Physical metallurgy of substitution

R A J E N D R A   K U M A R   and   V E D   P R A K A S H

INDUSTRIAL civilization is largely based on scientific and technological development in different countries and no country can today remain aloof from scientific and technological developments which take place elsewhere in the world. The industrial complex of developing nations has initially to import machinery and raw materials and even men from industrially advanced countries to gear up their rate of progress, but a stage comes in the growth of their industrial pattern that the import of either the machinery or raw materials is not economically possible specially if the balance of trade is adverse. In this context, development of substitute alloys has acquired two meanings. It primarily suggests development of new alloys based on metals produced in India and/or using minimum amounts of imported metals. Whenever substitution with indigenous alloys is not possible, its scope may be enlarged to include development of new processes and heat treatment which raise the strength so that utilization of thinner sections may reduce the cost of import.

Present day technology is essentially based on iron and steel including alloy steels. Although resources of iron are rich and extensive, those of its important alloying elements, nickel, chromium, molybdenum, cobalt, etc. are scarce. Similarly, most of non-ferrous metals are either not available in the country or their deposits too small to meet the entire industrial demands. In this category are tin, zinc, lead and copper. On the other hand, there are abundant resources of titanium, manganese, chromium, aluminium and magnesium. It is probably correct to say that most of these metals are only used to a very limited extent in India.

Evaluation of indigenous metals for alloy development

Based on considerations of alloying alone, the problem of designing a material from first principles would seem a fairly straight-forward one but the problem of developing an engineering material which resists both plastic yielding and brittle cracking, is complex as a number of other factors have also to be considered. If this were not so, a metal could be chosen according to the strength of the atomic bonds calculated from elastic or thermal properties.

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No precise measure of cohesive forces is available. If, however, the melting temperature is considered as a reflection of the binding energy, then the (cohesion/unit mass) decreases in the order Be, Ti (Mg, Nb) Cr, Mo, Al, Fe, W, Co, Mn, Cu, Pb as given in Table 1 which shows that the metals of potential Indian interest (Ti, Mg, Cr and Al) are amongst the more stronger metals on a unit mass basis. But scientific information about them has not advanced to an extent to permit their technological exploitation for alloy development.

TABLE I   Some physical properties of a few engineering metals

Metal	Compressibility $K = -(1/V)(dv/dp)$ near room temp. in 10^7 Cm²/kg	Cohesive energy in Kcal/mole at room temp.	Melting point °C	Density	Melting point/density or cohesive strength/unit mass.
Al	13·4	55	660	2·7	244
Cr	6·1	88	1850	7·1	260
Fe	5·9	94	1537	7·9	195
Mg	29·5	36	650	1·74	287
Mn	7·9	74	1244	7·4	168
Ti	8·0	100	1660	4·5	369
Be	7·8	75	1284	1·85	694
Co	5·4	85	1492	8·7	1·71
Cu	7·2	81	1083	8·9	122
Ir	2·7	120	2443	22·4	109
Pb	23·7	48	327	11·3	29
Mo	3·6	160	2825	10·2	257
Ni	5·3	85	1455	8·9	168
Nb	5·7	68	2468	8·6	287
Ta	4·8	97	3000	16·6	185
W	3·2	210	3380	19·3	175·12

## Inadequacy of chromium as a base for alloy development

The first metallurgical familiarity with chromium showed that (i) it has a very sharp transition in a narrow temperature band from ductile to brittle fracture (ii) the transition temperature is very sensitive to the impurity content—whereas it is less than 100°C for electrolytic chromium, it is between 300 and 400°C for chromium made from chromium hydride, and (iii) brittleness is probably due to the presence of minute quantities of dissolved nitrogen.[1,2] Sully et al[3] showed that variation of nitrogen content between 0.001 and 0.04% was without any significant effect on transition temperature. The main handicap in the extensive use of chromium is its high ductile to brittle transition temperature. Efforts to find an element to lower the transition temperature, as does manganese in iron, have so far failed. Fig. 1 showing the effect of added elements on the transition temperature, indicates[3] that (i) almost all alloying elements sharply raise the transition temperature and (ii) although oxygen has a marked effect on ductility above transition temperature its presence does not have any marked effect on the transition temperature. It appears[3] that the effect of alloying elements on the transition temperature is related to the lattice distortion, as measured by hardness, and it shows a sharp upward tendency with increasing hardness. Wain and Henderson[4] demonstrated that the transition temperature of chromium strip arc-melted and hot worked (by forging and swaging) can be brought down below room temperature. Even if ductile chromium could be produced economically on a large scale, alloying to increase its hardness and strength would simultaneously raise the transition temperature so that such alloys would again be severely embrittled. Unless alloys with super-pure chromium behave in a better manner, it cannot constitute a base for alloy development and its use will have to be restricted as an alloying element. Creep resistance[5] of chromium-base alloys (80% Cr-10% Fe-10% Ta) is reported to be very high but no use can be made because the alloys are very brittle at room temperature, besides being notch sensitive at high temperature. In this connection, it may be useful to study transition temperature of alloys prepared with high purity chromium. Non-traditional methods of metal processing as discussed later in this paper, are also now being explored to develop chromium alloys with adequate ductility.

