

Hardness Anisotropy, Deformation Mechanisms and Brittle-to-Ductile Transition in Carbides

D. J. ROWCLIFFE, G. E. HOLLOX*

Brown Boveri Research Center, 5401 Baden, Switzerland

The slip plane for $\text{TiC}_{0.8}$, $\text{VC}_{0.94}$ and substoichiometric tantalum carbide has been determined as $\{110\}$ using microhardness indentation at room temperature. Under the same conditions, $\text{HfC}_{0.98}$ also slips on $\{110\}$ but $\text{TaC}_{0.96}$ slips on $\{111\}$. At low temperatures $\{110\}$ slip is characteristic of the Group IV and substoichiometric Group V transition metal carbides while stoichiometric Group V carbides probably deform preferentially on $\{111\}$ at all temperatures. This behaviour is explained in terms of two models for the crystal structures of the carbides. The Group IV carbides are described by a close-packed metal lattice whereas the structure of stoichiometric Group V carbides is more open. Various physical and mechanical properties and the effects of changing carbon content have been correlated on the basis of the models. In particular, an explanation of the brittle-to-ductile transition in carbides is proposed.

1. Introduction

If a material is brittle at room temperature under uniaxial stress, it can usually be made ductile by raising the temperature. For example, the transition metal carbides appear to be completely brittle at ambient temperatures when tested in simple bending, tension or compression. However, at temperatures above the range 800 to 1200°C, depending upon the carbide, a permanent deformation by slip, usually on $\{111\}$ planes, precedes fracture [1]. The temperature at which this begins is called the brittle-to-ductile transition temperature. This is further characterised by the fact that the fracture strength increases appreciably and the crystal becomes less sensitive to the presence of flaws.

Brittle failure of solids can also be suppressed when they are subjected to a stress system which contains a hydrostatic component, since the necessary tensile stresses normal to the plane of a crack nucleus cannot develop. Local hydrostatic stresses are produced during hardness indentation and at room temperature, $\text{TaC}_{0.96}$ single crystals exhibit relatively extensive plastic flow and deform on $\{111\}$ planes in a manner similar to fcc metals [2, 3]. Clearly, under these stress conditions, a different description of a brittle-to-

ductile transition temperature is required to account for the more localised plastic flow, since such crystals appear completely brittle under uniaxial stresses. Different materials, however, respond in a different manner to such testing conditions. For example, the ostensibly similar carbide, $\text{HfC}_{0.98}$, shows much less extensive plastic flow than $\text{TaC}_{0.96}$ and, in addition, has a different slip plane, $\{110\}$ [3]. The purpose of this paper is to describe the deformation under hardness indentation of a number of carbides: $\text{TaC}_{0.96}$, $\text{HfC}_{0.98}$, $\text{TiC}_{0.8}$ and a substoichiometric tantalum carbide, and to discuss some conditions controlling their choice of slip plane. The results of this work also suggest factors which may be important in governing the brittle-to-ductile transition temperature in these compounds.

2. Experimental

Knoop Hardness measurements were made as a function of indenter orientation on the (001) surfaces of titanium carbide, vanadium carbide and substoichiometric tantalum carbide in the same way as discussed in the previous paper concerning tantalum carbide ($\text{TaC}_{0.96}$) and hafnium carbide ($\text{HfC}_{0.98}$) [3]. The titanium

*Now with International Nickel Ltd, Birmingham Research Laboratory

carbide and vanadium carbide crystals were grown using the floating zone technique [4]. Chemical analysis and lattice parameter measurements indicated that the compositions were $TiC_{0.8}$ and $VC_{0.84}$. Substoichiometric tantalum carbide crystals were obtained by decarburising $TaC_{0.96}$ crystals for 1 h at $2300^{\circ}C$.

3. Hardness Anisotropy

3.1. Titanium Carbide and Vanadium Carbide

The variation of Knoop Hardness as a function of orientation of the indenter to a $[100]$ direction in the (001) surface in $TiC_{0.8}$ and $VC_{0.84}$ is shown in fig. 1 and should be compared with fig. 1 of the previous paper [3] which indicates similar data for $TaC_{0.96}$ and $HfC_{0.98}$. In contrast both to $TaC_{0.96}$, which shows a continuously decreasing hardness from 0 to 45° indentations and to $HfC_{0.98}$, whose hardness increases over the same range of orientation, $TiC_{0.8}$ and $VC_{0.84}$ exhibit discontinuous variations in hardness. The hardness is lowest at 0° and rises to a maximum close to 30° , but then falls by a small but significant amount at 45° indentations.

