Strengthening mechanisms in alloys

T BALAKRISHNA BHAT and V S ARUNACHALAM
Defence Metallurgical Research Laboratory, Kanchanbagh P.O., Hyderabad 500 258

Abstract. Metals can be strengthened by methods appropriately combined to meet the operating conditions. In this 'alloy design', effort, we are guided by semi-quantitative relations that have been developed over the years and which relate the efficacy of the strengthening methods to the deformation modes. In this paper, the basic concepts are expanded with specific reference to dislocation glide, diffusional creep, grain boundary sliding and high strain rate deformation.

Keywords. Strengthening mechanisms; dislocation glide; dislocation climb; solution strengthening; precipitation strengthening; grain refinement; cell refinement; grain alignment.

1. Introduction

The term 'alloy design' may sound presumptuous as most of the commercial alloys of today are not products of deliberate design and development. It should not sound so any more, as there are now clear demands for materials with specific properties tailored to meet some specific applications. The materials engineer of today is better qualified to deal with such requirements as there is an improved understanding of the theoretical base for materials design and a variety of appropriate processing techniques available to synthesise them (Burte & Gegel 1980) accordingly. There is no one single route for designing materials, as property requirements vary. Designing for a radiation environment calls for optimising properties different from those required for designing a load-bearing structure. Materials thus have to be designed keeping their end applications in view.

Most of the metals and alloys used in engineering are load-bearing. This implies that these materials should have the necessary strength not to yield or fracture under load and retain their strength in service. It is the object of this paper to review the various strengthening mechanisms that can be effectively utilised to make metals and alloys meet the service requirements.

Strengthening of metals is necessary because metals are invariably weak due to the nature of metallic bonding, which is diffuse and non-directional, and also because of a large number of lattice defects. An important defect, dislocation, has high mobility because of the long-range periodicity of metallic lattices and the small translation vectors as compared to the spacing of planes on which they move (Cottrell 1966). Changing the nature of metallic bonding or the crystal structure to increase strength is not easy and cannot be recommended as it would lead to brittle solids.

A list of symbols appears at the end of the paper.
Strengthening efforts should therefore be directed towards strengthening the lattice against the easy movement of lattice defects. We shall first discuss the various flow processes that occur in metals and alloys and consider a number of strengthening mechanisms that can make this flow difficult. We shall also consider strengthening against high-temperature deformation and against large strain-rate effects.

It is important to emphasise that strengthening a metal is only one part of alloy design. The other is concerned with the building up of resistance to fracture. This in fact sets an upper limit for strengthening as increase in strength is generally accompanied by a reduction in ductility and fracture resistance (Tien 1975). Thus an upper limit to strength is imposed by other mechanical property requirements as well. While some strengthening methods, though very effective, bring in this limit too rapidly, others are more moderate. We have to optimise the various strengthening methods to evolve a successful strategy.

2. Plastic flow in metals and alloys

2.1 Deformation mechanism maps

Plastic flow occurs by a variety of mechanisms, their relative importance changing with temperature and applied stress. An elegant way to represent these flow properties is by deformation mechanism maps (Weertman 1968; Ashby 1972a, 1973; Mohammed & Langdon 1974; Frost & Ashby 1975). These maps graphically depict the response of a metal or an alloy to applied stress in terms of its shear modulus and homologous temperature. Various zones in the map characterising particular flow processes are determined by analysing the strain rate equations for different flow processes and evaluating the predominant one. A typical deformation mechanism map is shown in figure 1 for iron (adapted from Ashby 1972a; Lindholm 1974; Hockett & Zukas 1974; Oxley 1974). At very high stresses the flow is determined by the theoretical strength of the crystal (0.06G, where G is the shear modulus), athermal viscosity or twinning stresses. At high temperatures and low stresses, the flow is diffusional. An important area between these two extremes is governed by dislocation flow which falls in the range of usual temperatures and stresses in engineering applications.

2.2 Resistance to dislocation induced flow

Dislocation flow depends on some of the intrinsic properties of the host material, such as, elastic modulus E, diffusion coefficients D, and the crystal structure. This is because the energy of a dislocation is proportional to its modulus and the square of the Burgers vector b and its mobility at elevated temperatures is determined by the diffusion coefficients. As E, b and to a major extent, D are determined by the choice of the material they cannot be made to vary significantly by design. It is therefore necessary to seek other options available for reducing the dislocation mobility. This can be achieved by making the dislocation interact with the stress fields of other dislocations, sub-boundaries, grain boundaries, solute atoms and precipitates. These interactions, according to Fleischer & Hibbard (1973), can be ‘gradual’ or ‘rapid’ depending on the intensity of hardening. Rapid hardening has high $dr/df$ where $dr$
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2.3 Strengthening due to sub and grain boundaries

