = 1000$ K.

where z is a coordination number.

However, for particles which are not monatomic, only those atoms at the interface between the A and B particles will feel the influence of the unlike atoms. It follows that the enthalpy of mixing is not given by equation 5, but rather by

$$\Delta H_M = zN_a\omega - 2\delta S_V x(1-x) \quad (6)$$

where S_V is the amount of $A - B$ interfacial area per unit volume and 2δ is the thickness of the interface, where δ is a monolayer of atoms.

A further enthalpy contribution, which does not occur in conventional solution theory, is the structural component of the interfacial energy per unit area, σ :

$$\Delta H_I = V_m S_V \sigma \quad (7)$$

where V_m is the molar volume.

Both of these equations contain the term S_V , which increases rapidly as the inverse of the particle size m . The model predicts that *solution formation is impossible* because the cost due to interfaces overwhelms any gain from binding energies or entropy. And yet, solutions do form, so there must be a mechanism to reduce interfacial energy as the particles are divided. The mechanism is the reverse of that associated with precipitation (Fig. 7). A small precipitate can be coherent but the coherency strains become intolerable as it grows. Similarly, during mechanical alloying it is conceivable that the particles must gain in coherence as their size diminishes. The milling process involves fracture and welding of the attrited particles so only those welds which lead to coherence might succeed.

Another unexpected result is obtained on incorporating a function which allows the interfacial energy to decrease as the particle size becomes finer during mechanical alloying. Thermodynamic barriers are discovered to the formation of a solution by the mechanical alloying process, Fig. 8. When the enthalpy of mixing is either zero or negative, there is a single barrier whose height depends on the

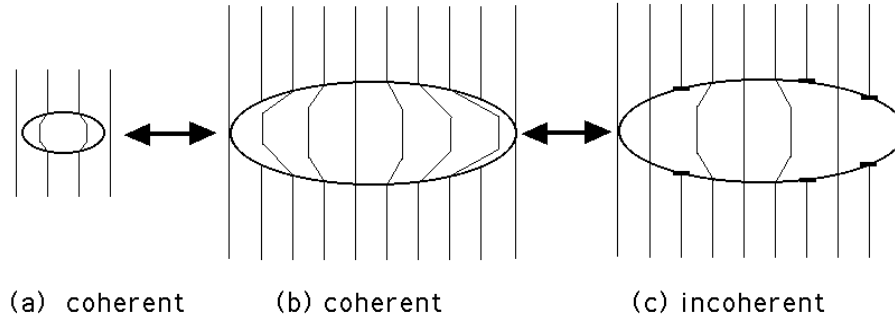


Fig. 7: The change in coherence as a function of particle size. The lines represent lattice planes which are continuous at the matrix/precipitate interface during coherence, but sometimes terminate in dislocations for the incoherent state. Precipitation occurs in the sequence $a \rightarrow c$ whereas mechanical alloying is predicted to lead to a gain in coherence in the sequence $c \rightarrow a$.

competition between the reduction in free energy due to mixing and the increase in interfacial energy as the particles become finer until coherence sets in. When the atoms tend to cluster, there is a possibility of two barriers, the one at smaller size arising from the fact that atoms are being forced to mix during mechanical alloying.

The composition dependence of the barriers to solution formation becomes more clear in plot of free energy versus chemical composition, as illustrated in Fig. 8c,d.

Shape of Free Energy Curves

There are many textbooks which emphasise that free energy of mixing curves such as that illustrated in Fig. 4b must be drawn such that the slope is either $-\infty$ or $+\infty$ at $x = 0$ and $x = 1$ respectively. This is a straightforward result from equation 4 which shows that

$$\frac{\partial \Delta S_M}{\partial x} = -kN_a \ln \left\{ \frac{x}{1-x} \right\} \quad (8)$$

so that the slope of $-T\Delta S_M$ becomes $\pm\infty$ at the extremes of concentration. Notice that at those extremes, any contribution from the enthalpy of mixing will be finite and negligible by comparison, so that the free energy of mixing curve will also have slopes of $\pm\infty$ at the vertical axes corresponding to the pure components[†] It follows that the free energy of mixing of any solution from its components will at first decrease at an infinite rate.