Titanium and its alloys

Titanium combines availability with lightness, strength and corrosion resistance. It has come into vogue only during the last two decades and precautions needed in working and using titanium alloys are now becoming generally understood. Titanium metal exists in two allotropic modifications—alpha titanium is close packed hexagonal and is stable below 882.5°C; the high temperature form is referred as beta titanium and is body centred cubic. It alloys with many metals and metalloids and its alloying behaviour is considerably influen-
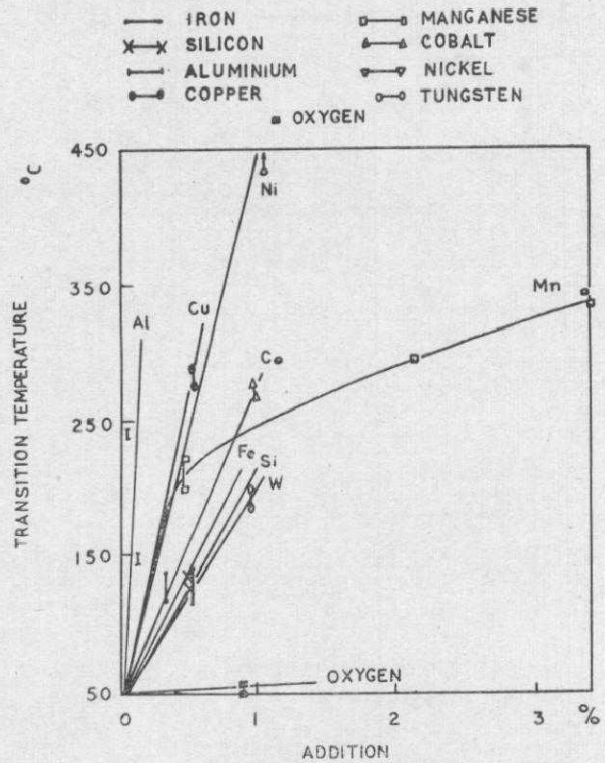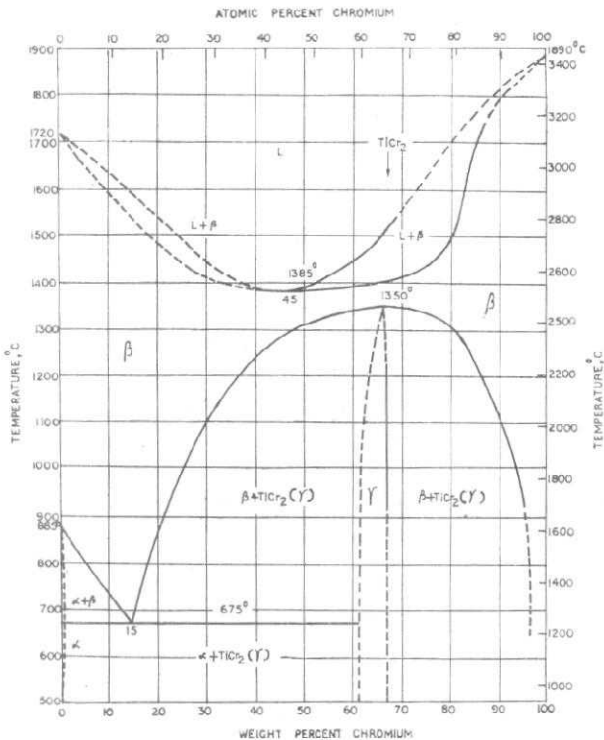

1 *Effect of added elements on the brittle/ductile transition of chromium in bend tests (after A. H. Sully, E. A. Brandes and K. W. Mitchll.)*

2 *System Ti-Al*

ATOMIC PERCENT MOLYBDENUM
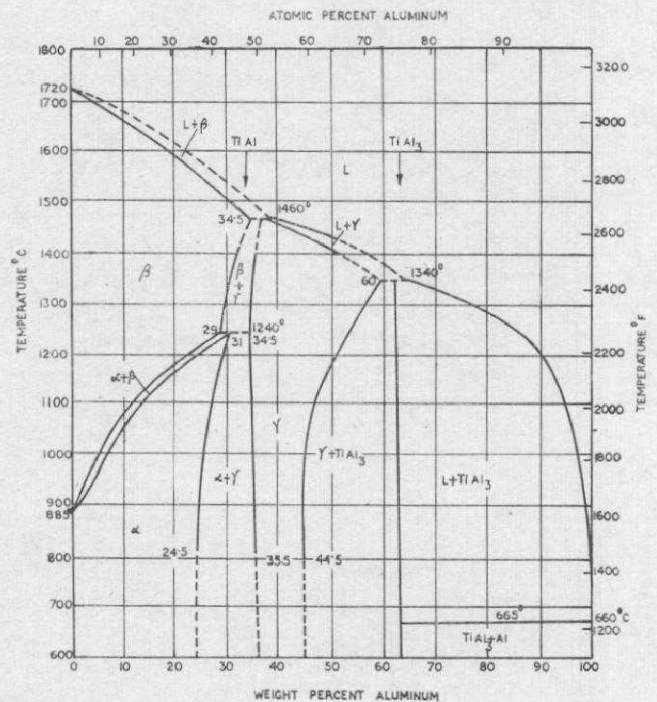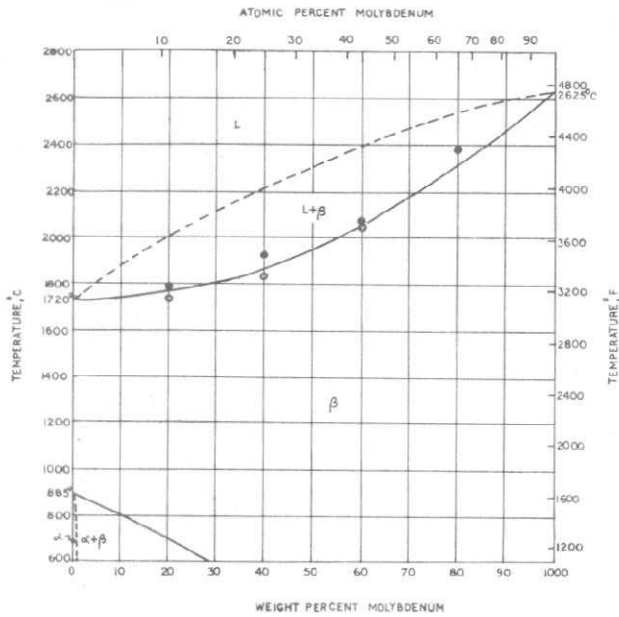
3 *System Ti–Mo after Hansen, et al.*

ced by the presence of impurities in the metal such as carbon, oxygen, nitrogen and hydrogen, with which the metal has strong chemical interaction. Since titanium alloys have been and are being primarily developed for high temperature service, their thermal stability is important. Titanium alloys rapidly lose strength above 500–600°C and are seldom used above this temperature range for the following reasons :

(i) they rapidly absorb oxygen above 500–600°C ;
(ii) in alpha-beta titanium alloys, the decomposition of beta phase is responsible for instability. Therefore, the structural stability of the alloys primarily depends on composition of the beta phase and the following are important factors which influence the structural stability.

(a) *Heat treatment*[6] The stability of alpha-beta alloys can be increased by heat treatment at a temperature high in the alpha-beta field followed by a stabilising treatment of either slow cooling or step cooling to a relatively low temperature. This treatment causes rejection of sufficient massive alpha-phase to obtain stability.