Dislocation cells, sub-boundaries and grain boundaries are effective strengtheners at low temperatures. However dislocation cells generated by cold work alone are not very useful because of poor ductility. This disadvantage can be overcome when the cold-worked structure is slightly annealed to produce well-developed dislocation sub-structures. The matrix is then devoid of dislocations except in boundaries or cell walls, where they are arranged in low-energy configurations. The interaction of dislocations with these walls does not drastically reduce the ductility and this route can effectively be utilised for strengthening. The increase in strength due to stable sub-structure is proportional to \( D^{-3} \) (\( D \) is cell size) (Embury 1972; Takeuchi & Argon)
Table 1. Mechanisms for strength and some of their characteristics

<table>
<thead>
<tr>
<th>Obstacle</th>
<th>Strength of the interaction $d\tau/d\phi$</th>
<th>Approximate formula for strength and some examples</th>
<th>Work hardening rate and some values</th>
<th>Effect of temperature</th>
<th>Limiting factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Substitutional atoms or interstitials at symmetric sites</td>
<td>Weak; $G/10$ to $G/100$</td>
<td>$a_1 \sqrt{\phi} (1 + a_2 \sqrt{\phi})$</td>
<td>Raises the saturation stress</td>
<td>Rapid drop with an apparent athermal breaking off at intermediate temperatures $\Delta F = 1/5 Gb^9$</td>
<td>Cost, solubility, segregation, weight penalty intermetallic formation</td>
</tr>
<tr>
<td>2. Interstitials in bcc, or strongly bonding interstitials</td>
<td>$1 \rightarrow 10G$ strong</td>
<td>$a_1 \sqrt{\phi} (Kocks et al. 1976)$ for Ti - 0 $a_1/G \sim 0.1$ (figure 2)</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>3. Grain boundaries, dislocations cells, two phase structures</td>
<td>$G/2 \rightarrow G/200$</td>
<td>$\sigma Gb/\rho$ (dislocation strengthening $KL^{-1/2}$ or $KL^{-1}$ (grain or interface strengthening) for Fe (Embury 1972) $a \sim 0.2m$, $G = 8.3 \times 10^4 MNm^2$, $b \sim 2.5 \times 10^{-4}m$ if $\rho = 10^3 m^{-2}$, $\Delta \sigma = 415 MNm^{-2}$, $K \sim 0.6 MNm^{-2}$ if grain size changes from $10^{-4}m$ to $10^{-5}m$, the strength would increase by $582 MNm^{-2}$</td>
<td>$1 d\tau \over \sigma G \over \partial \phi^{1/2}$ $\sim 1/2 \rightarrow 1$</td>
<td>$1/2 Gb^9$, weakly sensitive, can work upto $0.4 - 0.5$ TM</td>
<td>Coarsening, instability at elevated temperatures or in fatigue</td>
</tr>
<tr>
<td>4. Dispersoids</td>
<td>$G/10$</td>
<td>$0.81 Gb/L$ (Foreman &amp; Makin 1966)</td>
<td>$1/G d\tau/d\phi^{1/2} &lt; (b/2r)^{1/2}$ for $f = 0.01, r = 200b$ $1/G d\tau/d\phi^{1/2} = 1/2$ (Ashby 1970)</td>
<td>Strengths partly available even to high temperature; $\Delta F &gt; Gb^9$</td>
<td>Ductility reductions, inhomogeneity of dispersion</td>
</tr>
<tr>
<td>5. Precipitates</td>
<td>$G/100 \rightarrow G/200$</td>
<td>See table 2</td>
<td>No work hardening when cut, otherwise behaves like dispersoids</td>
<td>$\Delta F &gt; Gb^9$</td>
<td>Solubility and coarsening at elevated temperatures, slip concentrations in fatigue, ductility reductions with large misfit.</td>
</tr>
<tr>
<td>6. Ordering</td>
<td>$\Delta \tau \sim \gamma_{APB}^{(b)}$ $\sim G/100$</td>
<td>$\gamma_{APB}^{(b)}$</td>
<td>$1 d\tau \over G \over \partial \gamma^{1/2}$ $\sim 0.1$ to $0.3$ for ordered Fe-Co $\sim 0.3$ Marcinkowski (e.g. in Ni$_3$Al) 1974)</td>
<td>Weakly sensitive to temperature below disordering temperature. Strength may increase with temperature</td>
<td>Embrittlement</td>
</tr>
</tbody>
</table>
There is a 'memory effect' in these sub-structures on the mode of deformation employed to develop them. When the stress systems are altered, the sub cells developed during processing turn unstable and 'dissolve' causing flow instabilities. This should be borne in mind when dislocation cells are thought of as a strengthening route (Pattanaik et al. 1974). However, sub-boundaries can be stabilised by second phase particles, voids, or even by solutes (Rama Rao 1978; Kutumba Rao et al. 1975). The boundaries developed as a result of deformation-processing in the presence of dispersed particles have high stability and can be a source of useful strength over a range of temperatures. This coupled with grain refinement has led to the development of commercially viable processes under the generic name, 'thermo-mechanical processing'. High strength low alloy (HSLA) steels are products of such a processing.