However, these conclusions are strictly valid only when the concentration is treated as a *continuous* variable which can be as close to zero or unity as desired.

[†] The intercepts at the vertical axes representing the pure components are nevertheless finite, with values μ_A^0 and μ_B^0 .

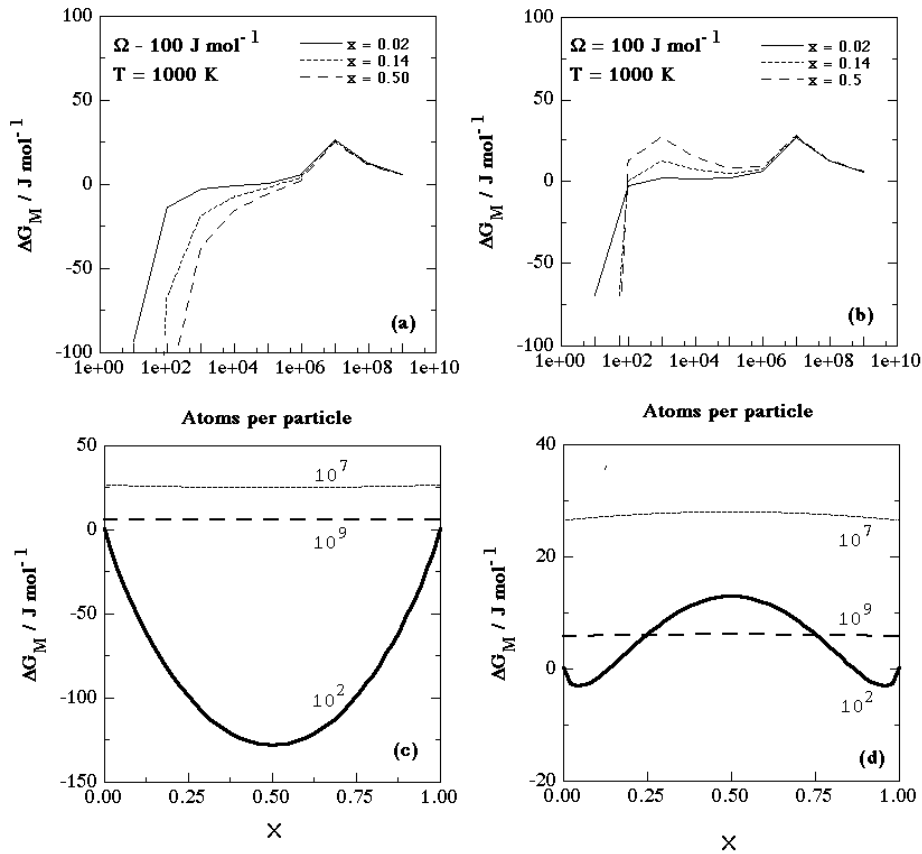


Fig. 8: Thermodynamic barriers to solution formation. (a) Case where the enthalpy of mixing is negative, *i.e.* unlike atoms attract. (b) Case where there is a tendency to cluster with a positive enthalpy of mixing. (c) As case (a) but plotted against chemical composition. The numbers alongside the curves refer to the number of atoms per particle. (d) As case (b) but plotted against chemical composition. The numbers alongside the curves refer to the number of atoms per particle.

The present work emphasises that there is a *discrete* structure to solutions. Thus, when considering N particles, the concentration can never be less than $1/N$ since the smallest amount of solute is just one particle. The slope of the free energy curve will not therefore be $\pm\infty$ at the pure components, but rather a finite number depending on the number of particles involved in the process of solution formation. Since concentration is not a continuous variable, the free energy is not represented by a curve, but rather by a set of straight lines connecting the discrete values of concentration that are physically possible when mixing particles. The shape approximates a curve when the number of particles is large, as is the case for an atomic solution made of a mole of atoms. But the curve remains an approximation.