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## Intrinsic mechanical properties and strengthening methods in inorganic crystalline materials

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**Résumé.** — Cet article traite de la résistance et de la fracture des métaux, des céramiques et des composés intermétalliques. L'accent est mis sur les correspondances entre la microstructure et le comportement macroscopique ainsi que sur la façon dont de tels concepts se reflètent dans la création de nouveaux alliages. C'est la nature des forces de liaisons qui distingue chaque type de matériaux. Dans les métaux, les liaisons métalliques dominent, ce qui entraîne une grande ductilité mais une médiocre résistance. En conséquence, dans le développement de nouveaux matériaux on cherche préférentiellement à produire des microstructures qui optimisent la résistance élastique sans perte inacceptable de ductilité. Dans les céramiques, les liaisons covalentes prédominent; ceci entraîne une dureté élevée, une grande rigidité, mais en même temps une extrême fragilité. Au contraire des métaux, le développement de ces matériaux vise à obtenir une pseudoductilité afin d'amener la tenacité à des niveaux suffisamment élevés. Dans les phases intermétalliques les liaisons atomiques correspondent à un mélange de liaisons métalliques et covalentes. La contribution de chacune d'entre elles varie en fonction du système allié. En conséquence, les propriétés des intermétalliques se situent entre celles des métaux et des céramiques. Par divers changements microstructuraux des propriétés peuvent être déplacées pour se rapprocher d'un comportement de type métallique ou de type céramique. Donner des règles générales pour la création de nouveaux alliages n'est pas possible car chaque système demande à être testé, les propriétés dépendent en effet, pour une part considérable, des propriétés intrinsèques des défauts de réseau comme les dislocations, les parois d'antiphase ou les joints de grains.

**Abstract.** — The paper deals with strength and fracture in metals, ceramics and intermetallic compounds. The emphasis is on the interrelation between microstructure and macroscopic behavior and how the concepts for alloy design are mirroring this interrelationship. The three materials classes are distinguished by the physical nature of the atomic bonding forces. In metals metallic bonding predominates which causes high ductility but poor strength. Accordingly material development concentrates on production of microstructures which optimize the yield strength without unacceptable loss in ductility. In ceramics covalent bonding prevails which results in high hardness and high elastic stiffness but at the same time extreme brittleness. Contrary to the metal-case material development aims at a kind of pseudo ductility in order to rise the fracture toughness to sufficiently high levels. In intermetallic phases the atomic bonds are a mixture of metallic and covalent bonding where depending on the alloying system the balance between the two contributions may be quite different. Accordingly the properties of intermetallics are in the range between metals and ceramics. By a variety of microstructural measures their properties can be changed in direction either towards metallic or ceramic behavior. General rules

for alloy design are not available, rather every system demands very specific experience since properties depend to a considerable part on intrinsic properties of lattice defects such as dislocations, antiphase boundaries, stacking faults and grain boundaries.

## 1. Introduction.

Throughout this century research activities in materials science have expanded steadily in aim as well as volume and an end of this development is not discernable. Industry is in need of continuously improved quality of conventional materials but also materials with advanced properties. Transportation systems in particular in air and space demand materials of high strength at low weight, shortage of energy resources asks for higher efficiency of turbines and combustion engines which requires materials with extreme temperature resistance and production techniques ask for materials with extraordinary wear properties to name only a few examples. This list can be extended as one likes e.g. by including electrical, electronic, magnetic, optical or chemical properties.

This paper is restricted to mechanical properties and will concentrate on the interrelation between microstructure, strength and fracture. It is a short summary of the microstructural basis of modern methods used in tailoring mechanical properties. Starting from the concepts for improving the strength of metallic materials subsequently methods will be described to promote the ductility of ceramics. Finally the potential and peculiarities of intermetallic compounds will be considered, which are candidates to bridge the gap between metals and ceramics.

## 2. Metals.

The typical lattice structures of metals with a strong preponderance of metallic bonding over other bonding contributions are closed packed structures like f.c.c. or h.c.p.. In these the stresses for movement of dislocations can come down to values below 1 MPa which are orders of magnitude below the fracture stress. Therefore pure metals generally exhibit excellent ductility but poor strength. In order to rise the stress to useful levels obstacles to dislocation motion can be introduced such as dislocations, grain boundaries, solute atoms and particles or precipitates as illustrated in figure 1. Quantitatively the dependence of yield stress on obstacle arrangement for each category obeys a specific law, the common feature, however, is an inverse dependence of yield stress on obstacle separation [1]. For point-like obstacles like solute atoms or particles and precipitates of sufficiently low volume fraction and for dislocations as line obstacles the yield stress is proportional to the inverse of the mean obstacle-distance, whereas for grain boundaries as planar obstacles the stress increases with the inverse square root of the grain diameter [2].

The actual relations are summarized in figure 1 where also an estimate is given of the maximum strength which can be reached with conventional metallurgical methods and this is compared with the theoretical yield strength. The maximum level of strength obtainable by the individual mechanism is limited by the maximum obstacle concentration. This level is usually fairly below the theoretical strength (which is roughly  $E/10$  with  $E$  = Young's modulus, [3]).

Ultrastrong materials take advantage of a combination of the different strengthening mechanisms by which thoroughly strength levels comparable to the theoretical limit can be attained as for example in ball bearing steels. For most applications, however, such high strength values are not needed and generally not even desired. Rather, by making skillful use

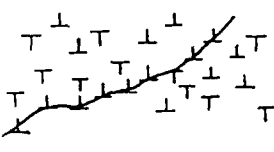
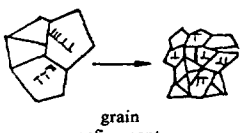
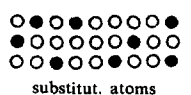
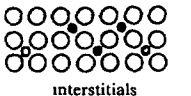
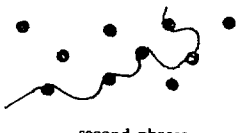
Mechanism	Process	Law	Theoret. strength $\tau/\tau_{\text{theor}}$ at	Obtainable values and corresponding relative strength $\tau/\tau_{\text{theor}}$	Effective for temperatures $T$ $T_M$ = melting temp.
ideal crystal	whisker	$\tau \sim 1/d$ $d$ = diameter	$d < 10^{-4}$ cm	$10^{-4}$ cm, 50 %	$T < T_M$
 dislocations	cold worked metals	$\tau = 0.3 G \cdot \sqrt{\rho}$ $\rho$ = disloc density	$\rho = 10^{14}$ cm $^{-2}$	$10^{11}, 10^{12}$ cm $^{-2}$ , 10 %	$T < 0.4 T_M$
 grain refinement	heterogeneous nucleation, thermomechanical treatment, powder metallurgy	$\tau = G \cdot \frac{5 \cdot 10^{-5}}{\sqrt{D}}$ $D$ = grain size	$D < 10^{-6}$ cm	$D \approx 10^{-4}$ cm, 5 %	$T < 0.4 T_M$
 substitut. atoms	alloying by solid solution	$\tau = \frac{G}{100} \cdot \sqrt{C}$ $C$ = concentration in at %	$C \gg 100$ %	$C = 10$ %, 3 %	$T < 0.7 T_M$
 interstitials		$\tau = \frac{G}{10} \cdot \sqrt{C}$	$C = 100$ %	$C = 1$ %, 10 %	$T < 0.5 T_M$
 second phases	precipitation, internal oxidation	$\tau = G \cdot b \cdot \frac{\sqrt{f}}{r}$ $f$ = volume fraction $r$ = radius of particles	$\frac{r}{\sqrt{f}} = 10b$	$r = 50 \text{ \AA}$ $f = 10$ %, 15 %	$T < 0.9 T_M$ (oxides) $T < 0.7 T_M$ (precipitates)