Strengthening due to grain boundaries is similar to sub-boundary strengthening except that the strength increment ($\Delta \sigma$) is generally proportional to $d^{-1/2}$ ($d$ is the grain size) according to the Hall-Petch equation: $\Delta \sigma = Kd^{-1/2}$ (Hall 1951; Petch 1953; Embury 1972; Margolin & Stanescu 1975). The proportionality constant $K$ is found to vary with strain and temperature and is derived to be equal to $M^2 r^{1/2} \tau_c$, where $M$ is the Taylor orientation factor, $r$, the distance between the head of the pile-up and dislocation source and $\tau_c$, the critical shear stress necessary to activate a dislocation source in the next grain (Armstrong et al. 1962). However, recent experiments suggest that the Hall-Petch equation is not universally valid and the reasons for this are not clear (Hutchinson & Pascoe 1972; Morris et al. 1976) and further work in this area is desirable.

Grain sizes can be reduced to micron and sub-micron levels by controlled micro-alloying additions followed by thermomechanical processing. Finely distributed insoluble particles can also inhibit grain growth. Fine grains generated as a result of thermomechanical processing are stable in many alloy systems (e.g. HSLA steels) and are capable of providing increase in strength upto intermediate temperatures.

It is worth pointing out that both sub-boundary and grain boundary strengthening are the only mechanisms which do not (Cottrell 1966) affect ductility and are therefore attractive for the designer. Figure 2 shows the relative hardening efficiencies of grain and cell boundaries as against various solute elements on a ' weight or volume percent' basis. This figure was generated by assuming the boundary thickness to be around $5b$ and a sub-boundary wall thickness of about $20b$ and calculating the volume fraction of the boundary phase as the obstacle density. The grain or cell boundary route stands out as the most rapidly hardening mechanism.

A novel approach to strength, for some metallic systems at least, is to turn them glassy. This is achieved by appropriate choice of alloying additions and cooling these rapidly to prevent the onset of crystallisation. The resulting structure can be considered to contain only disordered grain boundary structures. This is known to provide high strength and some attempts are being made to evolve a theory for understanding their behaviour (Ramachandra Rao 1980 private communication; Cahn 1980).

### 2.4 Precipitation hardening

Alloying to precipitate a second phase is perhaps the most effective and successful strengthening route. The second phase particles can be incorporated by precipitation
Figure 2. Effect of solutes, precipitates, dispersoids, grain or cell boundaries on strength. (Explanation to the curves are given in the table below)

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>Material</th>
<th>Strengthening element</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>bcc iron at 300(^\circ)K</td>
<td>Grain boundary</td>
<td>Embury (1972)</td>
</tr>
<tr>
<td>2</td>
<td>Ti at 300(^\circ)K</td>
<td>Grain boundary</td>
<td>Jaffee (1973)</td>
</tr>
<tr>
<td>2'</td>
<td>Ti at 450(^\circ)K</td>
<td>Grain boundary</td>
<td>Jaffee (1973)</td>
</tr>
<tr>
<td>3</td>
<td>Ti</td>
<td>N</td>
<td>Tyson (1970); Everhart (1954)</td>
</tr>
<tr>
<td>5</td>
<td>Fe</td>
<td>Cells</td>
<td>Morrisson (1966); Takeuchi &amp; Argon (1976)</td>
</tr>
<tr>
<td>6</td>
<td>Ni</td>
<td>Grain boundary</td>
<td>Embury (1972)</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>P</td>
<td>Pickering (1978)</td>
</tr>
<tr>
<td>9</td>
<td>Ti</td>
<td>Fe</td>
<td>Everhart (1954)</td>
</tr>
<tr>
<td>10</td>
<td>Ti</td>
<td>Mo</td>
<td>Everhart (1954)</td>
</tr>
<tr>
<td>11</td>
<td>Ti</td>
<td>V</td>
<td>Everhart (1954)</td>
</tr>
<tr>
<td>12</td>
<td>Fe</td>
<td>Si</td>
<td>Pickering (1978)</td>
</tr>
<tr>
<td>13</td>
<td>Ni</td>
<td>ThO(_3)</td>
<td>Sims &amp; Hagel (1972)</td>
</tr>
<tr>
<td>15</td>
<td>Ti</td>
<td>Al</td>
<td>Solonia &amp; Kuraeva (1973)</td>
</tr>
<tr>
<td>16</td>
<td>Fe</td>
<td>Mn</td>
<td>Pickering (1973)</td>
</tr>
<tr>
<td>17</td>
<td>Ti at 873(^\circ)K</td>
<td>Sn</td>
<td>Solonia &amp; Kuraeva (1973)</td>
</tr>
<tr>
<td>18</td>
<td>Ni</td>
<td>Al</td>
<td>Decker (1969)</td>
</tr>
<tr>
<td>19</td>
<td>Ni</td>
<td>Mo</td>
<td>Decker (1969); Pelloux &amp; Grant (1968)</td>
</tr>
<tr>
<td>21</td>
<td>Ni</td>
<td>Cr</td>
<td>Decker (1969)</td>
</tr>
<tr>
<td>22</td>
<td>Fe</td>
<td>Cr</td>
<td>Pickering (1978)</td>
</tr>
<tr>
<td>8</td>
<td>(K_f)^3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(K_f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>(K_f)^3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Dislocation-particle interactions