The origin of the different variations in Knoop Hardness of $TaC_{0.96}$ and $HfC_{0.98}$ with indenter

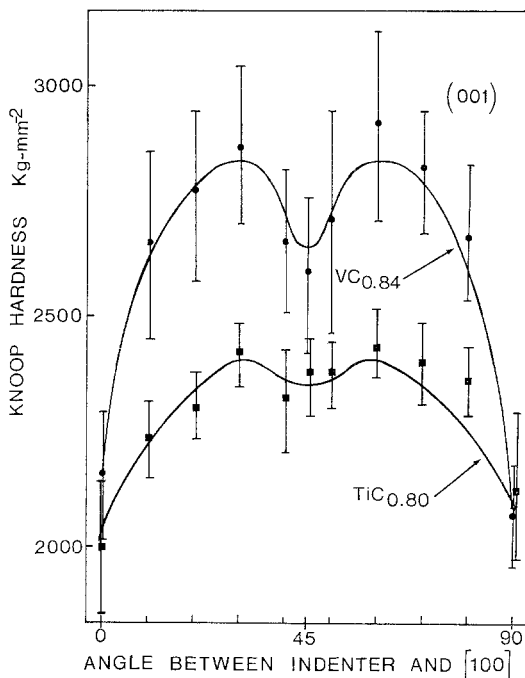


Figure 1 Variation of Knoop Hardness with Indenter Orientation in $TiC_{0.80}$ and $VC_{0.84}$ (100 g load). The hardness increases for 0 to 30° indentations, but then falls from 30 to 45° indentations.

orientation lies in a different operative slip plane in these two carbides at room temperature. Optical metallography has shown that $TaC_{0.96}$ deforms on $\{111\}$ while $HfC_{0.98}$ deforms on $\{110\}$ planes. According to Brookes *et al.* [5] (fig. 2), the effective resolved shear stress for deformation on the $\{111\} \langle 1\bar{1}0 \rangle$ slip system increases as indenter orientation changes from 0 to 45° and a continuously decreasing hardness is observed, while the opposite is true for slip on $\{110\} \langle 1\bar{1}0 \rangle$.

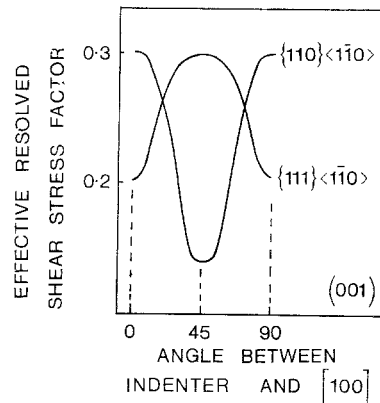


Figure 2 Effective Resolved Shear Stress on the $\{111\} \langle 1\bar{1}0 \rangle$ and $\{110\} \langle 1\bar{1}0 \rangle$ slip systems as a function of Indenter Orientation (after Brookes, O'Neill, and Redfern [5]).

Slip-lines could not be detected at indentations in $TiC_{0.8}$ and $VC_{0.84}$ by scanning electron microscopy, Nomarski interference or etch-pitting techniques. However, the first two techniques indicated that the surface adjacent to the indentations was slightly distorted which implies that local plastic flow had occurred. For indentations in the range 0 to 30° , the variation in hardness of $TiC_{0.8}$ and $VC_{0.84}$ is similar to that of $HfC_{0.98}$ suggesting that the active slip-plane is $\{110\}$. At orientations between 30 and 45° , however, the decrease in hardness is not consistent with the continuously decreasing effective stress on the $\{110\} \langle 1\bar{1}0 \rangle$ slip-system [5]. On the other hand, the effective stress on $\{111\} \langle 1\bar{1}0 \rangle$ and also on $\{100\} \langle 011 \rangle$ is high and increases with angle of indentation. Thus, the experimental observations are consistent with deformation on one of these other slip-systems and the hardness is lower at 45° than at 30° indentations. In view of the established deformation mechanisms at high temperatures it seems likely that this other slip-system is $\{111\} \langle 1\bar{1}0 \rangle$.

