

Influence of interstitials on the mechanical properties of group IV b metals

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THE spectacular progress in nuclear technology and space science researches has brought in a vigorous interest in the properties of IV b metals, titanium, zirconium and hafnium and their alloys. In most of the engineering applications, the properties of pure metals themselves would be clearly insufficient; alloying with other elements would be called for, be it for increase in strength and fracture toughness, or for better superconducting properties. Group IV b metals are somewhat unique in their alloying behaviour as they form solid solutions not only with substitutional alloying additions, but also rather extensively with interstitial elements hydrogen, carbon, oxygen and nitrogen. Generally, these elements are not soluble to any remarkable degree in metals and they readily form second phase compounds when present over few parts per million. IV b metals, perhaps helped by their crystal structure and accompanying large interstices, are able to accommodate these elements in their original lattices themselves, thus leading to drastic alterations in their mechanical and physical properties. It is the purpose of this review to consider the influence of interstitials on the mechanical properties of group IV b metals. This must be of recurrent interest to those engaged in investigations connected with the metallurgy of Ti, Zr and Hf and their alloys.

Geometry of interstices

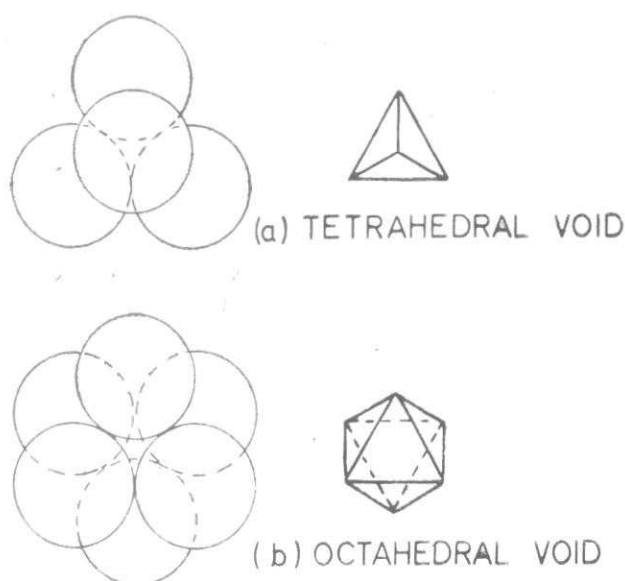
There are two types of interstices that are possible in a hcp structure which has an ABAB... sequence along $\langle 0002 \rangle$ direction. The tetrahedral void is formed between an A layer and a B layer (Fig. 1) such that the four spheres surrounding the void are arranged on the corners of a tetrahedron. An octahedral void is created when a triangular void pointing upwards formed by one closest-packed layer is covered by another triangular void pointing downwards in an adjacent layer. Such an arrangement results in a void that has six closest atom neighbours. It could be seen from the geometry of these arrangements, that the radius of a tetrahedral void is $0.225 R$ and that of an octahedral void is

SYNOPSIS

The influence of interstitial elements on group IVb hexagonal metals—Zr, Ti and Hf, has been reviewed in this paper. Starting from the crystallography of the interstices in this crystal structure, this review discusses in detail the influence of interstitials on the physical, mechanical and electrical properties of these metals. As interstitials are effective lattice hardeners, their interactions with dislocations are of paramount interest. A major portion of this review is devoted to this particular aspect.

$0.41 R$, where R is the radius of the metal atom. It is readily apparent from the radii values of the metal atoms and the interstitial elements under consideration, that the voids present in the crystal structure are being enough to accommodate the interstitial atoms. Comparatively big interstitials like oxygen could be expected to occupy octahedral interstices while hydrogen could fit in conveniently in the tetrahedral void. Actually, the tetrahedral void continues into the bcc structure which is the crystal structure of IV b elements at high temperatures (β -phase).

When comparisons are made between Goldschmidt atomic diameters of the metals and interstitials, it could be seen that a good fit obeying Hagg's law for interstitial solid solution formation is obtained for all the interstitial elements (Table I). From the excellence of fit between atomic diameters, it could be expected that hydrogen should form extensive solid solution with these elements followed closely in decreasing order by oxygen, nitrogen and carbon. As will be seen later, but for hydrogen this behaviour is indeed the rule. From a consideration of voids present in both alpha and beta phases of these metals, it could be seen that carbon, nitrogen and oxygen would fit better in the octahedral voids of the hcp structure than in the tetrahedral voids of the β -phase. This then neatly accounts for these three interstitials increasing the alpha-beta transformation temperature. When these two phases are in equilibrium at any particular temperature, the solubility of these interstitials will be greater in the alpha phase. Hydrogen, however, stabi-



1 Geometry of interstices in hcp lattice

ses the beta phase. This may either be due to the size of the tetragonal interstices in the bcc structure being bigger than in the hcp structure, or may simply be a consequence of larger number of tetragonal interstices available in the bcc structure. A novel hypothesis to predict the stabilisation of an allotrope due to a particular interstitial has recently been suggested by Nowotny.¹ He contends that the stabilisation can be viewed in terms of the structure of the next compound. For instance, carbon in TiC is surrounded by an octahedron and hence carbon would stabilise better in an octahedral environment. On the other hand, TiH_2 is a deformed body-centred structure and hence hydrogen would prefer a tetragonal interstitial position which is readily available in the beta phase. This hypothesis, thus takes into account the co-ordination of interstitial elements in addition to the usual considerations like the size-factor and electron-negativity.

Lattice parameter changes

Unlike substitutional solutes, interstitial additions alter the lattice parameters to such an extent that lattice parameter measurements themselves are often employed to estimate the interstitial content.

All the three metals under consideration, have a c/a ratio lower than the ideal value and this increases from 1.581 for pure hafnium to 1.587 for titanium and 1.593 for zirconium. Because of this lower than ideal axial ratio, the interstices are no more spherically symmetric, and asymmetrical distortion is to be expected when interstitials are added. This indeed is reflected in the variation of a - and c -values with interstitial additions. Table II shows lattice parameter values when one atomic per cent of oxygen is added to these metals. Values for expansion of the unit cell and the c/a ratios are also shown. It is seen that a maximum volume distortion occurs for hafnium followed by zirconium and titanium.

It is of interest to consider the relative expansion of the lattice with the addition of different interstitials. Table III shows such results for titanium when one atomic per cent of oxygen, carbon and nitrogen are added. As pointed out by Jaffe,⁵ the relative solubility of these interstitials are in inverse order to the volume expansion of the lattice. One may then ask whether the strengthening due to the addition of interstitials are also directly related to the volume of expansion they produce. If this were true, carbon which produces maximum distortion of the lattice, would also be the most potent strengthener. This however does not appear to be the case either for titanium (Table III) or for zirconium for which experimental results are available. Perhaps, the suggestion by Finlay and Snyder⁶ that strengthening is likely to depend on the 'eccentricity' of the void as reflected by the c/a ratio appears likely; a larger c/a ratio approaching the ideal value producing minimum strengthening. Any such correlation between volume expansion or c/a ratio and strengthening has only limited applicability. For, the volume expansion values are calculated from the lattice parameter data and hence they represent only gross changes involving