<table>
<thead>
<tr>
<th>mechanism &amp; order of magnitude</th>
<th>effective resisting force/2E</th>
<th>activation energy</th>
<th>representation of force</th>
<th>typical formula</th>
<th>example</th>
<th>comparison of experiment with theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>core energy</td>
<td>(21ΔF/F)^1/2 same</td>
<td>W/ΔF_dis</td>
<td>—</td>
<td>—</td>
<td>strong compounds</td>
<td>—</td>
</tr>
<tr>
<td>ΔF_{core} = F_{dis}/100</td>
<td>0.2</td>
<td>(W/b)/200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>modulus differences</td>
<td>[2</td>
<td>ΔG/2ΔG_{int}]^{1/2}</td>
<td>ΔG_{b}^2ω</td>
<td>8Gb (1 - E_{1}/E_{2})^2</td>
<td>Fe - Cu</td>
<td></td>
</tr>
<tr>
<td>ΔG ~ G/2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>interface step</td>
<td>(2β_{int}/L)^1/2</td>
<td>2bW_{int}</td>
<td></td>
<td>—</td>
<td>Al - Cu</td>
<td></td>
</tr>
<tr>
<td>Δν_{int} ~ Gb/100</td>
<td>0.3</td>
<td>(Wb)/50</td>
<td></td>
<td></td>
<td>Cu - Be</td>
<td></td>
</tr>
<tr>
<td>Δν_{void} ~ Gb/10</td>
<td>0.8</td>
<td>(Wb)/5</td>
<td></td>
<td></td>
<td>(Brown &amp; Ham 1972)</td>
<td>—</td>
</tr>
<tr>
<td>Orowan loop</td>
<td>strong</td>
<td>strong</td>
<td>W^2/L</td>
<td>0.8Gb/L</td>
<td>Cu - BeO (Hirsch-Humphreys 1970)</td>
<td>—</td>
</tr>
<tr>
<td>solid solutions</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>a_1/(f + a_2/f)</td>
<td>Ni - Mo</td>
<td>the concentration dependence of f^{1/2} is observed at low concentration and f at high concentration</td>
</tr>
</tbody>
</table>
Table 2. (Contd.)

<table>
<thead>
<tr>
<th>mechanism &amp; order of magnitude</th>
<th>effective resisting force/DE</th>
<th>activation energy $F_0/Gb^3$</th>
<th>representation of force</th>
<th>typical formula</th>
<th>example</th>
<th>comparison of experiment with theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>friction stress $G/100 = \tau_{ele}$</td>
<td>$W/b \times 100$</td>
<td>same</td>
<td>$\frac{\Pi}{4} \frac{W^2 b}{(W/b)^2/100}$</td>
<td>$W/b \times 100$</td>
<td>Al-Si</td>
<td>$-$</td>
</tr>
<tr>
<td>disordering $\tau_{APB} = Gb/100$</td>
<td>$W/b \times 100$</td>
<td>same</td>
<td>$\frac{\Pi}{4} \frac{W^2 \tau_{APB}}{(W/b)^2/100}$</td>
<td>$\frac{\tau_{APB}}{2b} - \frac{Gb}{W}$</td>
<td>nickel base alloy: mar M-200</td>
<td></td>
</tr>
<tr>
<td>misfit strains $</td>
<td>\epsilon</td>
<td>= 1/100$</td>
<td>$GbW$</td>
<td>small</td>
<td>$GbW^2</td>
<td>\epsilon</td>
</tr>
</tbody>
</table>
of unstable solutes from solution. The strength of interaction between dislocations and second phase particles is determined by the particle size and volume fraction and by the nature of the particles themselves. Table 2 summarises various parameters which determine this interaction, both for obstacles that are cut or bypassed.

The modulus differences (soft particle strengthening, solute clusters e.g. Cu in Fe, Russell & Brown 1972), antiphase boundary energy or the stacking fault energy (superalloys, $\gamma'$ in $\gamma$, Sims & Hagel 1972) and to a somewhat smaller extent, the misfit strains (Al-Cu alloys, Brown & Ham 1972) are usually the important factors for strengthening. On the other hand, the interface step energy and the core energy differences only lead to marginal strength benefits (Kocks et al 1973). Lattice mismatch, though a potent strengthener, adversely affects ductility. Lattice mismatch, in addition, enhances, the precipitate coarsening rate at elevated temperatures. Mismatch therefore is kept to a minimum in many alloy systems in spite of its rapid strengthening potential.

