

Fig. 1.3. Twinning. The crystal structure is reflected in the plane XY which forms the twin boundary. The vertical sides of the crystal as drawn are no longer smooth.

a special case of importance is that for which the orientation of neighbouring grains is very similar: such cases are termed low-angle boundaries. Their geometry is relatively simple and can be expressed in terms of dislocations.

We shall return to grain boundaries in Chap. 8 when we report atomistic structures with some realistic force laws. However, let us summarize here a few basic facts on twin boundaries.

Crystals are frequently produced with a fault which is such that one region of the crystal is a mirror image of the other part. The atoms in one region are in positions produced by reflecting the atoms in the second part at some symmetry plane of the crystal. Figure 1.3, reproduced from Rosenberg (1992), is an example of twinning. The crystal structure is reflected in the plane XY which forms the twin boundary.

Twinning frequently occurs in metals which have a small stacking fault energy as this fact then implies that the additional energy needed for any small atomic mismatch is small. Twinning can also happen during deformation. Twinning planes can often be seen by optical microscopy, and the presence of twins can be detected by X-ray diffraction. This is due to extra sets of spots which are produced from the twinned regions.

1.11. Alloy Formation: Rules and Models

1.11.1. Solid Solubility: Hume-Rothery Factors

Hume-Rothery *et al.* (1934, 1969) in very early work proposed several factors controlling the extent of solid solubility. Even at the time of writing, these factors form a useful basis for discussing the formation of extensive or restricted solid solutions (see also Alonso and March, 1989).

(a) Size effects

The 'size rule' asserts that solid solutions should not be anticipated if the atomic sizes of solute and solvent differ by more than 15%. Provided that 'other factors are favourable' solid solutions may form if the size difference is less than this value. Waber *et al.* (1963) applied this rule to some 1400 solid solutions. 90% of the systems predicted to be insoluble by the above 'size rule' were indeed found to have limited solid solubility, the distinction between a limited and an extensive solid solution being taken at 5 atomic %. However, of the systems predicted to form extensive solid solutions, only 50% were found to occur. In other words, it would appear to be the case that a favourable size factor is a necessary but not sufficient condition for the formation of solid solutions with extensive solubility.

(b) Electrochemical factor

The second rule of Hume-Rothery states that the electrochemical nature of the two elements involved must be similar for solid solutions to be expected. On the other hand, if their electrochemical characters are very different, compound formation is likely to occur. A measure of the electrochemical natures of the elements is afforded by their electronegativity. Introduced into chemistry by Pauling and by Mulliken, electron density theory, to be summarized in Chap. 6 holds promise that eventually a fully quantitative measure of this important chemical concept will be possible via the chemical potential of the inhomogeneous electronic charge cloud in an atomic (or molecular) system. Difference in electronegativity between two atoms, A and B say, drives the redistribution of charge as these approach one another to form, say, a stable AB molecule. Such charge transfer turns out to contribute to the enthalpy of formation.

Darken and Gurry (1963) made important progress in the prediction of solid solubility when they made simultaneous use of size and of electrochemical factors. In particular, these workers constructed a plot in which the coordinates are the electronegativity and the atomic radius. The values of these coordinates characterize the position of each chemical element in the plot.

Figure 1.4 reproduced from Alonso and March (1989), shows such a plot for various solutes in a Ag host. The solid circles indicate alloys in which extensive solution are found. The solid squares refer to alloys in which limited or zero solid solubility is obtained. The ellipse drawn in Fig. 1.4 approximately acts as a 'boundary' between soluble and insoluble impurities. To summarize the above very briefly, one can say that only chemically similar elements are mutually soluble (see also Alonso and March, 1989).

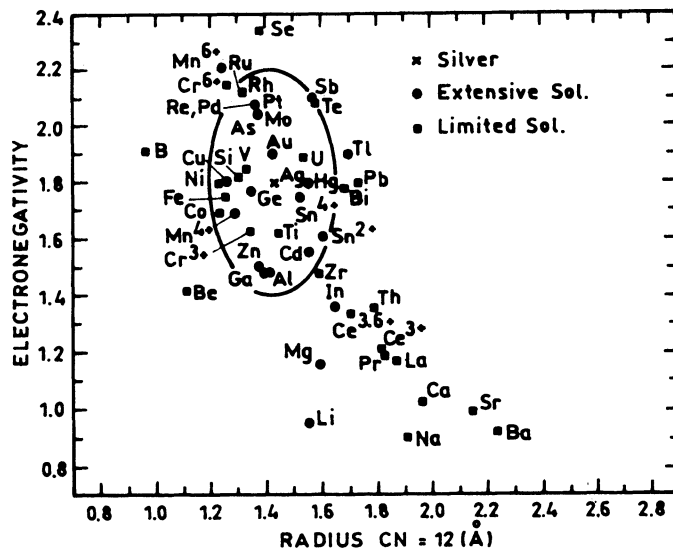


Fig. 1.4. Darken-Gurry plot for various solutes dissolved in Ag. Circles indicate alloys in which extensive solutions are found; squares indicate alloys in which limited or no solid solubility is found. The ellipse approximately separates soluble and insoluble impurities. (Redrawn after Waber *et al.*)

(c) Valence-difference effect

Hume-Rothery formulated a third rule which states that a higher-valent metal is more soluble in a lower-valent host than vice versa. Darken and Gurry (1963) have re-formulated this rule in a slightly broader framework by asserting (see also Alonso and March, 1989) 'a disparity in valence is conducive to low solubility and this disparity has an especially pronounced effect when the solute valence is lower than the solvent valence'

Alonso and March (1989) separate two aspects of the above rule:

- (i) The statement concerning absolute solubility: a difference in valence leads to low solubility and
- (ii) The assertion concerning the relative solubilities of A in B and B in A.