TABLE I Goldschmidt atomic diameters of IV b metals and the interstitial solutes

Element	Goldschmidt atomic diameter	Element	Goldschmidt atomic diameter	Atomic size of solute as a fraction of the atomic size of solvent				
	Å		Å	H	O	N	C	
Zr	3.20	H	0.92	Zr	0.2875	0.3750	0.4438	0.4813
Ti	3.42	O	1.20	Ti	0.2689	0.3508	0.4150	0.4501
Hf	3.18	N	1.42	Hf	0.2893	0.3774	0.4466	0.4843
		C	1.54					

TABLE II Changes in lattice parameters and volume expansion with 1a% oxygen in group IV b metals

Metal	c Å	a Å	c/a	with 1a% oxygen in solution			Volume expansion of unit cell Å ³ per atom per cent	Reference
				c Å	a Å	c/a		
Ti	4.6833	2.9502	1.5875	4.6888	2.9503	1.5893	0.043	2
Zr	5.1476	3.2317	1.5928	5.1497	3.2328	1.5930	0.048	3
Hf	5.0606	3.1971	1.5828	5.0638	3.1983	1.5833	0.062	4

thousands of atoms and do not reflect the true 'local' displacements introduced by the addition of interstitials. Only calculations involving local displacements are capable of yielding quantitative information about the lattice expansion that could have some relevance to the strengthening. Further, the nature of bonding existing between interstitials and host atoms in the lattice should also be taken into account while correlating the relative strengthening between interstitials. Such a study appears important for these metals as many experimental results⁷ suggest the presence of non-metallic bonding between host atoms and interstitials.

The solubility of hydrogen is negligible in the alpha phase at room temperature; hence the lattice parameters are not markedly affected. Recently, Straumanis and Wiebe⁸ have shown that it is possible to stabilise 310 ppm of hydrogen in α -zirconium when the alloy is slowly cooled. After such a stabilisation, the changes in lattice parameter values appear significant; a changes by +0.002 Å and C by +0.006 Å.

Mechanical properties

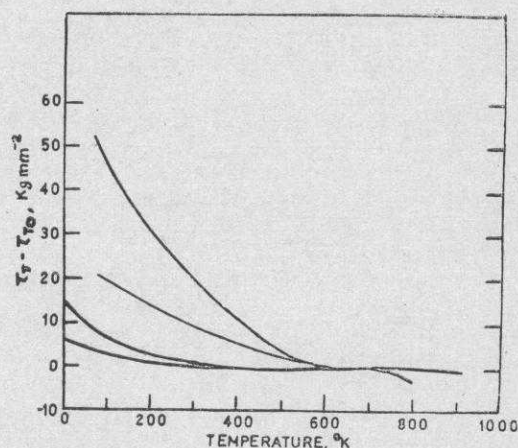
The mechanical properties of group IV b metals are greatly influenced by their interstitial contents. An

increase in interstitial concentration invariably shifts the stress-strain curves to higher values of stress and lower values of ductility. This behaviour is so marked at low temperatures, that sometimes ductile-brittle transition occurs at even moderate concentration of interstitials. This behaviour is observed for only nitrogen, oxygen and carbon in that order; hydrogen affects the strength only through its precipitation as metal hydrides. Hence the following analysis is applicable to only carbon, nitrogen and oxygen. The influence of hydrides would be considered later in this review.

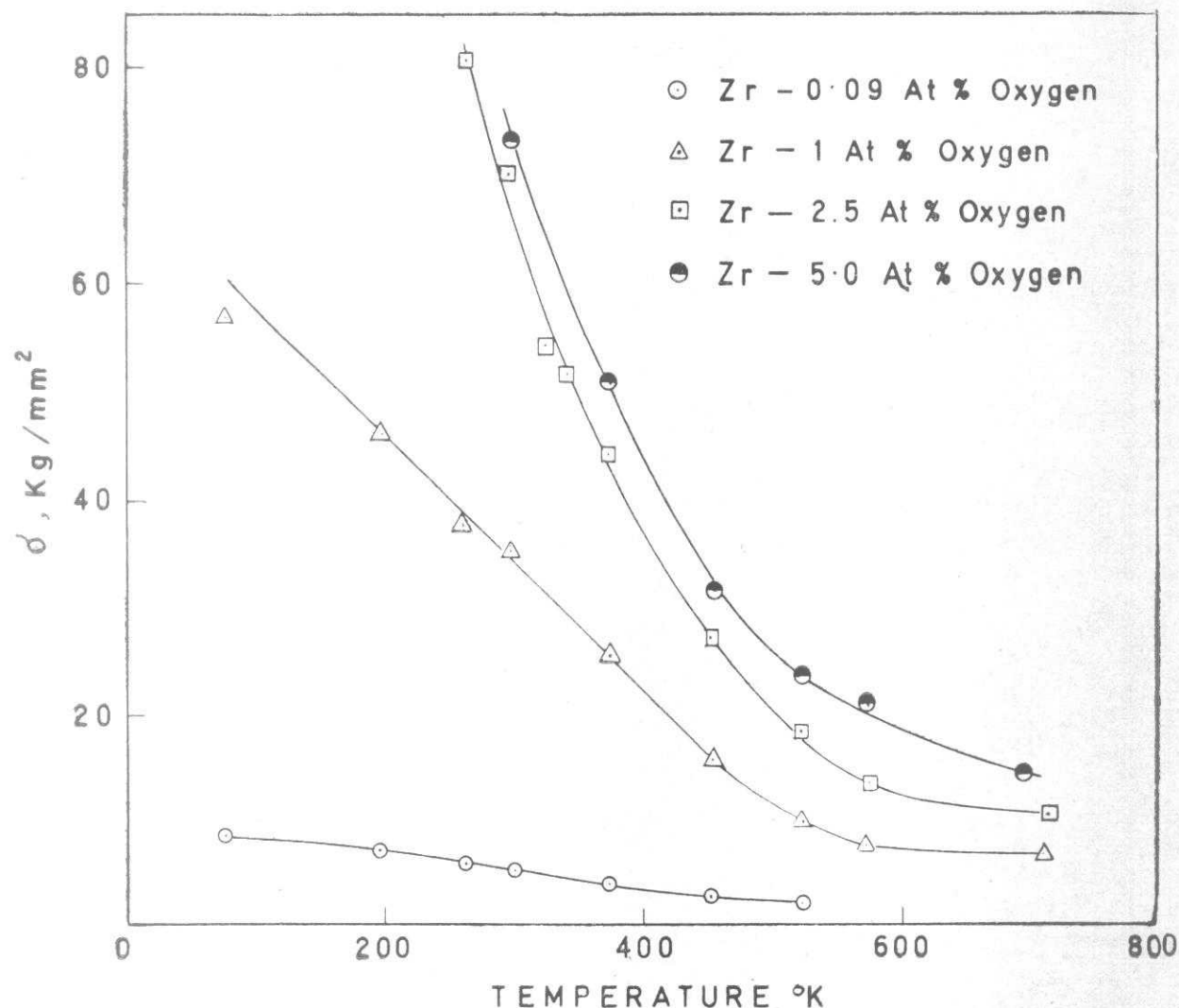
Fig. 2 shows the influence of interstitial contents on the plastic flow of titanium. The figure is after Conrad⁹ who has analysed the results of different workers. Fig. 3 shows similar curves obtained in zirconium containing varying amounts of oxygen.¹⁰ From these figures one notices that the strengthening due to interstitials is strongly temperature-dependent. It is now well established that such a dependence of flow stress on temperature arises from the overcoming of short-range obstacles by dislocations. As the temperature-depen-