An interesting feature of precipitation-hardened systems is the variation of strength with precipitate size (figure 3, Mitchell 1966; Decker 1969). The strength at first increases and then gradually decreases with increasing particle size, even though the volume fraction of particles and hence the antiphase boundary energy, stacking fault energy or misfit strain energy all remain constant. In the cutting region, with increasing particle size, the particle dislocation interaction becomes stronger, forcing the dislocations to adopt increasing curvatures before being cut. This increases the

![Figure 3. Effect of precipitate size on strength of the alloy.](image-url)
average number of obstacles per unit length of dislocation and hence the strength. With further increases in particle size, the random spacing continues to increase and a stage is reached where particles can no longer be cut but have to be looped by the dislocation. The strength then falls according to the Orowan equation: \( \Delta \sigma \sim Gb/(L-d) \) (Foreman & Makin 1966, 1967).

Orowan looping is a predominant deformation mechanism when particles are strong and when they are widely spaced. Even though the yield strength is lower in looping than when the particles are cut (figure 3), the material work hardens rapidly with strain due to dislocation foresting, and develops strength with deformation. The associated deformation is also more homogeneous. The influence of precipitate shape on strength has not received much attention so far. It is known however, that thin precipitates are powerful strengtheners. In fact the rapid grain boundary strengthening possibly arises from the almost infinite thinness of the boundaries.

Precipitation hardening often displays a temperature dependence that is not expected at first glance from such large obstacles. There could be many reasons for this anomaly. Dislocations can climb over the particles with increasing rapidity at elevated temperatures. The precipitates themselves tend to coarsen with time at elevated temperature (Ostwald ripening). Besides, dislocation interaction with particles can cause directional growth of the precipitates (Cary & Strudel 1976) facilitating the dislocations to find weaker channels to creep. For strength at elevated temperatures, it is therefore essential to choose only those precipitates which remain uniform and stable. If the particle distribution is non-uniform, dislocations would increasingly concentrate their activity in weaker zones once they could climb to reach there.

2.5 Two-phase hardening

There is an important class of alloys intermediate between precipitation hardening and grain size strengthening. The microstructures of these alloys contain an intimate mixture of two or more phases. Microstructures under this category include eutectic, eutectoidal, and other transformation structures. A typical microstructure is shown in figure 4 (plate 1) (Banerjee 1980 unpublished). Such alloys derive their strength from the fine structure of the colonies and the increase in strength shows a Hall-Petch type relationship to the colony size, the exponent ranging from \(-\frac{1}{3}\) to \(-1\) (Embury 1972), suggesting that the strength arises partly from an Orowan type interaction and partly from the Hall-Petch interaction.

A special feature of two-phase strengthening is that the composite exhibits good ductility and energy-absorbing characteristics even if one of the phases is brittle (Manganon & Thomas 1970) and hence deserves intensive study.

2.6 Solution hardening

This method is perhaps the oldest and was successfully practised by alchemists for developing bronzes, brasses and golden ornaments. In solution hardening, the host atoms are either replaced by solute atoms or the solutes occupy interstitial sites in the lattice. In explaining the mechanism of solid solution strengthening, Labusch (1972), Labusch et al. (1975) and Haasen (1979) have shown that the effect of mismatch strain for solutes could be significant while Stern (1975) and Collings & Gegel
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(1975) emphasise the importance of chemical and electrical effects. Similarly while Labusch (1970) emphasises the importance of dielastic interaction, Riddhagni & Asimov (1968) find it to be negligible. The solution-strengthening problem, being atomistic in scale, is outside the regime of normal microstructure-mechanical property rationale and is to some extent less understood.

Figure 2 shows the influence of increasing solute concentration \( f \) for several solutes on the strength of Fe, Ni and Ti. The strength of interaction varies over at least three orders of magnitude. Some elements cause rapid hardening, others only gradual. The rapid hardening by carbon in Fe is usually attributed to the asymmetry of distortion at the tetragonal site (Fleischer & Hibbard 1973). Ti is rapidly strengthened by interstitials such as O, C, N which has been attributed to the strong bonding effect (Tyson 1975). Strengthening in a fcc lattice like nickel is gradual and is governed mostly by size mismatch (Stoloff 1972) and lowered stacking fault energy (Gerold & Hartman 1968). The alloy with lower stacking fault energy is stronger as dislocations get extended into wider partials which have to be constricted before they can cross-slip over obstacles or interact with other dislocations to produce plastic deformation. Also plotted in figure 2 are two types of curves: (i) curves representing hypothetical Orowan type interaction by solute clusters, which gives \( f^{1/2} \) dependence and (ii) curves showing \( f^1 \) dependence. For rapid-hardening solutes \( f^{1/2} \) dependence correlates well, while for slow hardening solutes at higher concentrations, the \( f^1 \) function fits better. Inflexible dislocations arising out of a large number of solutes with weak force constants give rise to \( f^1 \) dependence (Gerold 1979).

