Chapter 7
Grain Boundary Segregation and Related Phenomena

Grain boundary segregation affects various physical and chemical properties of the materials, which further control material behaviour. It is mainly the consequence of the close relationship between the grain boundary segregation on the one hand and the grain boundary energy and bonding state on the other hand. The chart listing some metallurgical phenomena affected by grain boundary segregation is shown in Fig. 7.1.

In this chapter, we will present some examples of the effect of grain boundary segregation on material behaviour.

7.1 Grain Boundary Cohesion

Historically, the widely manifested consequence of the grain boundary segregation is its effects on grain boundary cohesion as expressed in a number of well-known forms of intergranular fragility. This continues to provide much of the focus for work in this field. The central problem is the role of solute atoms on atomic cohesion at the interface. As shown in Fig. 7.1, the embrittlement can be of different nature, for example temper embrittlement, hydrogen embrittlement and liquid–metal embrittlement.

7.1.1 Grain Boundary Cohesion and Temper Embrittlement

The majority of the work on grain boundary cohesion has been connected with the effect of additions in iron because of the technological importance of this material [643]. It is now well established that the elements such as copper, zinc, silicon, germanium, tin, phosphorus, arsenic, antimony, bismuth, sulphur, selenium, tellurium, oxygen and manganese all cause intergranular weakness in iron. Similar solutes also weaken copper and nickel. We now consider the two questions (1) why do certain elements weaken the grain boundaries? and (2) what is the relative embrittling potency of these elements? [13].
A number of theories have been proposed to account for the role of the solute atoms on grain boundary cohesion. All have a common approach but differ in their interpretation of the way to carry out the numerical calculations. As first, McLean [19] proposed in 1957 that the total work of fracture in low temperature intergranular fracture is the sum of the ideal work of fracture, $\gamma$, and the irreversible plastic work of deformation, $\gamma_p$. $\gamma$ is the energy to open the bonds across the interface, and $\gamma_p$ remains absorbed in the crystal as dislocations and phonons over a region well away from the boundary. $\gamma_p$ is principally much larger than $\gamma$, however, if $\gamma$ increases, the forces at a crack tip must also be enhanced to propagate the fracture and therefore, $\gamma_p$ will increase. For a given grain boundary, $\gamma$ and $\gamma_p$ are thus directly related. The precise relation will depend on the micro-structure and also on the orientations of the two grains and the grain boundary. The analyses showed that $\gamma_p \propto \gamma^n$ where $n = 2–5$ [644, 645]. To be able to answer the above questions the effects of segregated solutes on the ideal work of the grain boundary fracture must be understood.

The ideal work of fracture of a non-segregated grain boundary with the energy $\sigma^{\Phi,0}$ is [19]

$$\gamma^0 = 2\sigma^{s,0} - \sigma^{\Phi,0}, \quad (7.1)$$

where $\sigma^{s,0}$ is the surface energy of the pure material because by opening the grain boundary two free surfaces are created. An analysis of the values of $\sigma^{s,0}$ and $\sigma^{\Phi,0}$ for many metals shows that typically, $\sigma^{\Phi,0} \approx \sigma^{s,0}/3$ [371]. Accordingly, the ideal work of fracture of the pure grain boundaries is only slightly lower than that of an average plane in the crystal (approximately 5/6 of it). It does not mean automatically that the grain boundaries will always fail in preference to cleavage. The fracture manner will also depend on the orientation of the slip planes and the surface energy of the