TABLE III Changes in C/a ratio and volume expansion of unit cell in Ti with different interstitial solutes. Data from Clark² used for calculations

	C/a ratio	Volume expansion of unit cell Å a%	Hardening effect
Ti	1.5875		
Ti+1a% N	1.5895	0.060	Very large
Ti+1a% O	1.5893	0.043	Large
Ti+1a% C	1.5900	0.160	Moderate



2 Thermal component of flow stress versus temperature for titanium of different purities; the bottommost curve is for zone refined titanium (99.99%); increasing interstitial content raises up the curve; the topmost curve is for commercial purity titanium after Conrad⁹



3 Yield stress versus temperature curves for zirconium-oxygen alloys—after Das Gupta and Arunachalam¹⁰

dence of flow stress in IV b metals is increased by greater interstitial concentration, it is reasonable to assume that the rate controlling mechanism during deformation in these metals should have something to do with dislocation-interstitial interactions. This result is of interest in view of the current controversy about the role of interstitials in the temperature dependence of flow stress of bcc metals.¹¹

To analyse such problems of 'thermal activation', various thermodynamical parameters associated with plastic flow should be calculated. Seeger¹² has shown that the total applied shear stress τ is related to the thermal stress τ^* which is a function of strain-rate and temperature and τ_μ , the long range stress, through the relation

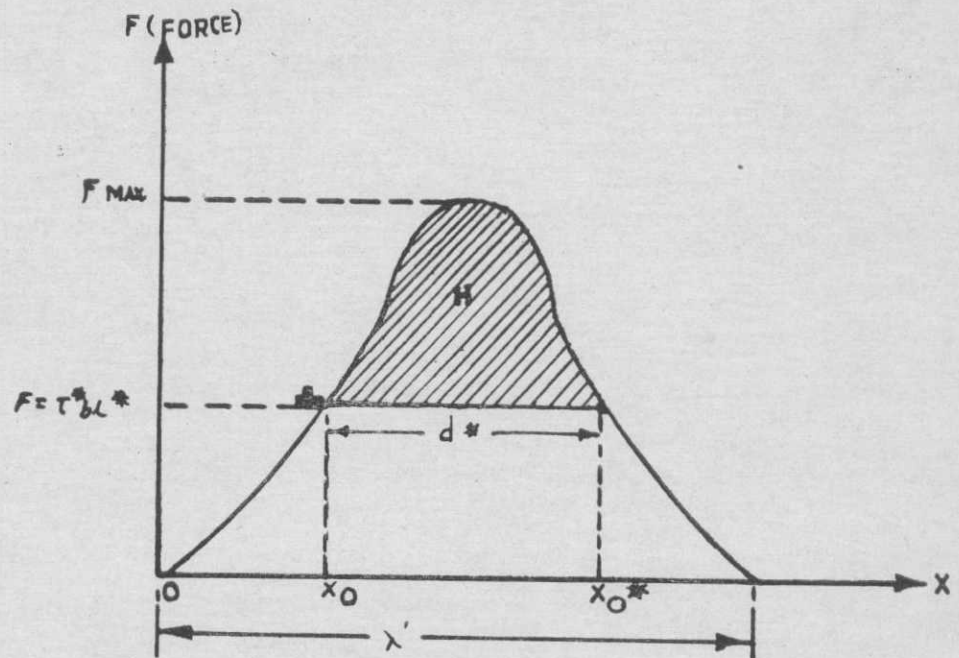
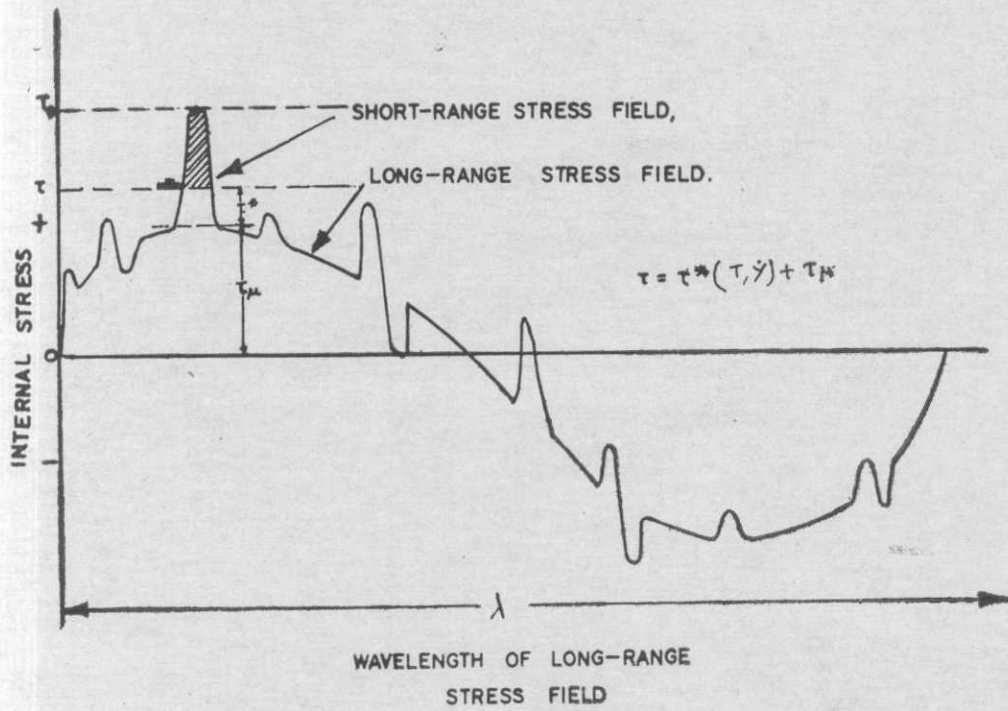
$$\tau = \tau^* + \tau_\mu$$

By separating τ_μ due to long range stress fields from the total applied stress, the thermal stress needed for dislocations to overcome the potential barrier created by interstitials could be calculated. By postulating the applicability of an Arrhenius type of equation to describe thermally activated deformation, the activation energy needed for overcoming the obstacle H , and the activation volume V^* participating in the event could be calculated using the following equation:

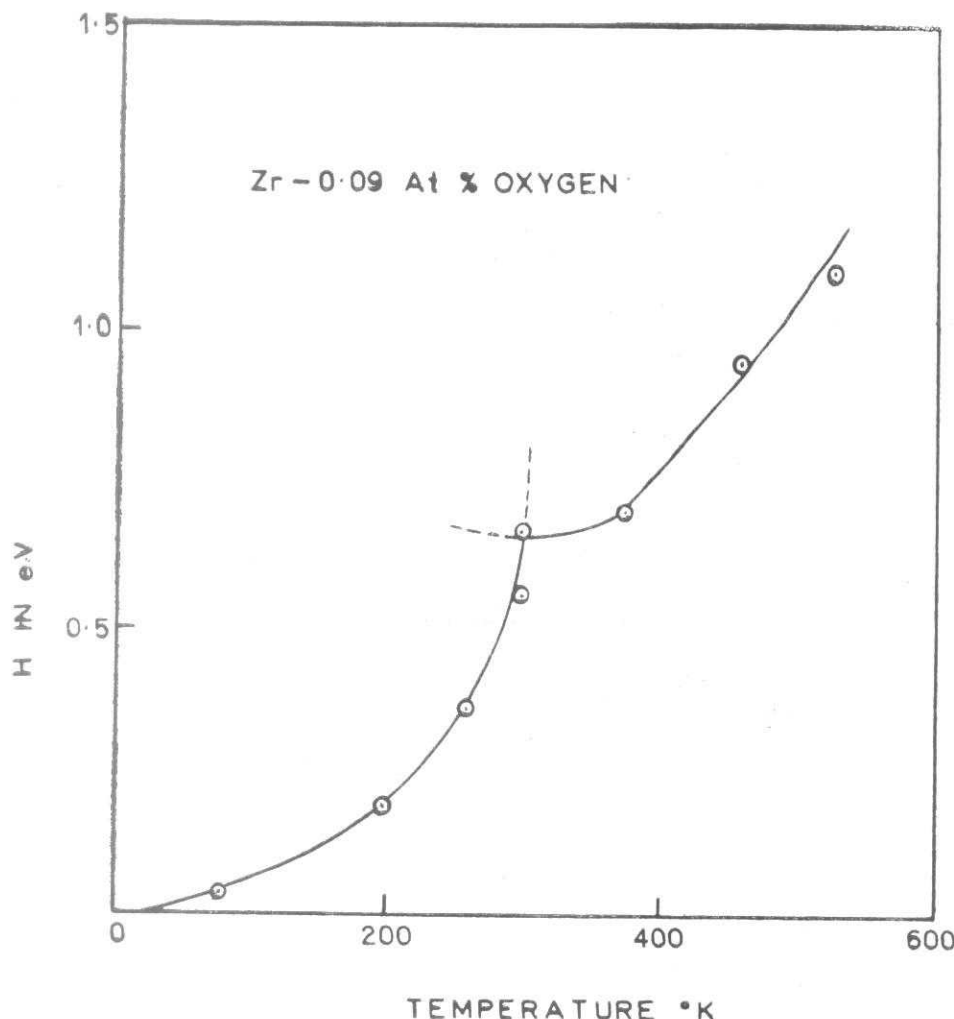
$$H = -kT^2 \left(\frac{\partial \tau^*}{\partial T} \right) \gamma' \left(\frac{\partial \ln \gamma'}{\partial \tau^*} \right)_T$$

and $V^* = kT \left(\frac{\partial \ln \gamma'}{\partial \tau^*} \right)_T$

τ^* , in these equations is the thermal component of flow stress, T , the temperature, γ' the shear strain-rate and K the Boltzmann's constant. For a detailed review on this approach to deformation studies and for the



4 Schematic representation of energy barriers "felt" by dislocations—after Conrad¹³

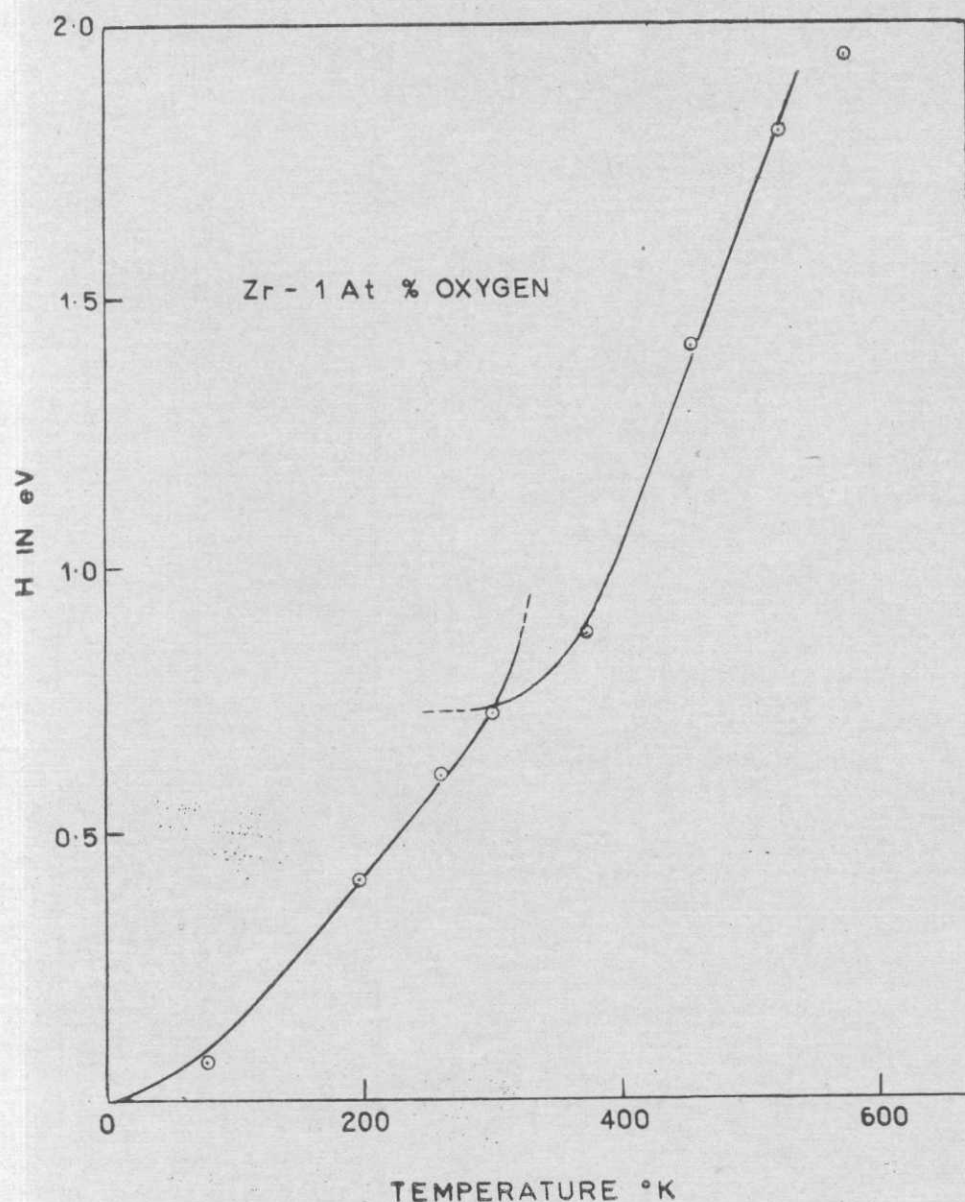


5a Activation energy versus temperature curves for zirconium-oxygen alloys—Zr-0.09 at % oxygen—after Das Gupta and Arunachalam¹⁰

experimental techniques for determining the deformation parameters, the reader is referred to an excellent review by Conrad.¹³ Here we shall discuss briefly only the physical picture of the activation energy (H) and the activation volume (V^*) before going to the experimental results obtained for group IV b metals. Fig. 4 shows schematically, the types of potential energy barriers that are 'felt' by dislocations. To make dislocations overcome these barriers at absolute zero, a high enough stress must be obtained. Once the temperature is increased, dislocations can climb these barriers at much lower stresses as part of the energy for overcoming is coming from thermal agitation. At some critical temperature, the thermal energy itself is high enough for the barriers to become transparent for dislocations. In order to estimate the work done by the external stress, the concept of activation (V^*) is useful. The activation volume is equivalent to bd^*l^* where b is the Burgers Vector of the gliding dislocations, d^* the width of the obstacle measured parallel to the Burgers Vector, and l^* the length of dislocation segment involved in the activated jump across the

obstacle. $V\tau^*$ then gives the energy supplied by the external stress so that we can write $H = H_0 - V\tau^*$ where H_0 is the total energy of the barrier and H the energy from thermal agitation at any particular temperature.