2.7 Order strengthening

The atomic order in alloys can lead to significant strengthening (Marcinkowski 1974; Westbrook 1974) giving higher yield strength, creep strength, as well as work hardening coefficient. The strength increment essentially arises due to dislocation interactions with domain boundaries and dislocations leaving a trail of antiphase domain boundaries. Increased work hardening rate (3–4 times higher than that for disordered alloys) is usually attributed to the accumulation of multipoles that are not annihilated owing to difficult cross slip of superdislocations. In non-cubic crystals these can arise from an interaction of dislocations with axial domain walls (Arunachalam & Cahn 1974). The decreased cross slip is beneficial to fatigue and creep properties (Marcinkowski 1974).

The strength of many two-phase alloys is due to the ordered intermetallic precipitates in them: Ni$_3$Al(\( \gamma' \)) in nickel base alloys, Ni$_3$Mo in maraging steels and CuAl$_2$/MgZn$_2$/Al$_2$Cu, in Mg, Cu alloys. A major drawback associated with order-strengthening (like many other modes of rapid strengthening) is the accompanying embrittlement. Structural application of fully order-strengthened materials depends on improving their ductility.

3. Strengths at high temperatures

At elevated temperatures materials deform by creep energized by a variety of diffusional and thermally activated processes. Strengthening at high temperatures should
therefore be directed towards slowing down these processes. The efficacy of a particular strengthening mechanism can be gauged from its effect on the various parameters in the relevant creep equation.

3.1 Strengthening against diffusional flow

Diffusional flow in polycrystalline materials occurs by flow of matter from grain boundaries under compression to boundaries in tension (Nabarro 1948; Ashby 1969; Herring 1970; Coble 1971; Raj & Ashby 1971, 1972; Burton 1972; Harris 1973; Ashby 1973; Burton & Beere 1978). This flow can occur either through grain boundaries (Coble creep) or through the bulk (Nabarro-Herring creep), the total flow being represented by a creep equation:

\[
\dot{\varepsilon} = A \frac{(\sigma_a - \sigma_b)}{G} \left( \frac{\Omega}{KTd^3} \right) D_{\text{eff}},
\]

\[
D_{\text{eff}} = D_o \left[ 1 + \left( \pi \delta \frac{D_o}{d} \right) \right],
\]

where \(A = \) a constant, \(\sigma_a = \) the applied stress, \(\sigma_b = \) the back stress that pins down the vacancy sources and sinks, \(\Omega = \) the atomic volume, \(G = \) the shear modulus, \(D_o = \) volume diffusion coefficient, \(d = \) the grain size, \(\delta = \) the boundary thickness, \(K = \) Boltzmann constant and \(T = \) temperature in K.

Creep can be minimised by reducing \(D_{\text{eff}}\) or increasing \(\sigma_b\). The effective diffusion coefficient \(D_{\text{eff}}\) can to some extent be reduced by alloying with heavy elements (Mo in Ti; W, Mo in Ni, Mo in steels), or elements that bind vacancies (Si in Ti). The back stress \(\sigma_b\) which opposes the grain boundary vacancy sources and sinks can be imposed on a polycrystalline array by incorporating a fine dispersion of stable inert particles in the material. More importantly, increasing the grain size \((d)\) decreases the creep rate as \(1/d^2\).

Polycrystals creep also by boundary sliding, with grains sliding past one another causing stress concentrations, which force the necessary local accommodation by diffusional flow, cavitation, or by dislocation creep. It is particularly important to suppress this mode as most of the high temperature alloys ultimately fail by shear and parting at grain boundaries (Perry 1974). The creep rate that can be attributed to sliding in a polycrystal can be empirically written to be (Raj & Ashby 1972; Gifkins 1977; Wilcox & Clauer 1972, 1966; Ashby 1972 b):

\[
\dot{\varepsilon} = C \left( DGb/KT \right) \left( b/d \right)^n \left[ (\sigma_a - \sigma_b) / b \right] \left( L^2 / r^3 \right) \left( f(1/d, \theta) \right)
\]

\[
\dot{\varepsilon} = \text{the strain rate due to sliding}
\]

\(C = \) a constant,

\(b = \) the Burgers vector,

\(D_b = \) the effective diffusion coefficient at the boundary zone,

\(d = \) the grain size,

\(\sigma_a = \) the applied stress,

\(\sigma_b = \) the back stress to moving boundary defects,

\(n = 1-3\) (usually about 2) (Gifkins 1977, 1978)