(b) *Alloy additions :* Alloying elements can influence the alpha-beta transformation kinetics in the following three manners :

(i) The alpha-beta transformation temperature may be raised as by aluminium (Fig. 2). The main feature of Ti-Al diagram is extensive solubility of aluminium in alpha-titanium i.e. 36·4 wt% at 400 C. It has not been possible to take full advantage of the extensive solid solubility of aluminium because Ti-Al alloys containing more than 6 wt% aluminium may be brittle due to the formation of intermetallic compounds—TiAl, TiAl$_3$. Their embrittlement[7,8] may be due to (i) precipitation phenomena (ii) precipitation (iii) local segregation of alloying elements or impurities at some interface and (iv) ordering. For this reason the Ti-6% Al-4% V alloy[7] is extensively used as it is metallurgically stable up to 500°C. If the embrittlement could de avoided or substantially reduced, superior titanium alloys would become available for aeronautical applications.
(ii) The stability of the beta phase may be increased by the addition of an alloying element which is isomorphous with beta-titanium such as molybdenum. The Ti-Mo phase diagram is shown in Fig. 3.
(iii) The addition of an alloying element like chromium which although beta-stabilizing, introduces eutectoidal reaction, increases the thermal instability of the Ti-Cr alloys.[6] The Ti-Cr diagram is shown in Fig. 4. The substitution of molybdenum for half of the chromium retards the eutectoid reaction and results in a more stable condition. Krossley,

4 *System Ti–Cr*

Carew and Kessler[9] have shown that these considerations are amply borne out if the hot hardness of binary titanium alloys is examined, as shown in Fig. 5. Columbium, nickel and tantalum are least effective in improving the elevated temperature tensile properties of titanium. They extend the field of the stability of beta-phase; columbium and tantalum form isomorphous solid solution with beta-titanium but nickel introduces an eutectoidal reaction at 5·5% Ni. Fig. 5 indicates that aluminium provides the best addition for retaining strength at elevated temperatures. It is well known that ternary solid solutions and distribution of a stable second phase in solid solution matrix increase the creep resistance at elevated temperatures. In accordance with this, Crossley et al[9] found that in Ti-Al alloys creep resistance can be significantly improved without detriment to ductility or stability by ternary additions of molybdenum, tin and zirconium. Of these, molybdenum, which produces a second phase (beta) appears to be the most desirable ternary addition. Tin and zirconium additions go into the alpha solid solution.

5 *Hot hardness comparison for binary alloys with 5 and 6 per cent additions*

Manganese

Although, on the basis of cohesive strength per unit mass manganese is not as strong as aluminium, it should be metallurgically developed as an engineering metal in view of its extensive deposits in the country. In view of its complex crystal structure its alloying characteristics have not been investigated. Since the complexity of crystal structure is anomalous, it may be due to the presence of impurities. The preparation of 'pure' manganese and a study of its properties and alloying characteristics is advocated here.
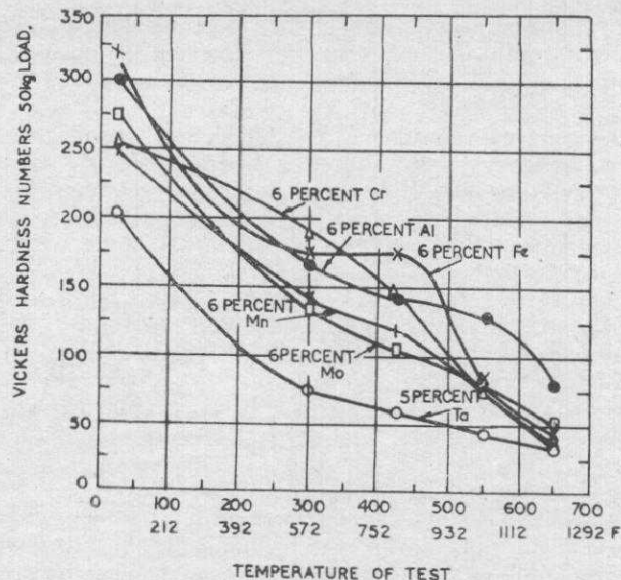
Formation of sigma-phase in transition metal alloys

Titanium, chromium and manganese are transition metals and the alloys formed amongst them and with other transition metals are likely to be brittle due to the formation of sigma phase. Important requirements[10] for the formation of sigma phase are :

(i) One component of the alloy should be body centred cubic and the other face-centred cubic.

(ii) The ratio of the two atomic ratio should not exceed 1·12 ; larger difference in atomic size does not favour the formation of sigma phase.

(iii) transition elements can substitute one another easily in sigma phases.

Conventional light metals—aluminium and magnesium

The metallurgy of aluminium alloys has been the subject matter of a large number of investigations and it is rather naive to summarise its important aspects.

Magnesium, however, is a new entrant in this field. Most of the magnesium-base casting alloys have coarse grains in the 'as cast' condition and it is well known that mechanical performance of cast metals can be considerably improved by refining the grain size. Although the mechanism of grain refinement of steel and aluminium is well known, that of magnesium and its alloys is only known emperically. Grain refinement in these alloys can be achieved through (i) superheating the melt or (ii) by inoculating the melt by carbon. Finely dispersed particles of the inoculant are produced by treating magnesium with carbon or carbon bearing compounds. Several solid and gaseous carbon-bearing compounds have been arbitrarily tried e.g. hexachlorobenzene, calcium carbide, peat, graphite, coke, pitch carbon dioxide, acetylene, propane, etc. The relative efficacy of the different compounds is not known and none of the inoculants find universal acceptance. Although there is general agreement that a nucleation process occurs, the process is not understood and inoculants are used in a rather empirical fashion. The inoculant is usually added in amounts to give a carbon concentration of 0·1–1% by weight in the melt, but the extent of its pick up by the melt is not definitely known.

The degree of grain refinement by superheat, however, seems[11] to depend upon the time taken to superheat, the temperature attained, the time at this temperature, the time taken to cool to casting temperature and the time of holding at relatively low temperatures before casting. Maximum grain refinement can only be obtained by holding the melt for a certain minimum time. The precise period of holding depends upon (i) the manufacturing process of magnesium (ii) the nature of the alloying elements, and is generally more at lower temperatures in the superheating range than

at higher temperatures. Once the melt has been held for the minimum period necessary to form the embryos the grain size is virtually independent of the superheating temperature.[12]

Grain refining tendencies of the once superheated melt are lost by (i) holding at a temperature less than the superheating range and (ii) solidification i.e. when superheated melts are remelted after solidification no grain refinement is observed ; superheat is again necessary for refinement.