We shall first consider the results obtained for zirconium containing oxygen. Experiments on this system have been carried out on single crystals by Soo and Higgins¹⁴ and on polycrystals by Das Gupta and Arunachalam¹⁰ and also by Baldwin and Reed-Hill.¹⁵ We shall discuss the results of Das Gupta and Arunachalam in detail in our attempt to assess the role of interstitials in increasing the yield stress. As in titanium, the thermal component of flow stress* increases while the activation volume V^* decreases with increasing additions of interstitials. The activation energy-temperature diagrams for different interstitial concentrations as shown in Fig. 5 bring out the characteristic features of thermally activated deformation for these alloys. There appear to be two rate-controlling mechanisms and the energy at which the second rate-controlling mechanism starts increases with increasing concentration of intersti-



5b Activation energy versus temperature curves for zirconium-oxygen alloys—Zr- ϕ 1.00 at % oxygen—after Das Gupta and Arunachalam

tials. Such dependence on interstitial concentration leads us to expect that at least one stage of this thermally activated deformation should in some way be connected with dislocation-impurity interaction.

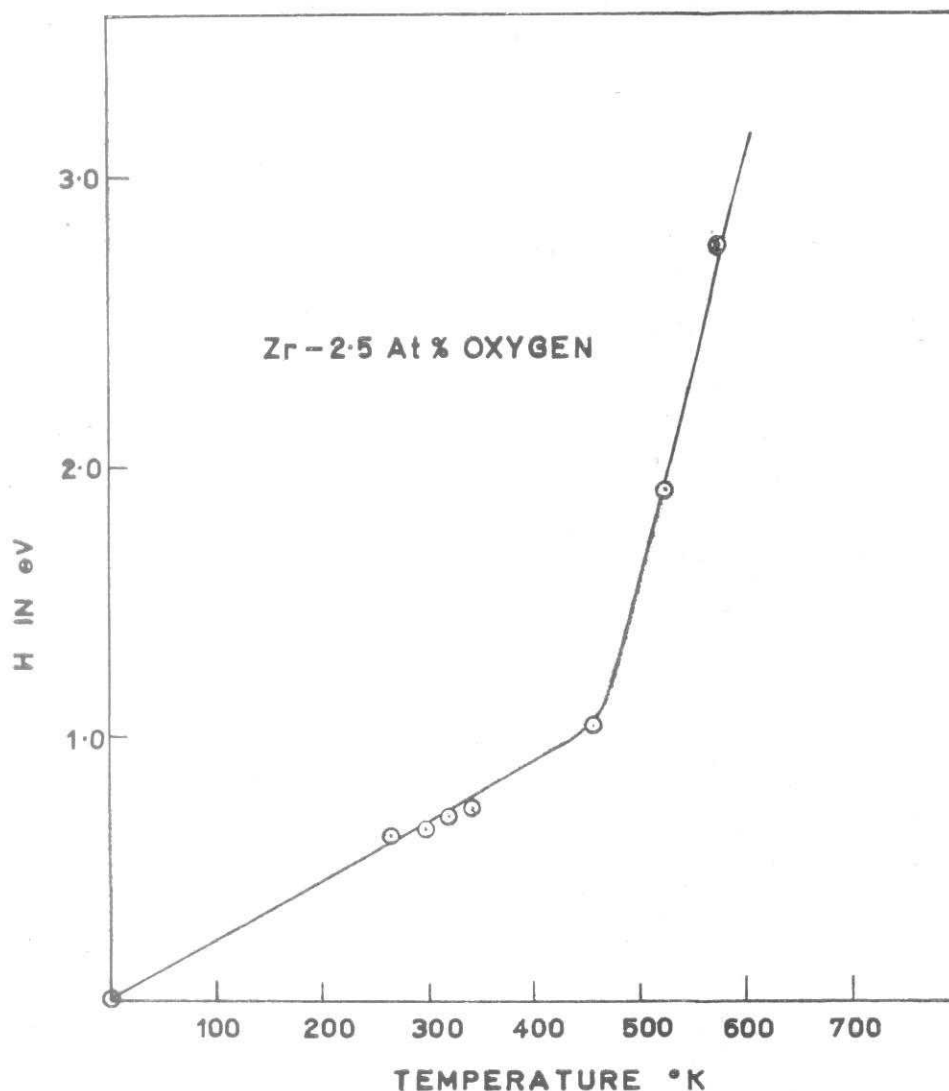
At first sight this result appears somewhat surprising as the octahedral interstices are 'almost' symmetric and their interactions with dislocation should therefore be somewhat weak. But the volume change produced by the insertion of oxygen coupled with a lack of spherical symmetry of the stress field appears to produce a strong enough effect that pin dislocations effectively. Fleischer¹⁶ has considered this problem of elastic interaction between solute atoms and dislocations and has found that for asymmetrical distortions, the interaction energy is

large. For such interactions, τ^{*+} is linear against $T^{\frac{1}{2}}$ and the activation volume V^* is a function of the interstitial concentration c through the relation

$$V^* = b^3 (\sqrt{\tau_0^*/\tau^*} - 1) / \sqrt{3C}$$

where τ_0^* is the zero temperature intercept in the τ^* versus temperature curve. As a rough approximation we could take V^* to be equal to $b^3/\sqrt{3C}$. For 1 at % oxygen alloy, these approximations lead to a value of V^* of about $6b^3$ and this fits in excellently with the measured value¹⁰ of about $7b^3$ at 77°K.