From these data, the primary slip-plane in $\text{TiC}_{0.8}$ and $\text{VC}_{0.84}$ can be deduced. If the critical resolved shear stress for slip on $\{111\} \langle 1\bar{1}0 \rangle$ were exactly equal to that for slip on $\{110\} \langle 1\bar{1}0 \rangle$, then a sharp change in slip-plane would be expected at the "cross-over" point when the effective resolved shear stresses on these two slip-planes are equal, i.e. at 22° indentations (fig. 2). In $\text{TiC}_{0.8}$ and $\text{VC}_{0.84}$ the "cross-over" is at about 30° , for which case the effective resolved shear stress factors are ~ 0.29 for $\{111\} \langle 1\bar{1}0 \rangle$ slip and ~ 0.19 for $\{110\} \langle 1\bar{1}0 \rangle$. Since slip takes place at a lower stress on $\{110\} \langle 1\bar{1}0 \rangle$, this must be the preferred slip-system in these two carbides. When the stress to produce slip on $\{110\} \langle 1\bar{1}0 \rangle$ is very different from that on $\{111\} \langle 1\bar{1}0 \rangle$, then no discontinuity in the hardness would be observed; this is the case for $\text{HfC}_{0.98}$ [3] and also for $\text{TiC}_{0.94}$ as indicated by earlier data of Williams [6]. On the other hand, if slip occurs on $\{111\} \langle 1\bar{1}0 \rangle$ at 0° indentations, a continuous variation in hardness is expected, since the effective stress factor for deformation on this slip-system is continuously increasing, as is the case for $\text{TaC}_{0.96}$.

3.2. Substoichiometric Tantalum Carbide

In decarburised $\text{TaC}_{0.96}$, a composition gradient exists from the surface to the centre of samples and previous results [2] have shown that the regions of constant composition are very narrow. Consequently, indentations were only made at 0 and 45° at constant distance from the decarburised surface. In all cases, the hardness was greater at 45° than at 0° indentations in contrast to the behaviour in $\text{TaC}_{0.96}$ [3]. Average values for the substoichiometric tantalum carbide were 2100 kg/mm^2 at 0° and 2575 kg/mm^2 at 45° indentations. This hardness anisotropy shows that slip must take place on $\{110\}$ planes.

4. Mechanical Behaviour of Carbides

In this paper the preferred slip-plane at room temperature of $\text{TiC}_{0.8}$, $\text{VC}_{0.84}$ and substoichiometric tantalum carbide has been shown to be $\{110\}$, the same as that observed in $\text{TiC}_{0.94}$ and $\text{HfC}_{0.98}$, but different from that in $\text{TaC}_{0.96}$. In the following sections, hard sphere models of the crystal structure of these different carbides are considered. On the basis of these models, a qualitative description of differences in physical and mechanical properties of the carbides will be given, with particular reference to the slip-plane and the brittle-to-ductile transition.

4.1. Lattice Structures of Carbides

The transition metal carbides have the NaCl-type structure. Assuming metal/metal contact, the atomic radii of the metals in the Group IV carbides are only about 3% greater than those in the metal crystal from which they are derived, table I. This suggests that a close-packed structure in which the ratio of the radii of the atoms, r/R , is geometrically fixed at 0.414, as shown in Model A, fig. 3a, describes these compounds. For the Group V carbides, however, the large difference between the metal atom radii in the metal and in the carbide suggests that a model of metal/metal contact is less likely, and a more open structure, shown in fig. 3b, describes their structure. In Model B, fig. 3b, it is assumed that the main contact is between metal and carbon and that the radius ratio is variable. If the radius of the metal atom is taken to be the same as that in the parent transition metal, the radii of the carbon atoms and hence the ratios r/R for each carbide can be calculated from the lattice parameter. The data are shown in table II. On the basis of this model, the effective radius ratio is about 0.46 for Group IV carbides and about 0.58 for Group V carbides.