The improvement in properties by grain refinement is the classical example which shows that deviation from the perfect crystalline state exercises marked influence on the mechanical behaviour.
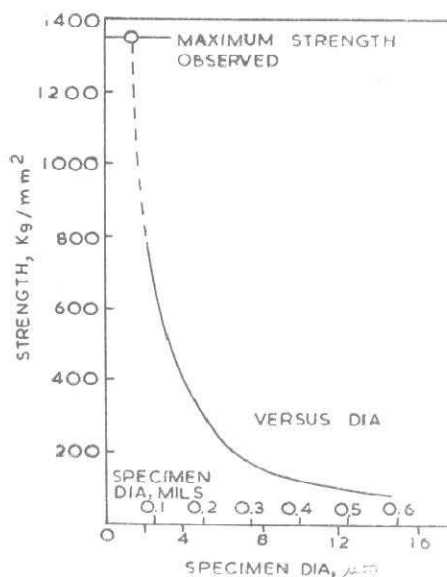
Mangnesium alloys are not easily workable because their close packed hexagonal crystal structure does not provide a large number of slip systems for extensive deformation to occur. Obviously its alloys can be made workable if their crystal structure is made either bcc or fcc. In other words, the problem becomes one of finding an alloying element whose crystal structure is not only body or face-centered cubic but one with atomic radius closely similar to that of magnesium so that the primary solid solubility extends to the magnesium-rich side. One such element is lithium and Mg-Li alloys are at present under development. In this context metallurgy of lithium is also important for our country.

Strong metals and alloys

It is derived from the theory of atomic forces that the strongest solids are amongst materials with regular and close packed arrangement of atoms and that the maximum theoretical value of their fracture of flow strength 0.1μ where μ is the shear modulus. The ideal shear and cleavage strengths of a few materials are summarised in Table II, but are seldom achieved. In practice, however, metals have much lower strength than 0.1μ and may vary by a factor of 100 or more. This observed weakness of metals is due to the presence of dislocations whose movement under the applied stress leads to slip process of deformation. Had there been no dislocations in metals, their strength would have closely approximated to the theoretical strength.

TABLE II Ideal strengths of single crystals

Substance	Ideal cleavage strength 1000 kg/sq. mm.	Ideal shear strength 1000 kg /sq. mm.
Copper	3·9	0·12
Silver	2·4	0·08
Gold	2·7	0·07
Iron	3·0	0·66
Diamond	20·5	12·10
Magnesium oxide	3·8	1·6
Sapphire	4·9	1·9

6 *Strength of Fe whiskers as a function of size (Brenner)*

It may be possible to grow dislocation free crystals, called whiskers on micro-dimensions. But as their size assumes macro-dimensions there is no escape from dislocations and other lattice defects as they originate from accidents of growth during crystallization and therefore, cannot be avoided. It has been shown[14] that the strength of iron whiskers decreases rapidly as their diameter increases (Fig. 6) and approaches the theoretical value for micro-dimensions. The whiskers, per Se, cannot be used for any engineering applications due to their small size and expensive production. Further, they are likely to lose shear strength catastrophically once the dislocations are somehow introduced in the lattice. In future whisker reinforced metal composites are likely to assume engineering importance and this development will call for revolutionary changes in the concept of engineering design.[13] One cencern of the science and technology of physical metallurgy is to raise the strength of the metals through structural features which obstruct the movement of dislocations. The ease of dislocation movement depends upon crystal structure and can be rendered difficult by (i) the introduction of solute atoms in the lattice (solution hardening). (ii) by introducing lattice distortion by coherent precipitates (precipitation hardening) and (iii) by introducing a fine dispersion of a metallurgically and chemically inert phase (dispersion hardening). The energy of dislocation movement is related to crystal structure : in simple crystal structures, such as the cubic, the dislocations move easily under applied stresses which are a small fraction of the theoretical strength. In complex structure as that of diamond or sapphire the dislocations are immobile except at high temperatures. But for materials for the same kind of crystal structure, the energy for dislocation movement is also related to their cohesive energy.
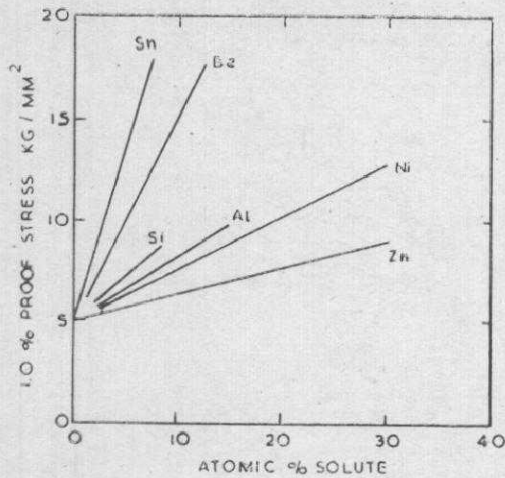
7 *Effect of soluble alloying elements on the 1·0% proof stress of Cu polycrystals at room temperature. (French and Hibbard)*

Solution hardening

The strength of metals can be increased by alloying with elements which form either substitutional or interstitial solid solutions. The solute atoms strengthen the parent metal by distorting its lattice and thus increasing the frictional stress opposing the movement of dislocations. The extent of lattice distortion depends upon the difference in the solute and solvent atomic diameters : the greater the difference, the greater is the distortion and therefore greater the hardening. However, the solutes which differ widely in their atomic diameter from their solvents and cause greater distortion have small solid solubilities. Since solutes having extensive solid solubility introduce little lattice distortion they do not produce marked hardening.

Stress-strain curve

Since the stress-strain curve provides a good indication of the mechanical behaviour of metals, the effect of solute atoms can be discussed in terms of it. A stress-strain curve can ideally be divided into the following three regions :

(i) Region of easy glide : in this region work hardening is almost absent as the moving dislocations, causing plastic deformation, do not interfere with one another. This region is mostly noticeable in single crystals of orientation favourable for single slip and of high purity.