\(m = \sim 1 - 1.5\) (Gates & Horton 1977),

\(L = \) the particle spacing at grain boundaries,
Strengthening mechanisms in alloys

\[ r = \text{size of particles at grain boundaries}, \]
\[ 1/d = \text{the grain aspect ratio}, \]
\[ \theta = \text{the orientation of the grain alignment with respect to stress}. \]

The tendency to slide is lowered by increasing the grain size, incorporating stable particles at the boundaries, and more powerfully by growing grains of large \(1/d\), aligned along the stress axis. Directionally solidified microstructures, such as those shown in figure 5 (plate 1), strengthened with precipitates, ideally fit into this requirement (Tiwari & Hema Reddy 1979, unpublished work) and provide excellent creep properties (figure 6). By suppressing boundary sliding, we, in effect, convert a polycrystal into a ‘single crystal’. Better still would be to go in for single crystals with no boundaries to worry about.

3.2 Strengthening against dislocation creep

All obstacles become increasingly transparent to dislocation motion at elevated temperatures. Dislocations assisted by diffusional processes climb or cross-slip over these obstacles. The flow rate by such a process can be given by an approximate equation of the form (Bird et al 1969; Kocks et al 1973; Ashby 1973; Balakrishna Bhat & Arunachalam 1977; Takeuchi & Argon 1976):

\[ \epsilon = A \left[ (\sigma_a - \sigma_b)/G \right]^n (DGb/KT), \]

Figure 6. Creep properties of directionally solidified ZHS-6K compared against as cast properties (Hema Reddy & Tiwari, private communication). (a) Investment cast. (b) Investment cast plus heat-treated. (c) Directionally solidified. (d) Directionally solidified plus heat treated.
where the terms have their meanings as defined in previous sections. In this case the diffusion coefficient $D$ is given by, $D = D_v f_v + D_c f_c$, where $f_v$ and $f_c$ are the fraction of atom sites associated with bulk and core diffusion respectively; $D_v$ is the volume diffusion coefficient and $D_c$ the core diffusion coefficient.

It is essential to subdue dislocation creep for it is generally too rapid. We can attempt to decrease dislocation creep through many routes. $D$ can be reduced a little by alloying. Some alloying elements segregate to dislocations (Si in Ti, Kehoe & Broomfield 1973) and form dragging obstacles. This leads to a reduced creep rate. Many elements in solution decrease stacking fault energy (Gallagher 1970). The dislocation reactions then become slower (Ashby 1973; Sastry et al 1974; Mohammed & Langdon 1974; Bird et al 1969) and the parameter $A$ in the creep equation is reduced. The separated partials could climb together by nucleation of jog pairs. However, such nucleation has a large energy barrier and would be extremely slow (Baluffi & Granato 1979). Hence the separated partials will have to be constricted before climb or cross slip, an event which effectively introduces a back stress ($\sigma_b$) to dislocation motion. Stable particles can strongly reduce creep by providing a back stress which the dislocations must first overcome before creeping and interacting with other dislocations. The back stress has been calculated to be around 0.5 $\sigma$ Orowan (Brown & Ham 1972) and recent calculations by Lagneborg & Bergman (1976) have suggested that this back stress is not constant but varies with applied stress. The back stress arises from the extra line lengths of dislocations that have to be created to form the climb configuration. The presence of this back stress explains the excellent creep resistance of nickel base superalloys. The back stress that is responsible for subdued creep also explains the anomalously high values of activation energy and stress exponents in the creep rate equation for these materials. Table 3 shows how incorporation of back stress in the creep equation brings down both $\theta$ and $n$ values in line with the observed values for precipitate free systems (Balakrishna Bhat 1980; Lund & Nix 1975; Parker & Wilshire 1975).

4. Strengthening against high rates of deformation

There are some applications where the materials are required to stand up to localized impulsive forces, as for instance when they are hit by high velocity projectiles.

A parameter that is important for such an application is plastic modulus, $\partial\sigma/\partial\epsilon$, a function related to the work hardening coefficient. This parameter determines the spread of deformation in the bulk since plastic deformation waves propagate with a speed $V_p$ given by $V_p = \left\{\left(\partial \sigma / \partial \epsilon\right)_p\right\}^{1/2}$ (Cottrell 1966; Johnson 1972). High 'plastic modulus' ensures that deformation rapidly spreads over a large volume which prevents strain localization and leads to the protection of the material against fracture. There are a number of ways of increasing this modulus; fine grain size, presence of fine non-deformable particles and solid solution alloying all increases this coefficient or shift the limit of work hardening to higher strain values. Precipitation hardening is not all that effective for this purpose as the precipitates are generally cut at high stresses and therefore do not lead to an increase in the work hardening. At strain rates between $10^2$ to $10^4$ s$^{-1}$, phonon drag has been claimed to be an energy dissipation mechanism (Klahn et al 1970; Kumar 1970). It is not clear how import-
Table 3. Incorporation of back stress in the creep equation removes the apparent anomaly in activation energies