Soo and Higgins¹⁴ in their experiments on single

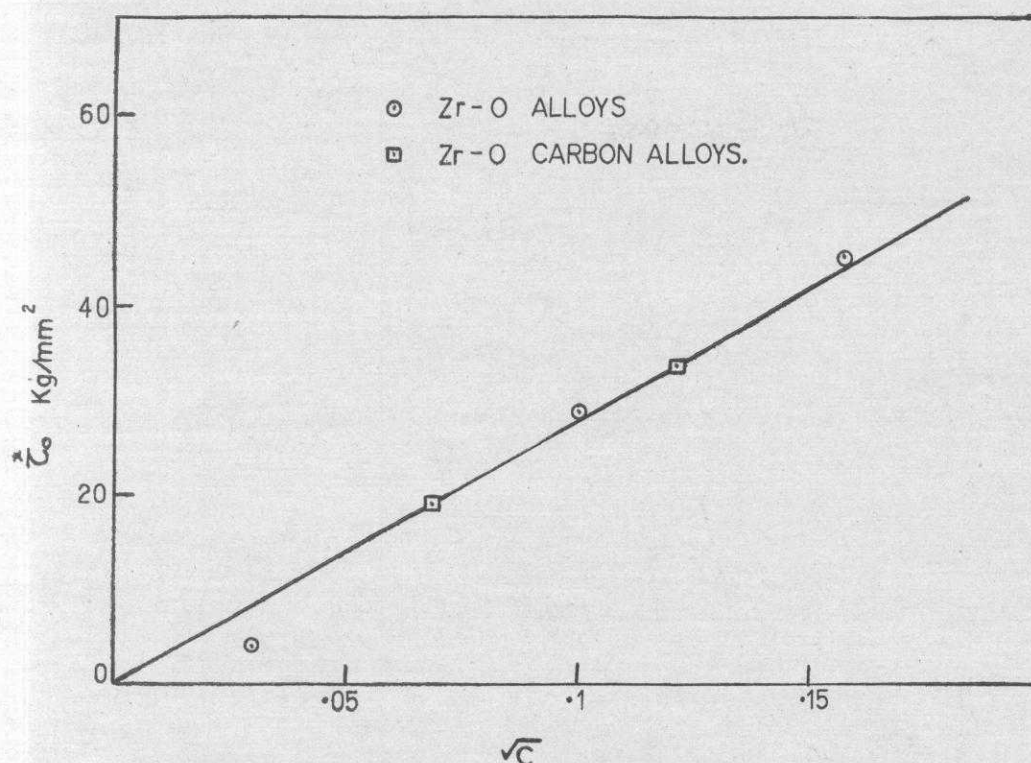


5c Activation energy versus temperature curves for zirconium-oxygen alloys—Zr-2.5 at % oxygen—after Das Gupta and Arunachalam¹⁰

crystals of Zr-O alloys have also detected double-stage activation. They have also attributed the lower temperature stage to dislocations overcoming the interstitial oxygen pinning. Similar experiments have been carried out on titanium with varying amounts of interstitial additions. Experiments on single crystals by Levine¹⁷ have shown the existence of two stages of activation for this metal. However, his interpretation of the first stage as due to the overcoming of the P.N. force has not been accepted by other workers. Conrad⁹ has ascribed this stage in titanium to interstitial hardening. Orava¹⁸ has shown that two stages of activation are present in polycrystalline commercial purity titanium also. Recently Evans¹⁹ has carried out deformation studies on commercial purity titanium and on Ti-8% aluminium alloy and found similar behaviour in these materials. From the results obtained and from an estimation of the force-distance profiles, he concludes that the retarding

force exerted by the obstacle towards dislocation is effective over larger distances from the obstacle with increasing interstitial additions. Similar experiments on thermally activated deformation of hafnium²⁰ and on zirconium-carbon²¹ alloys have been carried out by Das Gupta and Arunachalam.

As yet there is no unanimity in identifying the second mechanism which appears to be rate-controlling at higher temperatures. Das Gupta and Arunachalam¹⁸ have suggested that double-kink motion of dislocation loops that are no more pinned by impurities could be rate-controlling here. Soo and Higgins¹⁴ on the other hand, suggest that non-conservative motion of jogs could be responsible. Cross-slip is another mechanism that has been considered¹⁸ in this connection. Until further careful experimental results on this stage of activation clearly separated from the first stage are available, it is difficult to pinpoint the mechanism responsible for this stage.



6 τ_0 versus temperature curves for zirconium-oxygen and zirconium-oxygen-carbon alloys—after Das Gupta and Arunachalam²¹

In addition to the thermal component of flow stress, the long-range athermal stress (τ_0) also increases with interstitial concentration. This has been observed by Das Gupta and Arunachalam¹⁰ and also by Baldwin and Reed-Hill¹⁵ in zirconium-oxygen alloys. A model to account for this increase must be looked for. The following possibilities offer themselves for consideration :

1. Order-hardening
2. Strain-ageing
3. Higher forest-dislocation interaction
and
4. Increase in elastic constants.

It is well-known that oxygen-zirconium system is liable for interstitial ordering. As in substitutional ordering, this must also result in a large increase in strength. While this is a possible mechanism near the stoichiometric composition (33 at % O) for ordering, it is doubtful whether this could be responsible at such a low oxygen concentration. Even if this mechanism were present for these compositions, it would only be of minor importance.

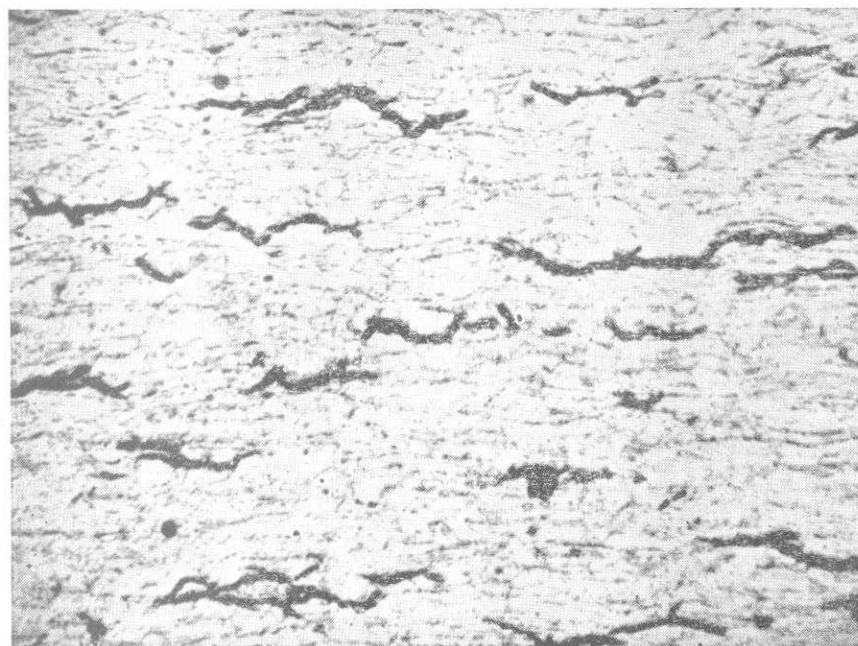
Strain-ageing is another likely mechanism that can increase τ_0 . Though earlier experiments have failed to detect strain-ageing in these systems, it appears quite likely that strain-ageing activated by a large volume distortion due to interstitials is possible. Some indirect evidence for such a process has been obtained from the values of activation volume measured through stress

relaxation and strain rate change tests. V^* Values from stress relaxation were always found to be higher implying the operation of another rate phenomenon in a direction opposite to that of stress-relaxation. Implications of this strain-ageing behaviour on thermal activation parameters have been discussed recently by Rodriguez.²²

The possibility of a stronger dislocation-forest interaction due to higher interstitial concentration is a very attractive mechanism for accounting this increase of τ_0 . Because of the influence of interstitials, slip planes of secondary importance could be activated leading to a larger forest interaction. This has generally been found to be true for titanium ; when impure, it slips on pyramidal planes in addition to prismatic ones. Similar results in zirconium have been reported by Baldwin and Reed-Hill.¹⁵ In microstructures of deformed specimens they have observed tendencies for both non-basal and cross slip to occur with increasing concentration of oxygen.

No data as yet are available on the values of elastic constants as a function of interstitial concentration ; from stress strain curves crude estimates on the Young's modulus could be made and these indicate that the Young's modulus increases with higher interstitial content. Any decisive correlation between τ_0 and the elastic moduli for these alloys must however wait for accurate experimental values.

Studies on relative strengthening between various interstitials in titanium have been carried out by Finlay



7 Microstructure showing quenched-in hydrides in zirconium $\times 20\,000$ (enlarged $4\frac{1}{2}$ times) after Rodriguez and Arunachalam³¹

and Snyder⁶ and also by Jaffe et al.²³ These have shown that nitrogen has the greatest strengthening effect followed by oxygen and then lastly by carbon. This increase in strength is invariably accompanied by a drastic reduction in ductility except for carbon. For instance, titanium alloys, containing carbon up to the solid solubility limit, do not exhibit any brittleness while it needs only 0.75 w% O or 0.5 w% N to bring down the tensile ductility at room temperature to zero.