Fig. 1. — The different strengthening mechanisms in metals due to obstacles to dislocation motion. The table contains the relationship between yield strength ( $\tau$ ) and obstacle density. Also an estimate is given for the maximum density which can be achieved by conventional methods and the corresponding stress level normalized by the theoretical shear strength  $\tau_{\text{theor}}$  ( $\tau_{\text{theor}} = G/10$  with  $G$  = shear modulus). The last column gives the temperature range in which an individual mechanism is effective.

of the different microstructural elements, mechanical properties, such as yield stress, fatigue strength, fracture toughness, and formability can be adapted to the special demands. Corresponding metallurgical techniques have been brought to perfection in the past and are well documented in the literature, so that they will not be followed up here in more detail. In summary it can be stated that for low temperature applications, metallic materials are superior to other material classes as long as corrosion and wear can be considered secondary. For certain applications (e.g. transportation systems and rotating parts) the relatively high specific weight of the majority of metals must be considered too.

For high temperature applications metallic materials are not so well suited because of the influence of diffusion besides corrosion. Microstructures when optimized in view of strength as sketched in figure 1 normally do not represent states of thermodynamical equilibrium and are transformed therefore at high temperatures by diffusional processes. A direct influence of diffusion on high temperature strength is due to climb-controlled creep. With regard to

hardening by dislocation accumulation, thermally activated recovery, i.e. annihilation and rearrangement of dislocations and as a result softening, takes place at reduced temperatures  $T/T_M > 0.4$ . Hardening by grain refinement is only effective as long as grain coarsening and recrystallization is excluded.

In the case of pure metals grain boundary migration leads to grain coarsening at reduced temperatures  $T/T_M > 0.4$ . For the effectiveness of solid solution hardening a distinction has to be made between substitutional and interstitial atoms [4]. The obstacle strength of interstitials is almost one order of magnitude larger than that of substitutionals, however the temperature range for interstitial hardening is much smaller than for substitutionals. Interstitial atoms commonly begin to diffuse already at rather low temperatures since the diffusion is not controlled by thermal vacancies. The associated hardening reduction occurs for interstitials already below half the melting point, whereas for substitutional solutes the hardening effect may be retained up to about  $T/T_M = 0.7$ .

The effectiveness of hardening by particles (or precipitates <sup>(1)</sup>) depends on the mechanisms by which these can be overcome by dislocations and on the thermal stability of the particles. In the case of coherent particles cutting by dislocations is possible, whereas incoherent particles commonly can only be surmounted by the Orowan process or by climbing of dislocations.

By its very nature the Orowan process is an athermal mechanism being influenced by temperature only through the temperature dependence of the elastic constants. Therefore climbing around particles has to be considered important for high temperature strength. In combination with dislocation accumulation at particles it can lead to a pseudo threshold behaviour [5] (Fig. 2). The stresses necessary to overcome particles by dislocation climb at

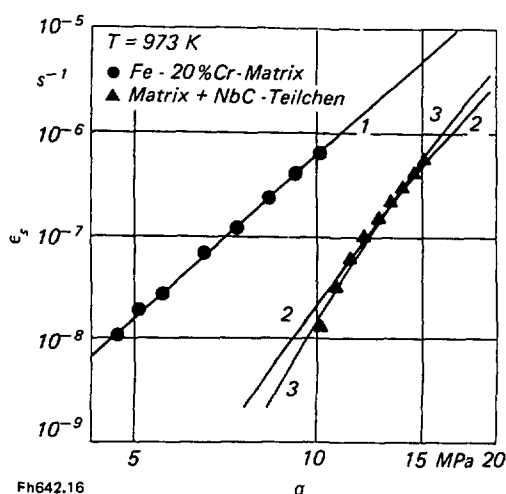


Fig. 2. — Stress dependence of steady state strain rate for particle-free Fe-20 % Cr and for particle-strengthened Fe-20 % Cr with 0.03 vol.% NbC [5, 6].

<sup>(1)</sup> Although usually a distinction will be made between particles and precipitates for brevity these terms will be used here alternatively.

higher temperatures depend not only on repulsive forces between particles and dislocations but also on attractive forces. It has been shown [6, 7] that the existence of attractive forces also can be the cause of a « threshold stress » below which the creep rate can be considered as negligibly small. The existence of such « threshold stresses » in dispersion strengthened alloys can lead to the retention of strength up to very high temperatures of  $T/T_M = 0.9$ .

Superior strength properties for cast alloys at high temperatures can be obtained with directionally solidified or single crystal alloys which exhibit a reduced level of Coble and Nabarro-Herring creep. As an example the creep properties of the nickel base superalloys single crystal 454 and directionally solidified MAR-M200 [9] are given here (Fig. 3, Tab. I). The strengthening in these alloys is obtained by a combination of solid solution hardening (elements Cr, Co, W) together with precipitation hardening by the intermetallic phase  $\gamma'$ -Ni<sub>3</sub>Al ( $\gamma'$  formed by Ta, Al, Ti). These materials offer a sufficiently high creep strength for operation up to temperatures of  $T \leq 1050^\circ\text{C}$ .

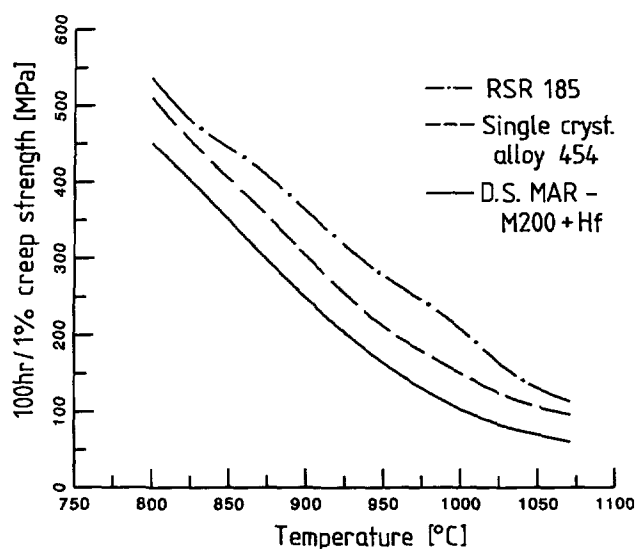


Fig. 3. — Creep resistance of nickel base superalloy RSR 185 (produced by rapid solidification technique) as a function of temperature in comparison with Single Crystal 454 and directionally solidified MAR-M200 ([9], c.f. Tab. I).

Table I. — Chemical compositions (wt.%) of cast and PM nickel base superalloys of figure 3 [9].