(ii) Region of multiple glide in which slip occurs on primary and secondary slip systems and the strong interaction of dislocations gives rise to steep increase in work hardening. The interaction of dislocations creates lattice imperfections of the type which include (1) forest or tangles dislocations (2) Lomer-Cottrell barriers and (3) jogs produced by moving dislocations. The rate of linear work hardening is approximately inde-

pendent of applied stress, temperature, orientation or impurity content.

(iii) Region of parabolic hardening which exhibits a lower rate of work hardening (than stage ii) due to cross slip and due to the formation of coarse slip bands. The onset of this stage is markedly dependent upon temperature and sets in at a strain which increases with decreasing temperature ; the lower the temperature of deformation, the higher is the stress corresponding to the onset of the third stage.

All the three stages of work hardening are usually observed in metals with low stacking fault energy such as copper and alpha brass. Others may show only the first and the third stage ; e.g. aluminium, which shows all the three stages of work-hardening at 78°C.

Effect of alloying elements on stress-strain curve

Alloying elements mainly raise the yield stress and intensify strain hardening. They make easy glide more extensive in single crystals and the onset of stage II is delayed for higher stress. When easy glide is particularly extensive as in Cu-30% zinc alloys, 'overshooting' occurs because the yield stress of inactive slip planes becomes higher than that of the active one.[15] Alloying elements (i) prolong strain-hardening (stage II) ; (ii) cause steeper strain hardening in stage III and (iii) delay necking. Fig. 7 shows that the variation of 1% proof stress is polycrystalline copper alloys and indicates that less soluble solutes, which distort the parent lattice more, cause steep work hardening. It should be noted from the Fig. 7 and Table III[16] that zinc does not raise proof stress as much as other alloying elements. The addition of zinc to copper is, therefore, helpful in operations involving tensile strength, for example, in deep drawing.

Figure 8 shows[17] the stress-strain curves of polycristalline alloys of copper with a number of alloying elements. It will be noted that different solutes have similar effects on the shape of stress-strain curve and that identical curves can be obtained with different concentrations of solutes. Thus the stress-strain curves

TABLE III Mechanical properties of copper and its alloys

	0·1% proof stress kg/mm²	UTS	E% on 2″ kg/mm²
Copper	3·0	15	40
70/30 brass	5·5	21	65
90 Cu-10 Sn	21·0	46	65
(0·5% proof stress)			

of Cu-19·8% Zn and Cu-9·15% Al alloys are closely similar. Similar results have been obtained on alloys of aluminium[18] and iron.[19] This naturally suggests that replacement of zinc by aluminium in copper-base solid solution alloys should be more vigorously explored than the altogether replacement of Cu-Zn alloys by aluminium base alloys.

The other important effects of solutes can be summarised as follows :

(a) There is not much effect on the true fracture strength except perhaps in those alloyed to high strength.

(b) in ternary systems, the yield stress is sometimes fairly accurately additive of those of binary alloys ; this has been found in Al-Mg-Zn alloys[20] and in iron base alloys.[19]

(c) the solute strain hardening tends to be less important as the testing temperature is lowered.

In case of iron, however, the effect of interstitial carbon seems to be different.[21] It strengthens the ferrite remarkably as the temperature of testing is lowered as shown in Fig. 9. The figure also shows that except phosphorus and beryllium, other substitutional alloying elements have weak strengthening effect.

Precipitation hardening

Precipitation hardening is now one of the effective methods of controlling strength of metals and classical examples are aluminium-copper, aluminium-zinc, aluminium-magnesium, aluminium-zinc-magnesium, copper-beryllium, nimonic and other supper-alloys mar-ageing steels, etc.

Precipitation hardening alloys have been extensively investigated, both scientifically and academically, and it is now generally accepted that strengthening is due to the formation of coherent metastable phases with optimum size and distribution.[22] The shape of the precipitate is important as it determines the number of slip planes that can be obstructed by a given volume fraction of the precipitate : their number increases in the order sphere-disc-rod. Maximum strengthening is produced when the particles are about 100 Å dia. and interspaced at 100-150 Å. Marked softening occurs when the precipitates become non-coherent or increase in size and acquire coarser distribution. Strengthening due to precipitation can be controlled by the following factors besides time and temperature of ageing and solute concentration.

(a) Vacancies : The thermally generated vacancies at the solutionising temperature are retained during quenching and help in the diffusion of solute atoms to nucleation sites which are additionally created by their condensation. The concentration of quenched in vacancies depends upon the relative difference in the atomic sizes of solute and solvent atoms.[23] When the solute diameter is appreciably smaller than the solvent e.g. Al-Cu, the vacancies are mobile and available for pro-
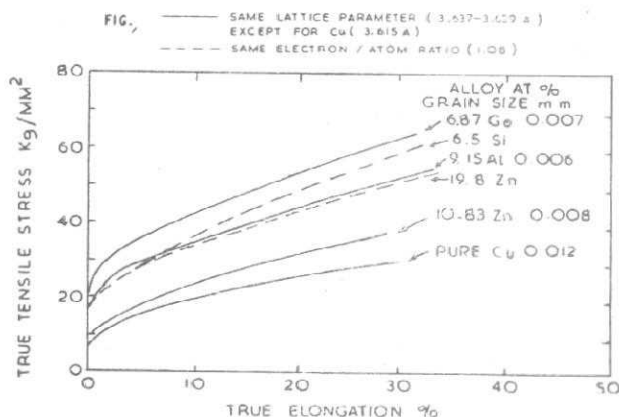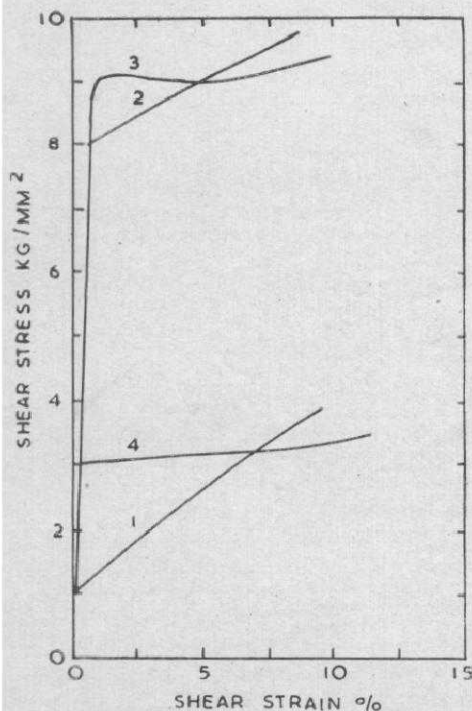

8 *Stress-strain curves of Cu and some Cu alloys at room temperature (Hibbard)*

moting the diffusion. The vacancies are immobilized and diffusion is slower if the solute diameter is larger than solvent as in Al-Mg. This has obvious bearing on the extent of precipitation strengthening which is more in Al-Cu than in Al-Mg.