At first sight, these findings do not appear to correlate well with the volume distortion produced in the metal lattice by oxygen, nitrogen and carbon. Carbon produces maximum distortion followed by oxygen and nitrogen. In spite of this, if carbon does not cause either rapid hardening or brittleness as compared to the other two interstitials, it only implies that factors other than pure elastic interactions are important in determining hardening. For instance, the nature of binding between oxygen atoms and the metal atoms in IV b is still to be identified. There have been suggestions of covalent and even ionic bonding existing. Differences in binding between carbon-metal atom and oxygen-metal atom can perhaps account for different hardening behaviours. Another likely hypothesis, as we have pointed out earlier in this review, contends that lower the axial ratio from the ideal value, higher is the hardening.

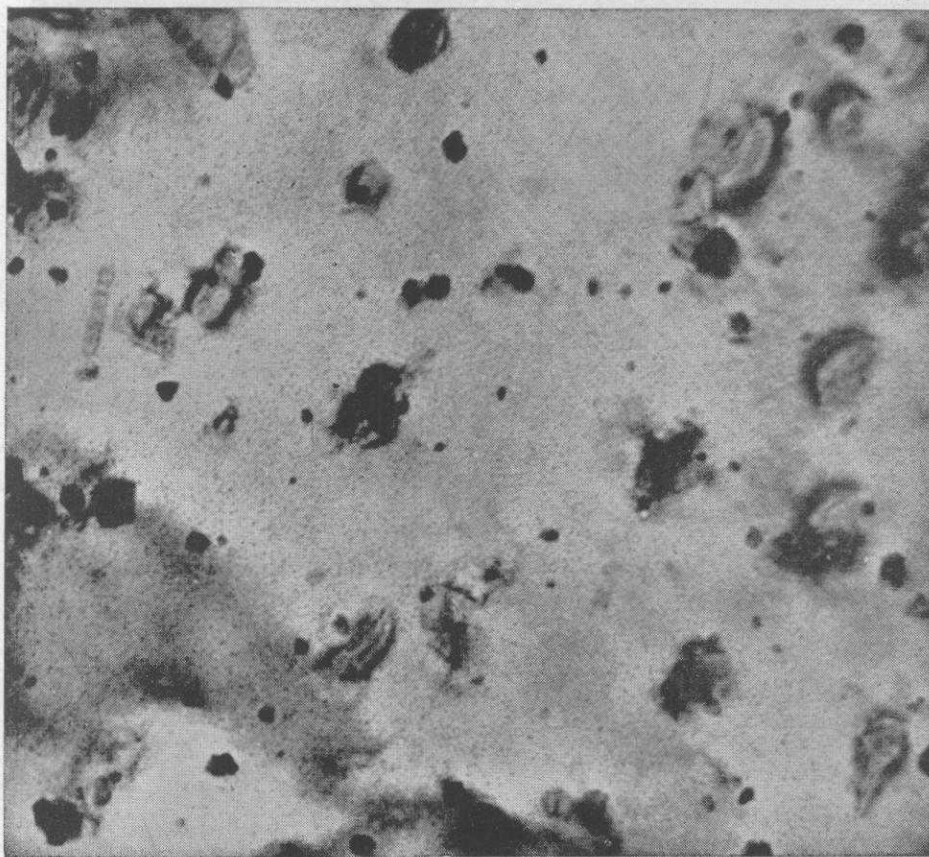
Similar investigations on relative hardening between zirconium alloys containing oxygen and oxygen with carbon have been carried out by Das Gupta and Arunachalam. From their experiments they have found that carbon is only one-fourth as effective as oxygen in hardening. Their values of τ_0^* (thermal component of flow stress extrapolated to 0°K), for both oxygen and oxygen-carbon alloys are shown in Fig. 6.

The ability of Zr-C and Ti-C alloys to remain ductile has possible technological applications. It appears practicable to design dispersion-hardened materials in this group of metal containing metal carbides as dispersions in the metal matrix. Such a dispersion is likely to lead to a significant hardening of the composite because of the non-deformability of the carbides and possible coherence that may exist between carbides and the matrix. This kind of blending is unfortunately not possible either with oxides or with nitrides as they cause brittleness.

Mechanical properties of alloys containing hydrogen

Among the interstitials that go into IV b metals, only hydrogen has such a poor solid-solubility at room temperature, that it exists almost invariably as second-phase hydrides in the metal. The mechanical properties of these two-phase structures are such that they have poor ductility, low fracture toughness and low impact strength. This behaviour has such a profound technological significance that a good deal of attention has been given to the embrittlement caused by hydrogen. For instance, in reactor technology, hydrogen pick-up by zirconium cladding as well as by pressure tubing during reactor operation has a damaging influence on the life time of zirconium or its alloys as structural material.

For understanding the mechanical properties of IVb metals containing hydrogen, it is necessary to study the different morphologies of hydride precipitates. Normally, hydrides precipitate as needles or platelets at grain boundaries and within the grains. But on rapid quenching from high temperatures, precipitates form as small circular discs, not unlike quenched-in dislocation loops (Fig. 7).



8 Microstructure showing stress-oriented hydrides in zircaloy-2 $\times 240$; after Sinha and Arunachalam²⁴

The mechanical properties of the material containing such quenched-in hydrides are markedly different from the samples having massive hydrides. We shall, therefore, consider the mechanical properties of these two types separately. In addition to this broad classification, we shall also consider the phenomenon of stress-orientation of hydrides. This, as the name implies, is a preferred precipitation of hydride platelets under applied elastic stress such that the precipitation takes place normal to the stress axis when under tension; while under compressive stress, the hydrides are oriented parallel to the stress axis. This phenomenon is similar to the 'stress-ordering' effect observed in martensitic transformations or in order transformations. This stress-orientation of hydrides has more than a mere academic significance. In internally pressurised tubes, stress orientation tends to precipitate hydrides in radial planes where they cause maximum embrittlement. As hydrides precipitate on particular crystallographic planes called the habit-planes, the texture of the material containing hydrides largely determines the mechanical strength. As there are more than a single habit-plane available for precipitation, it is observed that in the absence of stress-orientation, many habit-planes are activated for precipitation and hence there is no unwanted single orientation of hydrides which may cause embrittlement. This is altered when there

is stress-orientation as only those habit-planes which are normal to the tensile stress axis would now be activated. Such enhanced precipitation would provide a continuous fracture path leading almost to nil ductility. As an example of stress-orientation a micrograph showing hydride morphology after stress-orientated precipitation in zircaloy-2 is seen in Fig. 8.²⁴ Marshall and Louthan²⁵ were the first to show the seriousness of the stress-orientation in destroying ductility and strength; tensile specimens containing as little as 50 ppm of hydrogen precipitated as hydrides perpendicular to the axis, exhibited complete brittle behaviour. As we have pointed out earlier this is due to greater intergranular precipitation on a single or only a few habit-planes that are normal to the stress axis. Such a textured precipitation would naturally provide an easier chain for the link-up of micro-cracks initiated by hydrides. Various factors such as grain size,²⁶ texture²⁴ and fabrication strain²⁷ have been shown to play a role in determining the efficiency of stress-orientation. Studies on these variables are important as they could suggest fabrication paths that could avoid the unwanted stress-orientation. This stress-orientation phenomenon is not peculiar to zirconium alone. Louthan²⁸ has shown that stress-orientation of hydrides also takes place in titanium.