The work of Gschneidner (1980) and of Goodman *et al.* (1983), see also Watson *et al.* (1983), has clarified the situation regarding relative solubilities

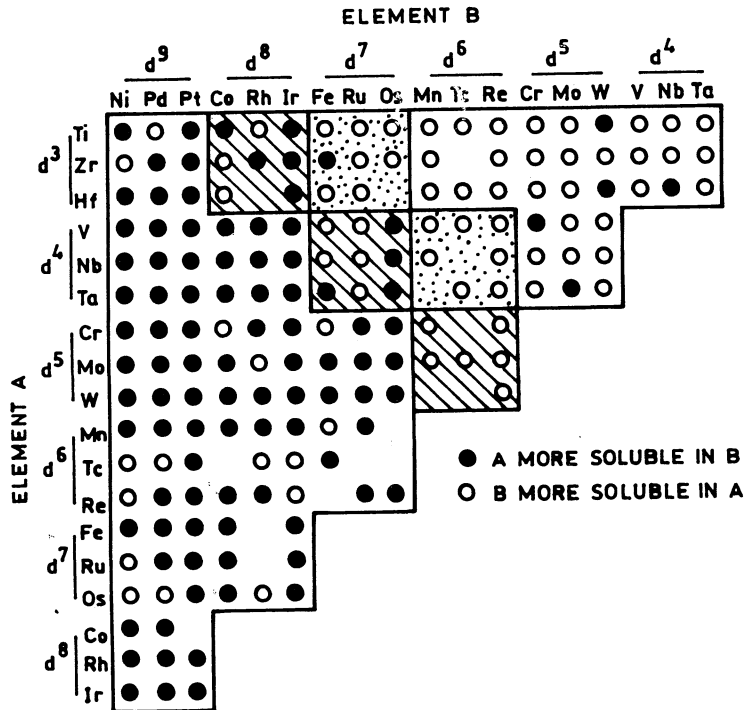


Fig. 1.5. Experimental relative solubilities in transition-metal alloys. The dotted region indicates systems where the d-bands of the constituents are equally far from half-filled; the hatched region indicates a diagonal boundary region in which no clear bias appears in the relative solubilities. (Redrawn after Watson *et al.*)

(see also Alonso and March, 1989). Gschneidner studied 300 systems formed by two metals having different valence and for which the terminal solid solubilities are known at both ends of the phase diagram. The result was that 55% of the systems do not confirm to the rule. The work of Goodman and co-workers deals with the relative solubilities in transition-metal alloys. Figure 1.5, reproduced from Alonso and March (1989) serves to illustrate the findings of these authors. The chart can be divided into two regions separated by a diagonal boundary (the cross-hatched region). Only in one of the regions is the relative-valence rule obeyed. In contrast, in the other region the rule obeyed is that 'the lower-valent metal is more soluble in the higher-valent one than vice-versa' (see also Alonso and March, 1989). We shall return to this point briefly in Chap. 6

on electronic structure, when we discuss the role of d-band filling in determining some of the physical properties of transition metals.

The final point to be made is that Chelikowsky (1979) has presented solubility plots in which the two coordinates are prompted by the semi-empirical theory of Miedema (Alonso and March, 1989). Since, however, electronic structure also enters this theory, we shall defer further discussion to Chap. 6.

1.12. *Friction Mechanisms**

The mechanisms of friction are discussed in early books on the subject (e.g. Bowden and Tabor, 1950). Here we refer to the subsequent account of Stoneham *et al.* (1993). These workers note the following mechanisms:

- (i) Adhesion: surfaces adhere and then work is done in separating them.
- (ii) Ploughing: one surface pulls away small amounts of the other and
- (iii) Anelasticity: here the assumption is that energy is dissipated by dislocation motion and plastic deformation in the material.

We shall, in later chapters, discuss friction on a mesoscopic scale as well as specific atomistic studies. As to the first of these, we shall see below that two main steps are involved. The first of these is the characterization of rough surfaces and their contact. The second step is to invoke some law of friction. In such a law, we want to stress here the central importance of atomic force microscope (AFM) data (see Appendix 2.5) and its interpretation.

Tribology, the study of surfaces in moving contact, is an important area for technology. In spite of this, friction, at the time of writing, is not well understood at an atomistic level. Persson (1994) has posed some fundamental questions as follows:

- (1) What is structure of sliding interface: both geometric and electronic?
- (2) Where does the sliding take place?
- (3) What is the physical origin of the sliding force?

Persson follows these somewhat general points with some more specific questions:

- (i) Why is the frictional force F usually proportional to the load N ?
- (ii) What is the microscopic origin of 'stick-and-slip' motion? (see following page).

*The reader who requires an advanced account should refer to the book *Physics of Sliding Friction*, Eds. B. N. J. Persson and E. Tosatti, NATO ASI series E: Applied Sciences, Vol 311 (1996): (Kluwer: Dordrecht).