	C	Ni	Cr	Co	Mo	W	Ta	Nb	Al	Ti	B	Zr	Other
RSR 185	0.04	Bal.	—	—	14.4	6.1	—	—	6.8	—	—	—	1.4Y <sub>2</sub> O <sub>3</sub>
S.C. 454	—	Bal.	10.0	5.0	—	4.0	12.0	—	5.0	1.5	—	—	—
D.S. MAR-M200	0.13	Bal.	9.0	10.0	—	12.0	—	1.0	5.0	2.0	0.015	0.05	—

Precipitates are usually dissolved or coarsened at higher temperatures if the properties determining the thermal stability (e.g. the difference in the free enthalpy between the matrix and a precipitate, the diffusion coefficient, the surface energy of the phase boundary) are met unfavourably. As a general rule it can be stated that only dispersions of particles which are

thermally stable up to the melting point cause efficient hardening at high temperatures. The possibilities for the introduction of particles in conventional cast metallurgy are limited by thermodynamic constraints. Modern powder based alloying techniques circumvent these limitations and allow for production of materials with a high volume fraction of dispersed refractory oxide particles ( $Y_2O_3$  etc.) or intermetallic phases. Methods of powder metallurgy (rapid solidification, mechanical alloying) are able to suppress thermodynamic equilibrium states which often cause the precipitation of undesired phases as well as a coarsening of the microstructure. Microstructures which are produced by these techniques have to fulfill the two conditions of effective hardening at high temperatures and of good thermal stability which demands highly sophisticated methods [10].

Microstructures produced by such methods not only contain a sufficiently high volume fraction of particles (for hardening and stabilization of grain boundaries) but also solute

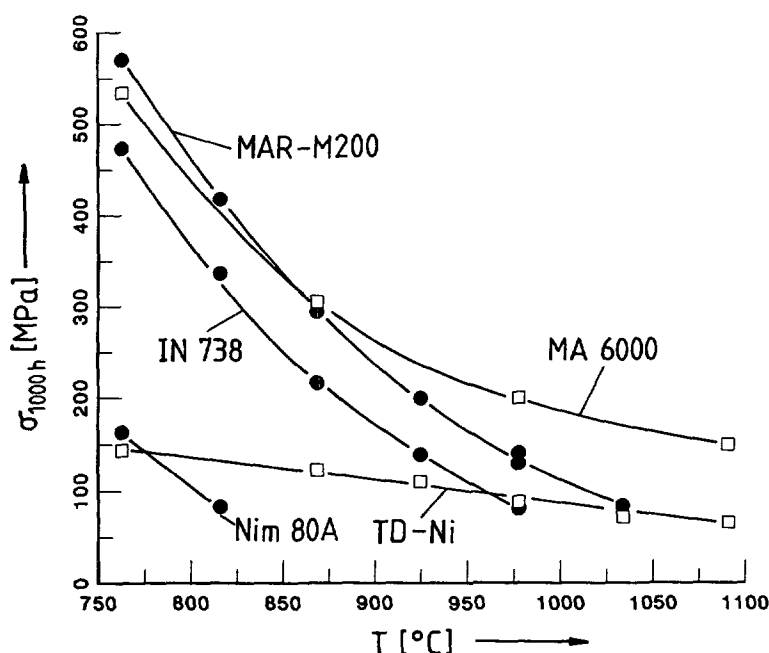


Fig. 4. — 1 000 h rupture strength as a function of temperature for several cast and wrought (○) nickel base superalloys in comparison with mechanical alloyed (□) superalloys ([9], c.f. Tab. II).

Table II. — Chemical compositions (wt.%) of the nickel base superalloys for which 1 000 h rupture strength is shown in figure 4 [9].

	C	Ni	Cr	Co	Mo	W	Ta	Nb	Al	Ti	B	Zr	Other
MA 6000	0.05	Bal.	15.0	—	2.0	4.0	4.5	—	4.5	2.5	0.010	0.15	1.1 Y <sub>2</sub> O <sub>3</sub>
TD-Ni	—	Bal.	—	—	—	—	—	—	—	—	—	—	2.0 ThO <sub>2</sub>
MAR-M200	0.15	Bal.	9.0	10.0	—	12.0	—	1.0	5.0	2.0	0.015	0.05	—
IN 738	0.17	Bal.	16.0	8.5	1.7	2.6	1.7	0.9	3.4	3.4	0.010	0.10	—
Nim80A	0.06	Bal.	19.5	—	—	—	—	—	1.4	2.4	0.003	0.06	—

elements causing solute dragging (for stabilization of phase boundaries and grain boundaries). As an example the creep properties of the rapidly solidified nickel base superalloy RSR 185 are shown here (Fig. 3, Tab. I) in comparison with the most advanced cast superalloys in which finely dispersed metastable  $\text{Ni}_3\text{Mo}$  phases are located at the  $\gamma\text{-}\gamma'$  phase boundaries in order to stabilize the  $\gamma'$  precipitate.

For applications at very high temperatures, microstructures can be produced by mechanical alloying and reaction milling which are highly stable after compaction and annealing. As an example of a successful application of mechanical alloying the oxide dispersion hardened Ni-base superalloy MA6000 is given here [9]. The thermal stability in MA6000 is met by an appropriate choice of the particle species ( $\text{Y}_2\text{O}_3$  in MA6000) and the solution hardened  $\gamma$ -matrix together with the  $\gamma'$ -phase as a second phase thereby fulfilling the above mentioned thermodynamic conditions. MA6000 exhibits a very high creep strength at temperatures  $T > 1\,050^\circ\text{C}$  (Fig. 4, Tab. II) compared with superalloys produced by conventional casting. The combination of dispersoids with a two-phase solution hardened matrix produces a further hardening by pinning of dislocations by oxide particles and pairwise shearing [11].

The last examples demonstrate the limit of the applicability of Ni-based alloys at high temperatures ( $T > 1\,100^\circ\text{C}$ ). At the same time they are intended to show that the possibilities to improve the creep properties and corrosion resistance are more or less exhausted with these alloy-systems. For service temperatures beyond  $1\,100^\circ\text{C}$  materials with much higher melting points are needed such as e.g. ceramic material.

### 3. Ceramics.

In contrast to metals ceramic materials exhibit no plastic deformation at low and intermediate temperatures. This is because plastic flow by dislocation movement, as treated in the last chapter, cannot be utilized in ceramic materials. High Peierls stresses, large Burgers vectors and high planar fault energies result in stresses necessary for dislocation glide which are generally much higher than the stress for cleavage fracture. Additionally the lack of slip systems may cause intergranular fracture in polycrystals.

As a consequence of the immobility of dislocations local stress concentrations (appearing for example at crack tips) cannot be relieved by local plastic deformation so that at the crack tip the theoretical fracture strength is already reached at relatively low macroscopic stresses. Therefore the excellent mechanical and physical properties of ceramics as for example high Young's modulus, good corrosion resistance and very high intrinsic strength cannot be fully exploited for engineering applications. At elevated temperatures creep based on diffusion activity occurs [12], but the main drawback is brittleness. To reduce brittleness is the primary challenge in developing engineering ceramics.

The « principal law of fracture mechanics » [13]

$$\sigma_c = \frac{K_c}{Y \cdot \sqrt{c}}$$

defines the interdependence between the fracture strength  $\sigma_c$ , the critical stress intensity at the crack tip  $K_c$  (fracture toughness), the flaw size  $c$  and a factor  $Y$  depending on specimen geometry. From this formula the two principal strategies for the improvement of mechanical properties can be anticipated: until the middle 1970's great effort was concentrated on the optimization of microstructure by minimizing the flaw size (Fig. 5). This strategy has been criticized not only because of the extraordinary demands for material production but also because of the difficulties of quality control by non destructive methods (NDM), since a single isolated not detected crack of sufficient length may lead to failure of the whole component.