It remains to consider the role of quenched-in

hydrides on the mechanical properties. It has been shown by Westlake²⁹ in zirconium and by Arunachalam et al.³⁰ in zircaloy-2, that when solution-annealed and quenched, hydrides precipitate as very fine circular platelets associated with vacancy loops (Fig. 7).

Mechanical properties of materials containing such quenched-in hydrides are of interest as they, because of their small size, could influence both the thermal component of flow stress (τ^*) and the athermal stress (τ_0). Experiments carried out in zirconium by Rodriguez and Arunachalam³¹ have shown that only the athermal stress is increased and τ^* is independent of the hydrogen content. In spite of the increase in strength, ductility is not seriously impaired perhaps due to the fine size of the precipitates.

Internal friction

One of the most sensitive methods for detecting the presence of interstitials and also for studying their migration in the lattice is through investigating the materials' damping capacity. Such internal friction measurements have been carried out for oxygen, nitrogen and hydrogen in group IV b metals.

In an earlier section, we have discussed the geometry of interstitials in the hcp lattice and have shown that while hydrogen occupies tetrahedral sites, other interstitial elements go into the octahedral holes. It can then be argued that as octahedral holes are symmetrically located in the lattice, there cannot be any stress-induced jumping of interstitials between sites leading to Snoek-like peak for elements occupying the octahedral sites. However, more subtle effects come into play even in this case leading to an internal friction peak. It has been suggested by Gupta and Weining³² that identity between octahedral holes would be destroyed if one hole has as its nearest neighbour a substitutional impurity atom. Such a combination is likely to lead to an internal friction peak. Such peaks in Ti-O alloys have been reported by Pratt et al.³³ and also by Gupta and Weining.³² The activation energy obtained for this peak (45 ± 5 kcal/mole), agrees well with the activation energy for the diffusion of oxygen in titanium. Similar experiments in hafnium-nitrogen and hafnium-oxygen alloys by Bosojni³⁴ et al. have shown that the internal friction peak appears around 480°C for a frequency of 0.9 c/sec. The activation energy for oxygen is about 55 kcal/mole while for nitrogen it is around 50 kcal/mole. These values also agree well with the activation energy for the diffusion of oxygen and nitrogen in hafnium. Results of similar experiments in zirconium are lacking.

Addition of hydrogen results in a somewhat different internal friction behaviour.³⁵ There have been as many as three peaks at temperatures of about -45, +5 and 230°C for zirconium-hydrogen alloys. The low temperature peak has been attributed to the stress-induced boundary movement of single hydrogen atoms while the peak at 5°C to the movement of hydrogen atom pairs. The peak at 230°C is believed to be due to an atom exchange between lattice sites which is influenced by coherency stresses between metal and hydride precipitates.

These interpretations at this stage appear a bit confusing; for all these results have been obtained on materials which were supersaturated with hydrogen. Considering the very poor solubility of hydrogen in these materials (10^{-4} at %), it is doubtful as to whether hydrogen in solution could actually give rise to these peaks. More likely these peaks are associated with the initial stages of precipitation. Careful experimental results in Hf-H, Zr-H and Ti-H are needed before building up the possible atomistic models associated with these peaks.

Fracture

The fracture behaviour of all the IV b elements are adversely affected when interstitials are present. The only exception to this rule is perhaps carbon; but then it does not dissolve to any remarkable extent in these metals.

Because of the practical implications, fracture properties of zirconium containing hydrogen have been extensively investigated and we shall draw on these results to discuss the hydrogen embrittlement of these metals. Though nitrogen seems to be most deleterious as far as fracture properties are concerned, no systematic experiments appear to have been carried out with this element in solution. With oxygen, the situation is somewhat better. Lehr and Debuigne³⁶ have studied the fracture surfaces of concentrated solid solutions of oxygen in zirconium. They found that for the concentration of interstitials they have used (5-20 a% O), fracture was completely brittle in both impact and slow strain-rate tests. The 'river' markings characteristic of brittle fracture were observed on fracture surfaces. Lehr and Debuigne interpret this brittleness as due to strong Zr-O bonds. The increase in strength due to this kind of bonding would be maximum near the composition Zr_3O because of ordering and hence complete brittle behaviour could be expected as this composition is approached. Similar behaviour could be expected in Ti-O system also, as this is also a system prone to ordering. As yet there have been no reports of ordering in Hf-O systems.

As has been pointed out earlier in this review the embrittlement of IV b metals containing hydrogen is due to the precipitation of second phase hydrides.

This embrittlement process is influenced by a large number of variables, such as hydrogen content, hydride orientation, grain size and crystallographic texture, and all of them should be correctly established to give a meaningful description of the process. In addition, strain rate and temperature also appear to be influential; low temperature and high strain-rate favour the embrittlement process. The hydride phase being brittle, acts as preferential crack nucleation sites and the fracture process can be conveniently considered to take place in three stages: First stage consists in the nucleation and propagation of crack within the hydride phase. In the second stage, this crack propagates into the zirconium matrix and the third one deals with the continuation of cracks into the matrix. According to Westlake³⁷, the nucleation of cracks could take place

through precipitate-twin or precipitate-dislocation interactions. Beevers³⁸ has also found that cracks originate through one of the following mechanisms :

- (a) interaction of the matrix twin with the precipitate
- (b) stress field generated by dislocation pile-up in the matrix at precipitate-matrix interface or
- (c) interaction of dislocations contained by the hydride lattice.

The first two mechanisms would nucleate crack at precipitate-matrix interface and the third one within the precipitate. Furthermore, once nucleated, the cracks are considered to have propagated to produce a crack-length equal to that of the precipitate. Beevers has shown by experimental observations and analysis that fracture of the hydride precipitate is more energetically favourable when the matrix is elastic than when it has become plastic. Coleman and Hardie³⁹ from their experiments on hydrided α -zirconium have concluded that hydrides precipitate directly at grain boundaries and act as crack nucleators. We have already pointed out in this review that this linking up of cracks become catastrophic when the hydrides are stress-oriented perpendicular to the tensile axis. In this case, Louthan³⁵ has suggested the mechanism of fracture as cleavage in the basal plane of the matrix. Such unwanted failures, often premature, continue to be a problem to the metallurgists engaged in utilising IV b metals for industrial applications.

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Discussions

Dr U. K. Chatterjee (Indian Institute of Technology, Kharagpur): Was any electron microscopy carried out for the study of dislocation pile-ups at the hydride precipitates and the nature of such pile-ups at different strain values?

Mr P. Rodriguez (Author): We have carried out electron microscopy studies on deformed specimens containing quenched-in hydrides. No dislocation pile-ups were observed in these, even in fractured specimens. The quenched-in hydrides are deformable and the absence

of dislocation pile-ups at the precipitates indicate that dislocation are cutting through them. This is also supported by the absence of any difference in the work hardening rate between specimens containing quenched-in hydrides and those that do not contain such hydrides. The details of these studies are being published elsewhere.¹

1. P. Rodriguez and V. S. Arunachalam—Effect of quenched-in hydrides on the mechanical properties of zirconium.

Journal of Nuclear Materials (to be published).