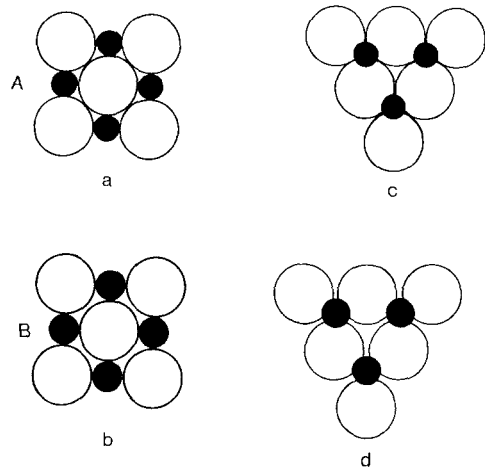


Figure 3 Schematic representation of the carbides by a hard sphere model of metal atoms (large circles) and carbon atoms (small circles). In fig. 3a, the metal atoms are in contact and the radius ratio is 0.414. Fig. 3b shows the more open lattice for a radius ratio of 0.50. In fig. 3c and 3d the projection of the $\{111\}$ slip-plane is shown for radius ratios of 0.414 and 0.50 respectively.

Using a similar model, Hägg [7] showed that the carbides have simple crystal structures for radius ratios < 0.59 , but above this ratio, the

TABLE I A comparison between radii of metal atoms in carbides and in the pure metal.

Carbide	Lattice Parameter (Å)	Metal Atomic Radius in Metal (Å)	Metal Atomic Radius in Carbide (Å)	Expansion of Metal Atoms in Carbide (%)
TiC	4.32	1.47	1.52	3.0
ZrC	4.70	1.61	1.66	2.8
HfC	4.64	1.59	1.64	2.5
VC	4.16	1.31	1.47	12.5
NbC	4.47	1.43	1.57	10.0
TaC	4.45	1.42	1.57	10.5

TABLE II Radius ratios of the carbides.

Carbide	Atomic radius in metal (Å)	Radius of carbon site (Å)	Radius Ratio
TiC	1.47	0.69	0.47
ZrC	1.61	0.74	0.46
HfC	1.59	0.73	0.46
VC	1.31	0.77	0.59
NbC	1.43	0.80	0.56
TaC	1.42	0.81	0.57

crystal structure changed. Here, it is proposed that the lattice becomes progressively less stable as the radius increases above 0.414.

In measuring the radius ratios, the dimensions that should be given to the radii of the different atom species are subject to some discussion, particularly if charge transfer takes place in compounds to alter the atom radii from those in the parent crystals. However, from these models which utilise dimensions in the carbide crystals, it would seem that a close-packed metal lattice such as that shown in fig. 3a more closely describes the Group IV carbides. If this is the case, the stability of the crystals may be expected to arise from metal/metal interactions, consistent with Lye's model for the band structure and cohesion in TiC [8]. As soon as the radius ratio exceeds 0.414, the metal/metal interatomic forces

would be expected to decrease sharply and the bond strength in $\langle 110 \rangle$ directions would be reduced. Consequently, metal/non-metal interactions may be expected to become of proportionally greater importance as the radius ratio increases.

The difference in directionality of the bonding in the carbides appears to be directly reflected in the elastic constants of these materials, shown in table III. The anisotropy factor $2C_{44}/C_{11}-C_{12}$ represents the ratio of the resistance to shear on a $\{100\}$ plane in a $\langle 001 \rangle$ direction to that of a $\{110\}$ plane in a $\langle 1\bar{1}0 \rangle$ direction. For all the Group IV carbides, the anisotropy factor is < 1 while for stoichiometric TaC, it is > 1 , in accord with the models discussed in fig. 3 and proposed for the structures of these carbides. Additional evidence for this picture is obtained from measurements on the phonon spectra of tantalum carbide which suggest that the metal/non-metal force constants are greater than the metal/metal interactions in this compound [13]. There are also other indications that the lattices of TaC and NbC are different from those of the Group IV carbides. For example, both are comparatively soft [14, 15] and both are superconductors at high carbon-to-metal ratio [16, 17] which suggests that the lattices are somewhat unstable.

TABLE III Elastic Constants (in units of 10^{12} dyn-cm $^{-2}$) and Anisotropy Factor for the carbides.