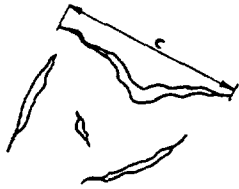

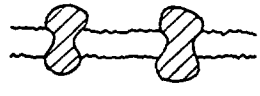
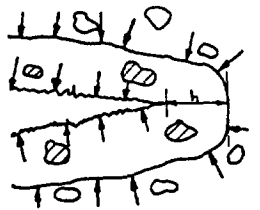
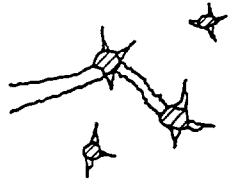

Mechanism	Example	Law	Max. toughness [MPa $\sqrt{m}$ ]	Temp. restriction [K]
 flaw size	fine grain ceramic	$\sigma_f \sim c^{-\frac{1}{2}}$ $\sigma_f$ = fracture strength $c$ = flaw size	8	none
 crack bridging	whisker/ fiber	$\Delta K_{Ic} \sim K_f (v \ell / (R E_f))^{\frac{1}{2}}$ $K_f$ = fiber toughness $\ell$ = fiber length $R$ = fiber radius $E_f$ = fiber modulus $v$ = volume fraction	15/ 20	< 1 500
 ductile particle	ductile particle	$\Delta K_{Ic} \sim \sigma_p (v R)^{\frac{1}{2}}$ $\sigma_p$ = strength $R$ = particle diameter $v$ = volume fraction	25	< 1 500
 process zone	stress induced transformation	$\Delta K_{Ic} \sim v \varepsilon^T h^{\frac{1}{2}}$ $2h$ = zone width $v$ = volume fraction $\varepsilon^T$ = transformation strain	10	< 900
 crack shielding	stress induced microcracking	$\Delta K_{Ic} \sim v \varepsilon^H h^{\frac{1}{2}}$ $2h$ = zone width $v$ = volume fraction $\varepsilon^H$ = respective volume strain	10	< 1 300
 crack deflection	platelet/ fiber/whisker	?	?	< 1 500

Fig. 5. — Reinforcement mechanisms in structural ceramics. The constitutive laws were taken from [14]. Estimates for the maximum toughness increase  $\Delta K_{Ic}$  were given by [15].

Therefore at present the other strategy is favored, namely improvement of the fracture toughness which results in a more « tolerant » material. Figure 5 is a listing of possible fracture mechanisms and corresponding quantitative estimates of the fracture toughness, where the constitutive laws have been taken from [14].

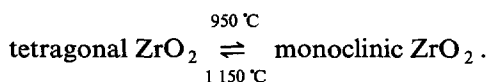
The limitations in the range of temperatures for which the quoted relations are applicable have been reported in [15]. Although they vary according to the considered material class

they are typical values for usual ceramics. For each mechanism a main representative is given in figure 5, it has to be noted, however, that a superposition of several different contributions occurs for every example.

In the case of fibre reinforcement for example the stress is released at the crack tip by spreading of the stress among the fibres bridging the crack. The stress distribution is controlled by the two energy dissipating mechanisms involved, namely, debonding at the interface between fibre and matrix and the friction during pull out of the fibres.

Another variant of crack bridging (Fig. 5) makes use of the ductility of metals. Here metallic inclusions embedded in a ceramic matrix counteract the crack opening. Thereby the load transfer by metallic filaments is strongly influenced by their strain hardening capacity.

Another very successful line of development for raising the fracture toughness has been set off by the utilization of the  $\text{ZrO}_2$  martensitic transformation [15]:



The tetragonal  $\rightarrow$  monoclinic transformation is associated with a shear strain and a volume increment of 3-5 % [16]. It is possible to adjust the transition temperature for this transformation in a wide range by a variety of different measures such as alloying with  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$  [16] and  $\text{CeCO}_2$  [14], variation in particle size and annealing treatments. Numerous examples for the application of stress induced transformation toughening are represented by many commercial ceramic materials. Localized transformation of  $\text{ZrO}_2$  particles occurs under the influence of tensile stresses near the crack tip so that by the volume increment of  $\text{ZrO}_2$ -particles crack path and crack tip are surrounded by a zone which superimposes strong crack closing compression stresses on the crack driving tensile stresses.

Nucleation of microcracks at the particles is already possible under stress free conditions if the  $\text{ZrO}_2$  particles are chosen sufficiently large so that the transformation takes place during cooling. A propagating crack will be deflected in directions toward micro-cracked regions thereby enhancing the disposition for further microcracking (Fig. 5). In this way the stress intensity at the tip of a crack is distributed among many micro-cracks whose stress intensities become uncritical. This mechanism is named crack shielding.

In a similar manner it is also possible to change the path of moving cracks by particles (mechanism of crack deflection). Thereby not only the crack mode ( $K_{Ic} \rightarrow K_{IIc} + K_{IIIc}$ ) is changed but also the stress intensity at the crack tip since the maximum normal stress changes its plane.

By three experimental examples the mechanisms and their interaction will be illustrated. A skillful technological method is reported in [17]. It is based on metal infiltration in reaction bonded silicon nitride (RBSN) with an open porosity of 18 %. Figure 6 shows the fracture behaviour for aluminium-infiltration at room temperature.

Between the crack flanks aluminium filaments are visible. The efficiency of this method is documented by the enhancement of fracture toughness as well as fracture strength given in table III. In addition to the crack bridging mechanism (visible in the micrograph) crack shielding occurs if the crack hits metallic particles. The radius of the crack tip then can be considered being comparable with the particle radius and the stress intensity is diminished by removal of crack driving energy through plastic deformation i.e. crack blunting. As a side aspect it is worth to be mentioned that metal infiltration in ceramics leads to such low values of electrical resistivity that permit the finishing of structural parts by spark erosion.

Similarly, reinforcement of 2Y-TZP (tetragonal  $\text{ZrO}_2$ -Polycrystals with 2 mol.% of  $\text{Y}_2\text{O}_3$ ) by SiC platelets as described in [18] enhances fracture toughness (Fig. 7, Tab. IV) but simultaneously the fracture stress clearly decreases. Actually three mechanisms are effective



Fig. 6. — Reaction bonded silicon nitride (RBSN) infiltrated with aluminium [17]. The arrows show crack bridging by aluminium in the crack wake (c.f. Tab. III)

Table III. — *The table demonstrates the beneficial effect of metals infiltration in RBSN on both fracture toughness and bending strength [17].*

Material	Fracture toughness [MPa $\sqrt{m}$ ]	Bending strength [MPa]
RBSN	2.7	227
RBSN + Al-Alloy	4.5	450
+ Al (99.9 %)	5.0	478
+ Si (99.99 %)	3.9	427

Table IV. — *Influence of 5 vol.% platelets on fracture toughness and fracture stress of 2Y-TZP. The reinforcement results in a slight improvement of fracture toughness but in a decrease of fracture stress due to an increase in flaw size ([18], cf. Fig. 7).*

2Y-TZP	$K_{Ic}$ [MPa $\sqrt{m}$ ]	$\sigma_F$ [MPa]
Without platelets	8.2	1 430
With 5 vol.% platelets	9.5	735

in this case. The SiC-platelets enforce crack deflection but the coarse platelets (100  $\mu m$ ) give rise to an increasing flaw size since they are much larger than the grain size of the matrix [18]. This makes a first contribution to the reduction of the fracture strength. The cause of a second contribution is the reduction of stress peaks at the crack tip below the critical values for

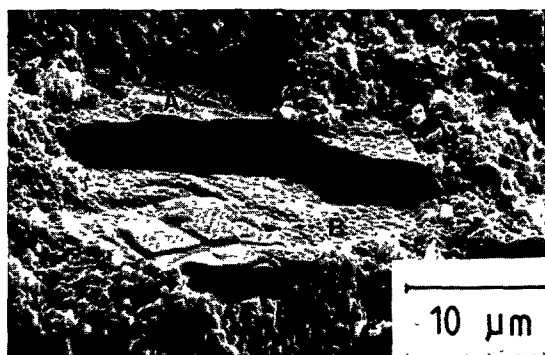


Fig. 7. — Fracture surface of 2Y-TZP (tetragonal zirconia-polycrystal with 2 mole% of  $Y_2O_3$ ) reinforced with 10 vol.%  $Al_2O_3$ -platelets [18]. A : Broken platelet, B : Fine grained 2Y-TZP-matrix. For mechanical properties see table IV.

transformation of  $ZrO_2$  [18]. An optimization of the transformation behaviour of the tetragonal phase by optimization of the microstructure would lead to an enlargement of the process zone. This example illustrates that the different methods of strengthening of ceramic materials do not act independently. Extraordinary experimental skill is required for an optimal combination of the strengthening mechanisms as well as for the optimization of the microstructure.