(b) Impurities in precipitation hardening alloys are important from four points of view, apart from their effect on phase relationships :

(i) if the impurity diameter is larger than the solvent, they immobilize the vacancies and suppress the natural ageing of the alloy and eliminate the necessity of refrigeration. Examples are the presence of indium, tin and cadmium in aluminium base but magnesium free alloys.[24]

(ii) they accelerate the artificial ageing by a factor of 3-8 : thus cutting down the heat treatment time. Examples are the effect of indium, tin and cadmium in aluminium base manganese free alloys and Ag, Cr and Mn in Al-Zn-Mg alloys.[25]

(iii) they promote general precipitation and, therefore, suppress stress corrosion.
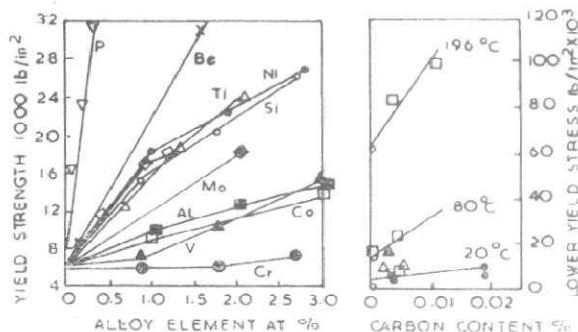
9 *Influence of substitutional solutes and carbon on the yield strength of iron (Allen)*

10 *Stress-strain curves of single crystals of Al–2 atomic % Cu oriented to favour single slip and tested at –196°C. Curve 1, aged 2 days at 350°C ; alloy contains noncoherent particles of CuAl₂ about 25 000 Å apart. Curve 2, aged 27½ hours at 190°C, alloy contains noncoherent particles about 400 Å apart. Curve 3, aged 2 days at 130°C ; alloy contains GP [1] zones, that is, platelets of Cu atoms 100 Å in diameter and 1 atom thick about 150 Å apart. Curve 4, as quenched ; alloy is a solid solution (Honeycomb)*

    (iv)   higher speed of extrusion can be used.

(c)   Other factors : such as prior plastic deformation, effect of specimen size[26] etc.

Stress-strain curve[22] of aluminium-copper alloys in different heat treated condition is shown in Fig. 10 which shows that the metal has its lowest yield stress in the over aged condition (curve I) and highest when aged to contain very small and closely spaced particles of precipitates (curves 2 and 3). When copper is in solid solution, the yield stress lies between these extremes (curve 4). The figure also shows that the overaged alloy has the maximum strain hardening effect.

Dispersion hardness

Alloys strengthened either by solute or precipitation hardening lose their strength much below their melting temperature. In the latter case, the strength is lost due to coarsening and re-dissolution of the precipitate particles. The strength could be maintained up to higher temperatures near the melting point if the re-dissolution and coarsening of the precipitates could be prevented. This is obviously impossible if the precipitate was 'born' of the solid solution but is feasible if

it could be 'adopted' by the metallic or solid solution matrix which then synthetically stimulates the conditions of precipitation hardening. Such precipitates or dispersions are usually the inert high melting oxides of aluminium, thorium, beryllium, magnesium, zirconium, etc. and carbides and nitrides which have high free energies of formation. The oxides are thermodynamically more stable than carbides and nitrides. This new and important direction of progress in metallurgy provides a structure with desirable properties to conform to preconceived design. As a result of extensive work during the last 10–15 years the process of strengthening metals through dispersions has gained widespread attention and products made from aluminium (having high strength up to the melting point) have been put in the market under the trade name S.A.P. (Sintered Aluminium Products) and A.P.M. (Aluminium Powder Metallurgy) products.

SAP and APM products are fabricated in various forms customary in wrought alloys for making pistons, piston rods, piston inserts, cylinder heads, jet engine compressor bladings, for the automative and air craft industries, etc. Widespread application of SAP and APM products in industry has apparently been handicapped by problems of cost and lower ductility.

These products show a marked resistance to recrystallization and grain growth up to temperatures near the melting point of aluminium. These are characteristic features of all the oxide-hardened alloys, and is one reason why they are potentially important for high temperature applications. It is possible that the high temperature strength of these materials is due to the formation of sub-grains, tangled dislocations and pinning of boundaries by the dispersed phase during the hot extrusion step in their manufacturing process. For SAP alloys containing 14% aluminium oxide, the room temperature ultimate tensile strength exceeds 50 000 psi, and the Brinell hardness 100. A sign of the excellent retention of properties after long periods of high temperature soaking is the fact that after 1 year at 500°C, SAP still has a room temperature UTS of 44 000 psi. When tested at 500°C after soaking for 1 month at the same temperature the UTS is over 13 500 psi i.e. more than six times that of heat treated Y-alloy tested under identical conditions.[27]

The properties of the SAP material can be further improved by adding alloying elements such as copper and magnesium[27,28] to the matrix. An Al-Cu-Mg-Mn type SAP alloy showed a 50% higher tensile strength at room temperature than unalloyed SAP, due to an age hardening effect being superimposed on the dispersion strengthening process.

Little work has been reported on similar dispersions in magnesium-matrix alloys.[29] Since the formation of coarse grains is an important handicap in the utilization of magnesium alloys, it is scientifically permissible to speculate that magnesium-matrix dispersion hardened alloys can be produced which are not only fine-grained but in which grain coarsening at elevated temperatures has been prevented.

Dispersions have also been successfully introduced in nickel and are known as T.D. nickel.[30] Thorium oxide

which is relatively stable in nickel has been used in place of aluminium oxide. The oxide can be added to nickel by mechanical grinding of nickel and thoria powders as in SAP. Much finer dispersions can be obtained by taking a mixture of colloidal oxides of the two metals and reducing NiO at low temperature. Its room temperature strength persists up to the melting point of nickel.