Carbide	C_{11}	C_{12}	C_{44}	$\frac{2C_{44}}{C_{11} - C_{12}}$	Reference
TiC _{0.91}	5.145	1.070	1.788	0.88	[9]
ZrC _{0.94}	4.720	0.987	1.593	0.86	[9]
HfC					not known
VC _{0.84}	5.01	0.84	1.55	0.75	[10]
NbC					not known
TaC _{0.90}	5.05	0.79	0.73	0.34	[11]
			- 0.91	- 0.43	
TaC _{0.97}	6.10	2.10	2.30	1.15	[12]

4.2. Slip-Planes in Transition Metal Carbides

Slip on $\{111\}$, $\{110\}$ and $\{100\}$ planes has been observed in crystals with the face-centred cubic structure. For metals, $\{111\}$ is preferred and is explained by the simple consideration that these planes are the furthest apart of any type. In ionic crystals slip is usually on $\{110\}$ or $\{100\}$ depending upon the polarisability [18, 19]. For covalent compounds all three planes have been observed and the choice of slip-plane has been correlated with the ratio of the radii of the atoms involved, on the basis that the preferred plane for slip is the one on which there is the least distortion of the lattice as the atoms move [20]. The generally accepted interpretation of bonding in carbides is that it is predominantly covalent in nature so radius ratio criteria are expected to be applicable. According to Van der Walt and Sole [20], the primary slip-plane will be $\{110\}$ for a radius ratio of 0.414. For radius ratios between 0.414 and 0.633, $\{111\}$ will be preferred.

TABLE IV Slip-planes in the carbides at room temperature and above the bulk brittle-to-ductile transition temperature.

Carbide	Slip-Plane	
	Room Temperature	High Temperature
TiC	110	111
ZrC	not known	111
HfC	110	not known
VC	110	111
NbC	not known	111
TaC	111	111

Table IV presents the observed slip-planes in single crystals of the transition metal carbides deformed by indentation at room temperature. $\text{TiC}_{0.8}$ and $\text{HfC}_{0.98}$ both deform on $\{110\}$, while $\text{TaC}_{0.96}$ deforms on $\{111\}$, exactly as expected from their radius ratios. From these correlations, it would be expected that zirconium carbide would deform on $\{110\}$ planes in the same way as titanium carbide and hafnium carbide; niobium carbide should be similar to tantalum carbide. Moreover, the proposed close packed nature of the lattice of the Group IV carbides suggests that these compounds would be harder than the Group V carbides, and this is indeed observed. Vanadium carbide is exceptional since it behaves more like a Group IV carbide, and will be discussed in the next section.

4.3. Effects of Non-Stoichiometry

The models illustrated in fig. 3 describe stoichiometric carbides. For the Group IV carbides, any deviations from stoichiometry should not change the arrangement of atoms significantly, since the lattice is already close-packed. At low carbon contents, the deformation mechanisms may not differ much from those of the stoichiometric compounds although a reduction in hardness would be expected as a result of the change in the Peierls stress. However, in the Group V carbides, deviations from stoichiometry would be expected to affect the positions of metal atoms in the lattice. As carbon atoms are removed, the metal atoms will be displaced towards each other. This difference between Group IV and Group V carbides is reflected in the change in lattice parameter with carbon content. Over the range in carbon-to-metal ratio from about 1.0 to 0.8, the lattice parameter of tantalum carbide decreases by about 0.7% while that of TiC is invariant [21]. In the carbon-deficient Group V carbides, the metal/metal interactions should become more important, and the lattice may be more appropriately described in terms of a model that approaches Model A, shown in fig. 3a, although the radius ratio is above 0.414. Consequently, non-stoichiometric Group V carbides may tend to resemble Group IV carbides, i.e. they would become harder and also deform by slip on $\{110\}$ planes.

The available experimental data support this view. The hardness of titanium carbide only decreases from about 2700 kg/mm² at $\text{TiC}_{0.97}$ to about 2000 kg/mm² at $\text{TiC}_{0.8}$ [6], while that of tantalum carbide increases from about 1500 kg/mm² at $\text{TaC}_{0.96}$ to above 4000 kg/mm² at $\text{TaC}_{0.83}$ [2]. Moreover, the Knoop Hardness anisotropy indicates that there is no change in slip-plane of titanium carbide over the same composition range, the presence of a slight tendency to produce slip on $\{111\}$ planes at 45° Knoop Indentations in $\text{TiC}_{0.8}$ suggesting that the covalent bonding in the carbide is reduced to the extent that more metallic behaviour is observed at low carbon contents. In substoichiometric tantalum carbide, slip is almost completely suppressed [2], but measurements of hardness anisotropy indicate that deformation takes place on $\{110\}$ planes in contrast to that in $\text{TaC}_{0.96}$, in which the operation of a $\{111\}$ slip-plane has been clearly demonstrated. Moreover, the elastic anisotropy factor of $\text{TaC}_{0.9}$ is < 1 , while that of $\text{TaC}_{0.97}$ is > 1 , suggesting that at low carbon-to-

metal ratio this carbide is similar to Group IV carbides.