The last example (Tab. V) illustrates a very successful combination of two mechanisms where the superposition of the two strengthening contributions are multiplicative rather than additive [19]. It is a combination of reinforcement of  $Al_2O_3$  by SiC-whisker and by tetragonal  $ZrO_2$ . The increase of the fracture toughness ( $\Delta K_{Ic} = 8.8 \text{ MPa } \sqrt{m}$ ) by the combination of the two mechanisms is much greater than the sum of the individual contributions ( $\Delta K_{Ic} = 3.8 \text{ MPa } \sqrt{m}$  for SiC-whiskers and  $\Delta K_{Ic} = 1.5 \text{ MPa } \sqrt{m}$  for transformation toughening by tetragonal  $ZrO_2$ ). This effect is according to [20] not only due to ideal utilization of the individual strengthening mechanisms but in addition due to a supporting interaction consisting in an enlargement of the process zone by transfer of critical load for the transformation of tetragonal  $ZrO_2$  by the SiC-whiskers.

A common goal of all mechanisms listed in figure 5 is to oppose the crack growth by stress release at the crack tip. In preventing crack opening the crack bridging protects the crack tip against stresses. The distribution of a high stress intensity to several small cracks or the

Table V. — *The positive interaction of stress induced transformation toughening and whisker reinforcement results in a more than additive toughness increase of the matrix [19].*

Matrix	t- $ZrO_2$ vol.%	SiC- whisker vol.%	$K_{Ic}$ $\text{MPa } \sqrt{m}$	Strength
$Al_2O_3$	—	—	4.7	520
$Al_2O_3$	15	—	8.5	650
$Al_2O_3$	—	20	6.2	1 080
$Al_2O_3$	15	20	13.5	700

propagation of the crack tip into a softer second phase equals a crack blunting. Since the crack path depends strongly on the local loading geometry at the crack tip, a crack deflection leads to a drop of stress intensity at the crack tip. As a summary it can be stated that arrangements in order to improve the fracture properties and defect tolerance of ceramics for structural applications have led to considerable progress through the last years. The aimed breakthrough in the form of a general application however has not taken place until now because of the still restricted margin of safety.

#### 4. Intermetallic compounds.

As has been discussed in the foregoing chapters materials with transient properties between metals and ceramics can be manufactured by combining these two material classes in a suitable two phase mixture with appropriate microstructure. In this way the ductility of ceramics can be considerably improved by introducing a ductile metallic phase while the strength of metals, in particular in the high temperature regime, can be drastically increased by dispersions of ceramic particles as is common practice in ODS-alloys.

Basically different possibilities to design materials with intermediate properties are offered by ordered, intermetallic alloys. These resemble either metals or ceramics depending on whether the atomic bonding forces are either of metallic or covalent nature. Figure 8 illustrates the interrelation between the types of atomic bonds and the materials classes by a tetrahedron in which the 4 corners represent the 4 different kinds of atomic bonds, namely : metallic, covalent, ionic and adhesive (van der Waals). While in metals metallic bonding

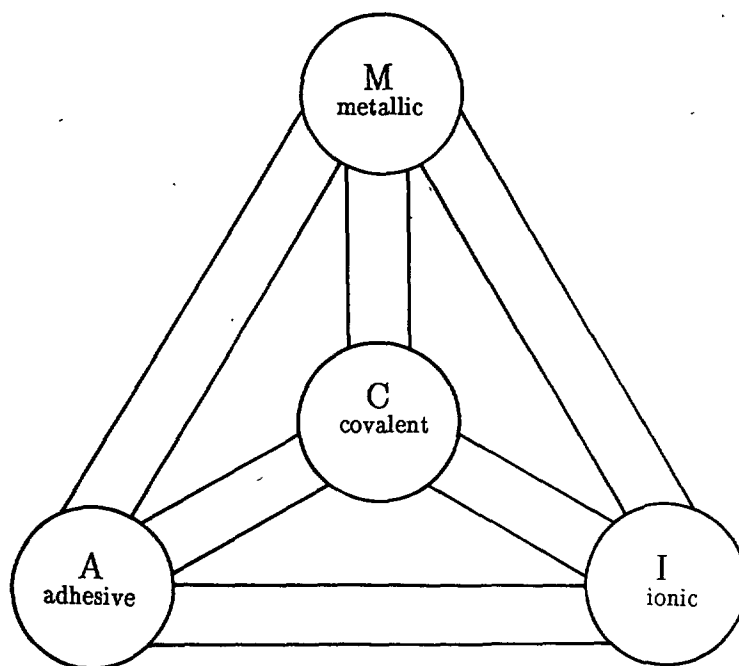


Fig. 8. — Tetrahedron of atomic bonding types of the solid state. A shift along an edge corresponds to a change of the relative contribution of the bonding type and a continuous transition towards an other materials class : A – C → polymers, I – C → salts, C – I → ceramics, M – C → metals, C – M → intermetallics.

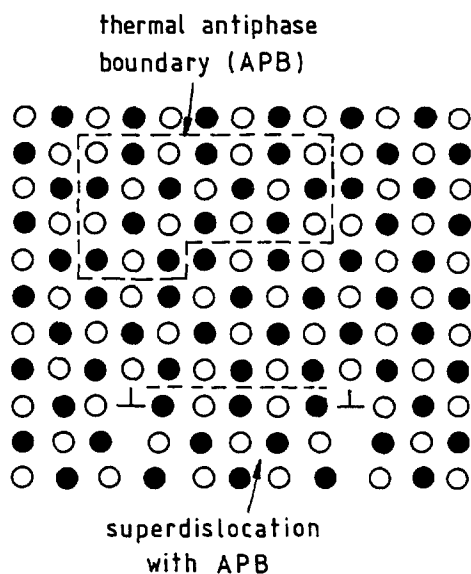


Fig. 9. — Specific faults in ordered alloys : thermally and dislocation induced antiphase boundaries (APB).

prevails, covalent bonding predominates in engineering ceramics. On the other hand in intermetallic compounds usually a mixture of metallic and covalent bonding is simultaneously present where, depending on the alloying system, the relative weight of the two contributions can be quite different. Correspondingly the properties may resemble those of a metal or a ceramic.

The total number of intermetallic compounds is practically unlimited [21]. Already the binary intermetallic alloys are estimated to consist of about 6000. From these approximately 1000 are known and these again represent more than 100 different lattice types. Considering also ternary and even quaternary systems, the enormous potential of this material class becomes obvious.

Not only are the bonding relations quite complex in intermetallic systems, but there are microstructural elements such as stoichiometry, degree of order and antiphase boundaries (APB) which offer possibilities for changing and adjusting the mechanical properties in addition to the procedures which are in use in metals and ceramics.