Methods are now being evolved to strengthen important b.c.c. metals like iron, chromium, tantalum, etc. by suitable dispersions. In case of iron, dispersions of aluminium oxide[31] are being produced in iron-aluminium matrix. Dispersion hardening of chromium by titanium nitride[32] is important not only in itself but also because it eliminates the embrittlement of chromium due to nitrogen through the formation of stable titanium nitride. The ductile to brittle transition temperature is considerably depressed as a result of the removal of nitrogen. The transition temperature[32] of the recrystallized Cr-0.5 Ti-0.1 N alloy was –57°C and that of chromium in corresponding condition 250°C. Its tensile properties at 20°C are given below :

Condition	Yield stress 1000 kg./ sq. mm.	Fracture 1000 kg./ sq. mm. strength	Elonga- tion %	Reduction area
As extruded	3 55	69·5	15	8·4
Extruded annealed at 1250°C, 2 hours	20·5	51·0	30·0	60
Pure chromium, extruded, annealed 1250°C, 2 hours	—	31·4	0	0

The idea of dispersion hardening has been extended to alloy steel for increasing their strength through refining of martensite needles.[33] The austenite is worked with meta-stable austenite range in the pearlite bainite band and then quenched to form martensite. The properties and structures of such a martensite are different from those of the quenched and tempered martensite. The yield and tensile strength of martensite increase significantly with increasing amount of deformation at a given deformation temperature, at 900°F the yield strength increases from 300 to 380×10^3 p.s.i. when rolling deformation increases from 30 to 94%. For a particular deformation the deformation temperature has smaller effect on the yield strength.

Electron micrscopy of martensite formed from strain hardened austenite revealed the presence of deformation markings. The extra dislocations produced perhaps provide additional nucleations sites for carbides and martensite thus refining the structures.

Conservation of conventional alloying elements

Much of the present discussion is confined to alloy steels where most of the alloying elements are at present imported. Substitution of one metal with another, merely on the basis of similar effects on phase boundaries, is not a simple and straight forward process as a number of other complicating factors are introduced due to the effect of substitute alloying elements on (i) phase transformations including kinetics (ii) structural features such as vacancies and stacking faults and their influence on plastic deformation (iii) volume change (iv) nature of carbides and carbide transformations in alloy steels and (v) embrittlement.

Phase transformations including kinetics*

The kinetics of transformation depend fundamentally on the ratio of rates of nucleation and growth and these are modified by : (a) the nature of alloying elements in austenite (b) the degree of heterogeneity of austenite and presence of undissolved carbides (c) grain size of austenite. It is easy to appreciate the retardation of austenite decomposition by alloying elements—nickel and manganese which stabilise it. Both nickel and manganese retard the decomposition of austenite at all temperatures in to pearlitic range. Although manganese has much weaker austenite forming tendency than nickel, it renders the austenite to pearlite transformation extremely sluggish ; 6–7% manganese steels may be required as much as 4 weeks to complete the decomposition at 525°C. Manganese is therefore very effective in increasing the hardenability of steel and any replacement of nickel by manganese in low alloy steels must consider the resulting sluggishness of the transformation.

As far as the carbide forming elements are concerned, they retard the pearlitic decomposition of austenite as they also form strong carbides. This provides a good illustration of the widely appreciated fact that the kinetics of any phase transformation are not determined by the relative stabilities of the phases but by the mechanism of transformation. Alloying elements forming stronger carbides, therefore, appear to retard the decomposition of austenite to a greater extent than those forming weaker carbides. Chromium is more effective in retarding the transformation than manganese but less so than molybdenum. Naturally, the retarding influence of the alloying elements is seen more on the diffusion controlled pearlitic decomposition than on the bainitic transformation in which diffusion plays relatively minor role. Thus both chromium and molybdenum are more effective in retarding the pearlitic transformation than they do the bainitic transformation.

Martensitic transformation in low alloy steels is important as it provides the basis for obtaining tempered aggregates of ferrite and carbide which have better combination of strength and ductility than equivalent aggregates produced by direct decomposition of austenite. The Ms temperature is determined by chemical composition and with the exception of cobalt and aluminium, all alloying elements lower it. For the development of

*Much of the subsequent discussion is summarised from Physical Metallurgy of Iron and Steel by R. Kumar to be published by Messrs Asia Publishing House Pvt., Ltd., Bombay.

substitute stable austenitic stainless steels it is important to suppress the austenite to martensite transformation. Eichelman and Hull[34] found that the relative effectiveness of elements in lowering the Ms temperature in the 18-8 stainless steel is in the following order of increasing effectiveness : silicon, manganese, chromium, nickel and carbon or nitrogen. The nickel equivalents of silicon, manganese, chromium, carbon and nitrogen are 0·45, 0·68, 27 and 27 respectively.[34] The effect of the alloying elements in weight per cent on the Ms temperature in °F can be calculated approximately with the equation.

$$Ms = 75 (14·6 - Cr) + 110 (8·9 - Ni) + 60 (1·33 - Mn) + 50 (0·47 - Si) + 3000 [0·068 - (C + N)] \qquad ... \quad (1)$$

The equation shows that chromium retards[34,35,36] the martensitic transformation when it is over 14·6%. Hsiao and Dulis[35] showed that the minimum amount of carbon plus nitrogen required for a completely austenitic structure increases with increasing amount of chromium and this relationship can be represented by the following equation.

$$C + N = 0·078 (Cr - 12·5) \qquad ... \quad (2)$$

This equation is applicable for steels that contain from 5 to 14% manganese. Whether the austenite that formed at the solution treating temperature can be retained at room temperature and whether it is stable after being subjected to ageing treatments depend on the composition of the austenite. When the chromium is over 15%, about 12% manganese is required to stabilise the austenite to avoid a martensite transformation. When the chromium is between 12 to 15%, the amount of manganese required to stabilise the austenite to avoid a mertensitc transformation varies from 12 to 18%. In addition to the effect of chromium, the variation in the amount of manganese that is required to stabilise the austenite also depends upon the amount of (C+N) in the steel. That is, for lower chromium and (C+N) contents, higher manganese contents are required for stabilisation of the austenite.[34]

Structural features

The substitution of nickel by manganese has other structural implications as well. Although the structure of austenites is relatively simple and dislocation free as compared to that of the martensites, it has a propensity of stacking faults. Stacking faults are important not only from the point of view of resistance to deformation of the matrix but also for the nucleation and growth of very fine particle of precipitating phase, not more than one millionth of an inch across, on a very fine scale. Chromium, titanium, molybdenum, columbium and nitrogen lower while nickel raises the stacking fault energy of austenites containing nickel and chromium. Wide stacking faults are characteristics of metals with low stacking fault energy and may be formed by the splitting of moving dislocations into two partials which bound the region of stacking fault and are immobile. The work hardening capacity of many metals is therefore related to their stacking fault energies. Metals which have low stacking fault energy work harden considerably. This may be one of the reasons to account for the greater extent and higher rate of work hardening in nickel free manganese-nitrogen stainless steel than in their conventional 18-8 grades.