It was mentioned earlier that $VC_{0.84}$ is anomalous since it does not resemble other Group V carbides, but shows many similarities with Group IV carbides. $VC_{0.84}$ does not exhibit slip lines when indented, but the hardness anisotropy shows that the slip-plane is $\{110\}$. In addition, the elastic anisotropy is < 1 . The behaviour does, however, correlate well with the behaviour of non-stoichiometric Group V carbides. It should be noted that vanadium carbide is also different from the other cubic carbides since its upper limit of composition is only at a carbon-to-metal ratio of 0.89 [21] and throughout its composition range, a series of ordered compounds is formed [22-24]. It may be significant that vanadium carbide has the highest radius ratio of all the carbides. Ordering and a limitation of the carbon content may be the mechanisms by which stability is retained in this material.

4.4. Brittle-to-Ductile Transition in Carbides

Three of the features of the observed slip-planes in carbides at different temperatures, table 4, are: (i) that $TaC_{0.96}$ deforms plastically at room temperature under hardness indentation and the slip-plane is $\{111\}$, (ii) $TiC_{0.8}$, $HfC_{0.98}$ and $VC_{0.84}$ exhibit little plastic flow and slip on $\{110\}$ planes at room temperature, and, (iii) at high temperatures, when the carbides are ductile under uniaxial stressing conditions, the slip-plane is $\{111\}$, although $\{110\}$ slip is also observed in $ZrC_{0.95}$ [25]. These data suggest that for ductility in the carbides, $\{111\}$ must be the operative slip-plane, while only limited flow can take place on $\{110\}$.

There are two possible explanations for greater ductility associated with $\{111\}$ slip as opposed to $\{110\}$. The first is that there are three possible $\langle 1\bar{1}0 \rangle$ slip vectors in each $\{111\}$ slip-plane, while there is only one for each $\{110\}$ slip-plane. This suggests that strains can be more easily accommodated by slip on $\{111\}$ planes. The second is concerned with the possibilities of dislocation dissociation on $\{111\}$ or $\{110\}$ planes. Kelly and Groves [26] point out that for slip on the $\{110\}$ plane the lowest energy configuration is for unit dislocations with Burgers vectors $a/2 \langle 1\bar{1}0 \rangle$. There appear to be no intermediate sites to which atoms could move without creating a very high energy stacking fault, so dissociation of dislocations is unlikely.

Several dissociation mechanisms for forming partial dislocations on $\{111\}$ planes in carbides have been proposed, such that atoms move in $\langle 112 \rangle$ directions [27]. The greater ductility of $TaC_{0.96}$ is due to the fact that dislocation dissociation is easier in its more open structure, fig. 3d, than in the close-packed structure of Group IV carbides, fig. 3c. A necessary condition for ductility in the Group IV carbides and non-stoichiometric Group V carbides may be the movement of dislocations on $\{111\}$ planes. Such a deformation mechanism may only be possible at high temperatures when the separation of metal atoms becomes greater as a result of their increased amplitude of vibration. At these temperatures, the more open structure, Model B, fig. 3b, will describe these carbides.

It should be emphasised that the brittle-to-ductile transition temperature will not be defined by the operation of the $\{111\}$ slip-plane alone. This is only one of the necessary conditions for ductile behaviour. The brittle-to-ductile transition temperature will also depend upon the stress system, the strain rate and the amount of plastic flow which is considered necessary to define a ductile failure. Thus, the high hydrostatic stress component allows considerable plastic flow in $TaC_{0.96}$ indented at or below room temperature, though no dislocation motion can be detected under conditions of uniaxial stress at similar temperatures. Bulk plastic flow under simple stress systems is only possible at relatively high temperatures when the stress to move dislocations is lower than the stresses developed at critical crack nuclei.

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