When moving across its slip plane a dislocation in an ordered structure can destroy order by leaving an APB behind. The order has to be restored by a second dislocation following on the same plane (Fig. 9). Thus in an ordered structure often superdislocations appear in which normal dislocations are bound together by APB ribbons whose width is determined by the equilibrium between the fault energy of the APB and the elastic repulsion between the dislocations. The simplified description of superdislocations in figure 9 has to be modified taking into account stacking faults (which are split into different types depending on the direction of displacement vectors in the stacking fault plane). In more complicated crystal structures superdislocations often consist of more than one pair. An example is given in figure 10 with a dislocation quadruplet in  $\text{Fe}_3\text{Al}$  where the first and the second superpartial dislocation as well as the third and fourth are interconnected by a nearest neighbour APB of relatively high energy, whereas the second and the third dislocation are bound together by a more complex next nearest neighbour APB with lower energy (Fig. 10 [22]). Cross slip and

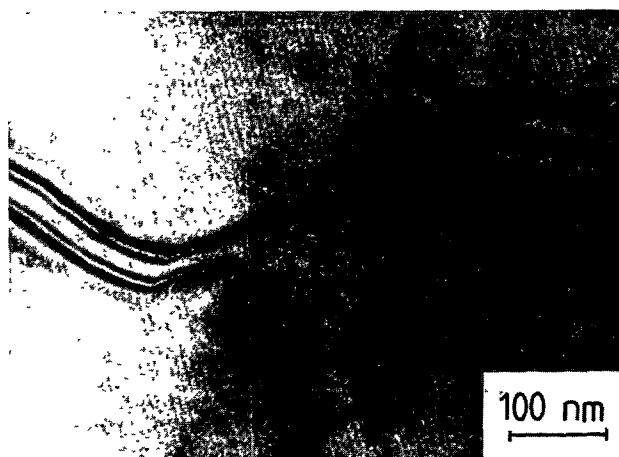


Fig. 10. — Superdislocation in  $\text{Fe}_{70}\text{Al}_{30}$  consisting of four superpartials which are interconnected by two different types of antiphase boundaries (APB) [25].

climb of superdislocation are complex mechanisms similar to that of extended dislocations in metals with low stacking fault energy [23].

Till now the detailed mechanisms controlling the mechanical properties are far from being understood so that no general guidelines are available for alloy design like in metals and ceramics, rather it seems as if every system has to be treated individually. Nevertheless, although empirical observations and theoretical considerations are only provisional they point out the directions which research in this field should follow.

Figure 11 shows the elementary cells of three different representatives of simple intermetallic systems namely  $\text{Ni}_3\text{Al}$ ,  $\text{Fe}_3\text{Al}$  and  $\text{TiAl}$  which are of  $\text{L}_{12}$ -,  $\text{B}_2(\text{DO}_3)$ - and  $\text{L}_{10}$ -type respectively. The following discussion is based on these 3 examples.

Many intermetallic compounds reveal an increase of the yield stress with increasing temperature resulting in a stress maximum at high temperatures. This behaviour is very advantageous for high temperature applications since a high strength at high temperature is obtained without the detrimental effect of reduction of ductility and fracture toughness through a similarly raised strength at lower temperatures. As an example the critical resolved shear stresses as functions of temperature for single crystals of the two intermetallic compounds  $\text{Ni}_3(\text{Al}, \text{Nb})$  [24] and  $\text{Fe}_3\text{Al}$  [25] are shown in figure 12.

The intermetallic compound  $\text{Ni}_3\text{Al}$  with  $\text{L}_{12}$ -structure is the strengthening phase in nickel based superalloys, and correspondingly  $\text{Ni}_3\text{Al}$  has been the subject of many investigations during the last twenty years. A detailed model for the explanation of the « stress anomaly » in  $\text{Ni}_3\text{Al}$  has been given taking into account the core structure of superdislocations [26]. In this structure the APB-energy for an APB on the slip plane  $\{111\}$  is higher than for APB's on  $\{100\}$ -planes. Thus a tendency exists for cross slip of superdislocations together with a reaching of the minor APB-energy [27] resulting in thermally activated generation of dislocation segments on  $\{100\}$  planes which give rise to an increase of the yield stress with increasing temperature. Another view of the cross slip event in  $\text{Ni}_3\text{Al}$  is based on the assumption that the APB energies on  $\{111\}$ - and  $\{100\}$ -planes can be considered as equal [28]. Atomistic simulations of cores of superlattice dislocations in  $\text{L}_{12}$ -structures including splitting into partials give an explanation for the dependence of critical resolved shear stresses on crystal orientation and stress state [26].

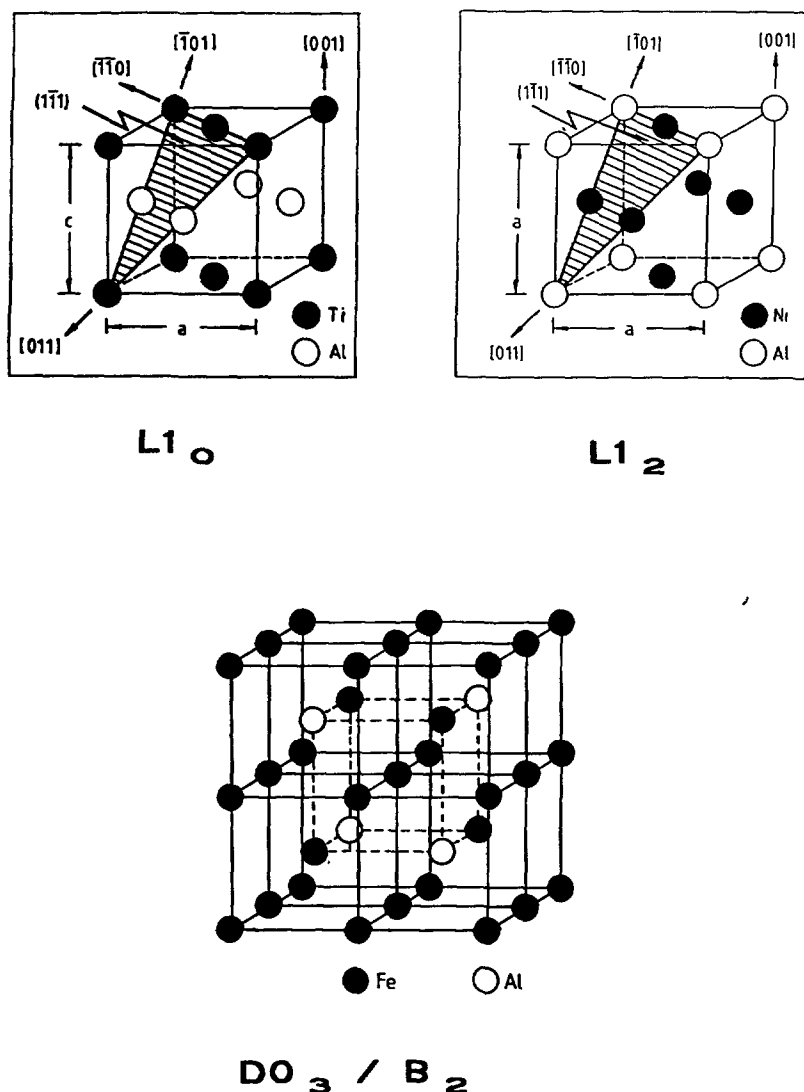


Fig. 11. — Lattice structure of TiAl ( $L1_0$ ),  $Ni_3Al$  ( $L1_2$ ) and  $Fe_3Al/(DO_3/B_2)$ .