The concept of the effect of alloying elements on the stacking fault energy of austenites also accounts for the inability of the Fe-Mn system to give a fully austenitic structure at higher manganese content as in the binary Fe-Ni system. The high temperature gamma-iron exists as a single phase solid solution down to liquid nitrogen temperatures only in the composition range 30-60% Mn. Up to 30% manganese, Fe-Mn alloys contain one or more of the phases : alpha, gamma and epsilon. It is not generally realised that iron-rich gamma phase in Fe-Mn alloys decomposes into two different phases (alpha martensite and epsilon martensite) through shear type of transformations and very often the two types of decomposition products are simultaneously present in the structure. Epsilon martensite is a transition phase having cph crystal structure and is closely related to the occurrence of stacking faults in the fcc matrix. Theoretically a stacking fault can act as a nucleus for cph epsilon phase. That this is so, has been confirmed experimentally by Mukherjee and Kumar[37] who introduced additional stacking faults in the austenite through plastic deformation and found that the treatment promotes the gamma to epsilon transformation. Structurally, therefore Fe-Mn austenites have to contain certain amounts of nickel to raise the stacking fault energy to thereby impart workability to the austenite.

Volume change

Volume changes in steels are important from the point of view of the susceptibility of steel to distort and crack during heat treatment and the development of non-distorting die-steels. The volume change due to the transformation occurs because of the change in crystal structure involving a change in the number of lattice points per unit cell and its size. The magnitude of the volume change is significantly influenced by the temperature of austenite decomposition and by the presence of alloying elements. Kenneford[38] studied the effect of alloying elements on the volume change. His results show that (i) increasing amounts of carbon up to 0·5% have very little effect on the volume change but there is rapid diminution between 0·5% and 0·8% and (ii) chromium, nickel, cobalt and manganese increase the volume change and silicon and molybdenum decrease it, the latter only slightly.

In non-distorting die-steels, the transformation of austenite is not complete and the basis of dimensional stability is the presence of retained austenite. Apart from negating the expansion on the formation of martensite, retained austenite is important in the structure as its decomposition (hence expansion) during tempering balances the contraction accompanying the break-

down of martensite. Chromium is an important constituent in die-steels as its carbides impart wear resistance but it increases the transformational volume change. The diverging requirements of tool and die steels are met by so adjusting the composition that controlled amounts of austenite is retained. This is usually done by increasing the carbon content and non-distorting steel containing 1-2% carbon, 5-11% chromium and up to 1% molybdenum is widely used.

Tempering of martensite

Alloying elements—chromium, molybdenum, tungsten and silicon have little influence on the first stage of tempering but may raise the second by as much as 100 to 200°C. Special carbides form in the range 500–550°C and cause retardation of softening and development of secondary hardening. As temperature is further raised, carbide particles coalesce and ferrite grains develop either by recrystallisation or by selective boundary movement.

Although all alloying elements retard softening of steel, significant retardation is introduced by carbide forming elements. If an alloying element is more soluble in cementite than in ferrite, as are manganese, chromium, molybdenum and tungsten, it is not likely to have a pronounced effect upon the rate of growth of carbides precipitated from ferrite but may effect the structure and nucleation rates when present in sufficient concentration. Alloying elements which are insoluble in cementite but soluble in ferrite—silicon, aluminium, phosphorus and nickel only affect the rate of growth of carbides and do not affect the types of carbide formed. Amongst the non-carbide forming elements, silicon is most effective in arresting the softening of martensitic steel. Since silicon is not soluble in carbide[39] it remains in solution in ferrite and thereby strengthens it as a very potent ferrite strengthener. The addition of up to 2·18% silicon[40] to a 3% nickel steel retarded the tempering of martensite. Similarly, addition of 1·5% silicon to 1·8% Ni-Cr-Mo steel retarded[41] the softening of martensitic structure and permitted higher tempering temperature without introducing the 350°C embrittlement. It has been observed[42] that in presence of silicon much higher tempering temperatures are required to cause appreciable reaction in the third stage. In recent years silicon is being increasingly used for these purposes. It has been reported that silicon confers the advantage only in steels of commercial purity but in high purity steels, silicon up to 1·5% may have detrimental effects on impact properties and tensile strength.[30]

Nickel and manganese are partially soluble in the carbide but partition in favour of ferrite. They are less effective in preventing the softening of martensite but may promote retained austenite in the structure. In all such steels, hardness and strength fall off gradually with increasing time and temperature.

Conclusions

The paper has attempted to show that substitution of one metal by another in an alloy can be considered on a national basis if its unified behaviour is considered from the point of view of its effect on (i) phase boundaries (ii) structural features (iii) kinetics of phase transformation and (iv) volume change on transformation, etc.

It advocates fundamental investigations to develop new alloys based on indigenous metals utilising both conventional and new techniques of fabrication and heat treatment.

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Discussions

Mr **L. J. Balasundaram** (NML) : I compliment the authors on the useful survey they have made on the physical metallurgical principles that govern substitution of alloys. I would like to ask Dr Kumar if he would consider the occurrence of epsilon martensite in Fe-Mn alloys as evidence of massive transformation. I wish the paper had mentioned about the phenomenon of K-effect and its possible relationship to marageing.

Dr **Rajendra Kumar** (Author) : The terminology of massive transformation is of recent origin ; but in the light of information available with us, I would not like to comment whether the formation of epsilon martensite in Fe-Mn alloys is the result of massive transformation.

We have not referred to the K-effect and its role in strengthening steels as we were concerned in showing the principles which underline the substitution of one element with another in alloys.