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°K)</th>
<th>n</th>
<th>$Q_{app}\ K\ mole^{-1}$</th>
<th>Correction to $Q$ due to variation of elastic modulus, K. cal, mole$^{-1}$</th>
<th>Correction to $Q$ due to variation of back stress K. cal, mole$^{-1}$</th>
<th>$Q_{real}\ K\ cal\ mole^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD Nickel</td>
<td>1174</td>
<td>4</td>
<td>768</td>
<td>40</td>
<td>444</td>
<td>284</td>
</tr>
<tr>
<td>(Wilcox and Clauer 1966)</td>
<td>1218</td>
<td>4</td>
<td>768</td>
<td>43</td>
<td>442</td>
<td>283</td>
</tr>
<tr>
<td>Dispersion strengthened superalloy</td>
<td>1343</td>
<td>4</td>
<td>980</td>
<td>56</td>
<td>650</td>
<td>274</td>
</tr>
<tr>
<td>Dispersion strengthened superalloy</td>
<td>977</td>
<td>4</td>
<td>640</td>
<td>9</td>
<td>238</td>
<td>392</td>
</tr>
<tr>
<td>Dispersion strengthened superalloy</td>
<td>1200</td>
<td>4</td>
<td>810</td>
<td>45</td>
<td>434</td>
<td>331</td>
</tr>
<tr>
<td>Dispersion strengthened superalloy</td>
<td>1311</td>
<td>4</td>
<td>835</td>
<td>72</td>
<td>406</td>
<td>357</td>
</tr>
</tbody>
</table>

At high strain rates, the dislocation density can reach very high values which are not seen during normal rates of deformation. To provide strengthening, the obstacle density should therefore be high enough to match the increased dislocation density. Viewed from this angle, most of the strengthening mechanisms are ineffective and solute hardening may perhaps be the best.

5. Conclusions

Metals can be strengthened in a variety of ways appropriately combined to design alloys that can stand up to the major operating deformation mechanisms. There exist semi-quantitative relations to assess the efficacy of these strengthening routes, which can be used to guide us in alloy design.

Some of these techniques are well-understood and are being effectively used, while a few others deserve a better in-depth study so that they can also be utilised effectively. Newly emerging processing techniques provide challenges to the alloy designer to use them to synthesise alloys with still better properties. It is this challenge that makes alloy design intellectually stimulating and technically rewarding.

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List of symbols

\( A \) \quad \text{constant in phenomenological relation}
\( b \) \quad \text{Burgers vector}
\( c \) \quad \text{constant}
\( D \) \quad \text{diffusion coefficient}
\( D_b \) \quad \text{boundary diffusion coefficient}
\( D_v \) \quad \text{volume diffusion coefficient}
\( D_{\text{eff}} \) \quad \text{effective diffusion coefficient}
\( E \) \quad \text{effective line tension}
\( F_{\text{dis}} \) \quad \text{energy per unit length of dislocation}
\( f_c \) \quad \text{fraction of sites associated with core diffusion}
\( f_v \) \quad \text{fraction of sites associated with volume diffusion}
\( \Delta F \) \quad \text{activation free enthalpy}
\( \Delta F_{\text{dis}} \) \quad \text{difference between high energy and low energy positions of the dislocation}
\( G \) \quad \text{shear modulus}
\( k \) \quad \text{Boltzmann constant}
\( K \) \quad \text{Hall-Petch coefficient, a constant}
\( L \) \quad \text{obstacle spacing}
\( m \) \quad \text{exponent for (1/d) for boundary sliding}
\( n \) \quad \text{stress exponent}
\( r \) \quad \text{particle radius}
\( T \) \quad \text{absolute temperature}
\( w \) \quad \text{obstacle width}
\( 1/d \) \quad \text{aspect ratio}
\( a_1, a_2, a_3 \) \quad \text{constants}
\( \gamma \) \quad \text{surface energy}
\( \gamma_{\text{APB}} \) \quad \text{antiphase boundary energy}
\( \epsilon \) \quad \text{strain}
\( \dot{\epsilon} \) \quad \text{strain rate}
\( \Delta \sigma \) \quad \text{strength increment}
\( \delta \) \quad \text{boundary thickness}
\( \sigma_a \) \quad \text{applied stress}
\( \sigma_b \) \quad \text{back stress}
\( \rho \) \quad \text{dislocation density}
\( \tau \) \quad \text{shear stress}
\( \tau_c \) \quad \text{critical stress}
\( \tau_{\text{ele}} \) \quad \text{element glide resistance}
\( \partial \tau / \partial \gamma \) \quad \text{variation of shear strength with strain}

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Figure 4. Two-phase structure in a typical titanium alloy.

Figure 5. Directionally solidified ZHS-6K alloy.
Figure 7. Adiabatic shear bands in steel with associated cracking failure.