These considerations have to be modified for an explanation of the stress maximum in other intermetallic compounds as for example  $Fe_3Al$  in figure 12. The crystal structure of  $Fe_3Al$  is  $B2$  at high and  $DO_3$  at low temperature with a more complicated ordering behaviour than  $Ni_3Al$ . It has been shown that the stress anomaly persists in samples which were quenched from high temperatures and tested at room temperature [29]. This observation excludes a model which is solely based on the production of sessile dislocation segments by thermal activation.

The yield stress in an ordered phase is often lower than the yield stress in the corresponding disordered phase since solid solution hardening is reduced by ordering. On the other hand strain hardening coefficients in ordered phases are anomalously high [30].

As another peculiarity in intermetallic compounds often a strong influence of alloying



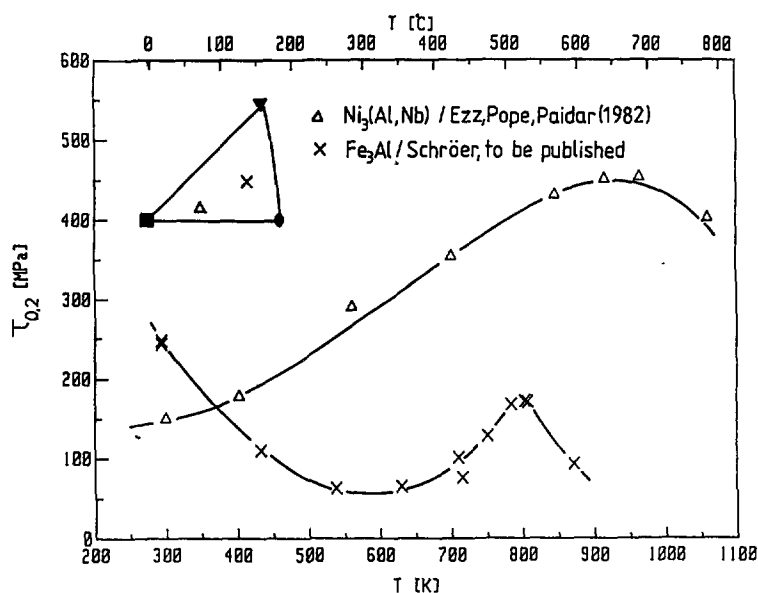


Fig. 12. — Temperature anomaly of the resolved shear stress  $\tau_{0,2}$  for two cubic intermetallic compounds with  $L1_2$ -structure ( $\text{Ni}_3(\text{Al, Nb})$  [24] and  $\text{Fe}_3\text{Al}$  [25]).

elements on mechanical properties has been observed. As an example in figure 13 the influence of Si-additions is illustrated when Al is replaced by Si in  $\text{Fe}_3\text{Al}$ . This effect is due to the influence of Si on the critical temperature for ordering as also shown in figure 13 and in this case is easily explained since with increasing Si-content the balance between the bonding forces is shifted from metallic towards covalent bonding.

Strong alloying effects have been documented in many intermetallic systems but general rules not yet have been established. In this context the atomic structure of APB and grain boundaries is of particular importance since they obviously can be strongly influenced by small amounts of alloying elements. It is well known that boron in  $\text{Ni}_3\text{Al}$  improves the ductility of polycrystals *via* a very strong influence on the grain boundary cohesion. Another example of the effect of alloying elements on the strength of  $\text{Fe}_3\text{Al}$ -polycrystals is given in table VI: the alloying of  $\text{Fe}_3\text{Al}$  with Cr leads to a considerable improvement in fracture strength and ductility. This result is ascribed to an enhancement of the resistance against transgranular cleavage fracture as compared to the intergranular cleavage fracture strength thereby causing a mixed fracture mode of grain boundary and cleavage fracture [32].

Other examples illustrating the combined effects of microstructure, slight changes of the crystal structure and impurities on ductility are titanium aluminides based on the intermetallic phase  $\text{TiAl}$ . They offer the opportunity for substantial density reductions without considerable losses in creep strength at high temperatures thereby exceeding the specific creep strength of conventional superalloys. The ordered  $\gamma$ - $\text{TiAl}$  phase (Fig. 11) has a face-centered slightly tetragonal structure. The layered arrangement of titanium and aluminium atoms on successive (002) planes results in different types of dislocations: ordinary dislocations with Burgers vectors  $\frac{1}{2} \langle 110 \rangle$  and superdislocations with Burgers vectors  $\langle 011 \rangle$  (both gliding on  $\{111\}$ -planes).

Figure 14 shows the temperature dependence of the yield stress of  $\text{TiAl}$  produced by

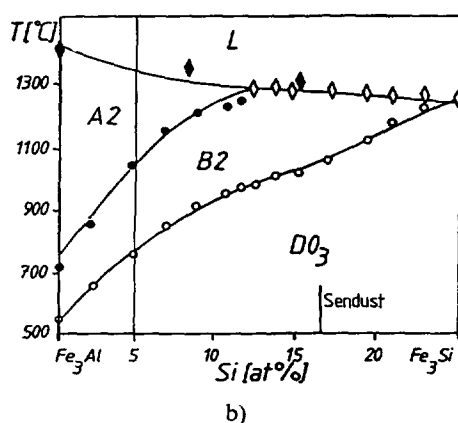
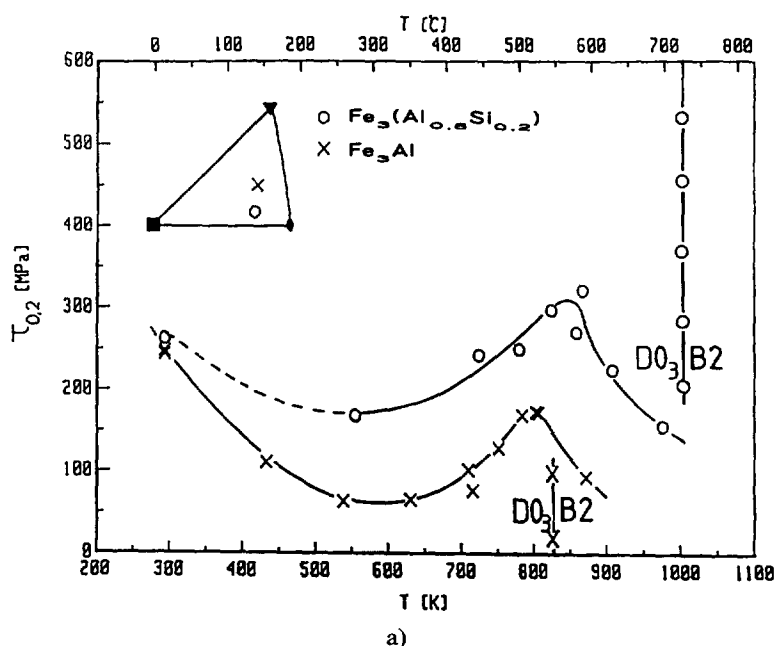


Fig. 13. — a) Enhancement of critical resolved shear stress by alloying of  $\text{Fe}_3\text{Al}$  with 5 at% Si [25], b) quasi binary section  $\text{Fe}_3\text{Al}-\text{Fe}_3\text{Si}$  of the ternary system Fe-Al-Si [31]: order transition temperatures as a function of Si-concentration grows with Si addition.

powder metallurgy with small additions of Nb and V which have a strong influence not only on strength (as seen from the Fig. 14) but in addition on the corrosion resistance.

Figure 15 summarizes the effect of different alloying elements on the room temperature ductility showing that Mn and Cr are of particular advantage.

The mechanical behaviour of TiAl-alloys is not only influenced by ternary alloying elements but also by microstructure, purity and flaws (oxide particles, microcracks). In the composition range of technological interest TiAl-alloys are composed of the two phases TiAl and  $\text{Ti}_3\text{Al}$ . A proper distinction of different factors which ductilize or embrittle these intermetallic alloys is difficult because they cannot be isolated in every case to give a complete description of the physical mechanisms [34].

Table VI. — *Room temperature tensile properties of Fe-28 % Al modified by Cr additions [32].*

Property	Fe-28 % Al	Fe-28 % Al + Cr		
		+ 2 % Cr	+ 4 % Cr	+ 6 % Cr
Yield strength (MPa)	279.2	247.2	228.2	232.4
Ultimate strength (MPa)	514.4	638.5	553.4	535.4
Elongation (%)	3.7	9.4	8.2	8.4
	cleavage fracture	mixed grain boundary and cleavage fracture type		

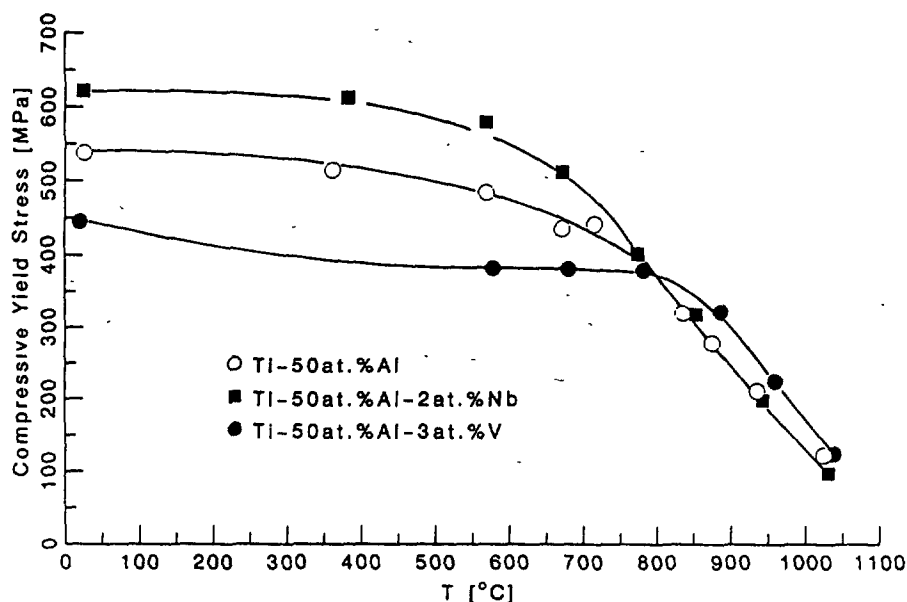


Fig. 14. — Temperature dependence of compressive yield stress of TiAl based alloys produced by powder metallurgy [33].

General problems with intermetallics are based on the brittleness which makes it difficult to reach predictable and reproducible behaviour for application in critical components. But the success in alloy development during the last years makes intermetallics a hopeful materials class and certainly justifies major research efforts.

#### Concluding remarks.

This paper gives a short review of the microstructural concepts which are used in designing mechanical properties of different material classes in relation to each other. Two extreme

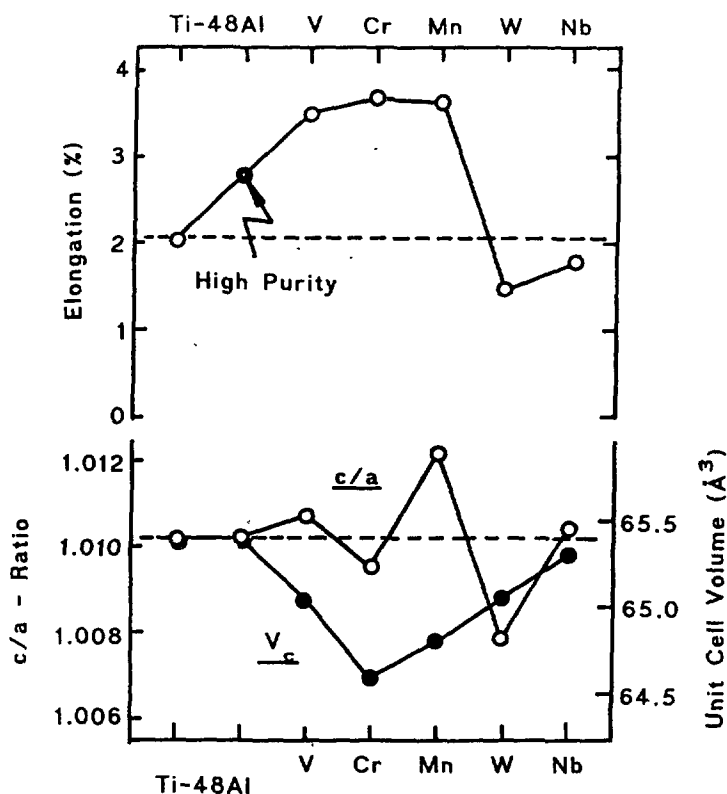


Fig. 15. — Influence of additions of 2 at% of different alloying elements on ductility and lattice parameters of TiAl [34].

positions are occupied by metals on the one side of the spectrum and of ceramics on the other side while intermetallic alloys take an intermediate position.

Metals, by their very nature, are extremely ductile due to the high mobility of lattice dislocations and correspondingly they normally suffer from low strength. Hence the task of alloy development consists in tailoring microstructures which increase the strength but at the same time preserve enough ductility to ensure sufficiently high fracture toughness. To this goal, certainly, methods and processes in metallurgy have been brought to a highly advanced level.

In engineering ceramics dislocations are totally blocked at least in temperature ranges of technological relevance. Correspondingly, although exhibiting high hardness levels, usually ceramic materials are totally brittle. Nevertheless they have gained continuously growing interest in engineering applications due to the excellent corrosion resistance, low specific weight, their practically unlimited availability and easy recycling. Improvement of mechanical properties which in this case is identical with reduction of brittleness, by principle, demands strategies in microstructural design which are contrary to the metal case. In ceramics the aim is always to introduce some kind of nonlinear stress strain behavior or pseudo yielding in order to reduce stress concentrations in the vicinity of crack tips. Various methods have been successfully applied but the achieved values for fracture toughness are still too low for a general breakthrough in the application of ceramic materials; this is particularly true for applications where safety requirements are important.

Intermetallics represent a materials class with a large variety of lattice structures and with intrinsic properties somewhere between metals and ceramics. In some intermetallic systems, predominantly those with cubic lattice, dislocations are observed to be mobile down to very low temperature but they can be totally blocked in others. To a large part the actual behavior is controlled by the specific geometrical arrangement of the different species of the alloying atoms in the center of lattice defects such as dislocations, stacking faults, antiphase boundaries and also grain boundaries. It has been demonstrated by many examples that small amounts of alloy addition can have drastical effects on mechanical properties probably due to their effect on fault properties. General rules, however, for selection and combination of suitable alloying systems could not yet be established. Every system seems to have its specific peculiarities so that guide lines for systematic materials development are primarily based on empirical experience but not on theoretical knowledge. Here considerable research efforts are needed to exploit the potential of this material class.

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