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FINAL REPORT

INVESTIGATION OF THE MECHANICAL PROPERTIES
OF TRANSITION METAL CARBIDES AND BORIDES

to

U. S. ATOMIC ENERGY COMMISSION

prepared by

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I. INTRODUCTION

Transition metal carbides and borides have received attention in the past because of their high melting points, elastic modulus and hardness, and their relatively good thermal and electrical conductivity for refractory materials. In general the marginal oxidation resistance and more importantly their brittleness has limited their usefulness as high temperature materials of construction.¹

Until recently, descriptions of these classes of materials were limited to information obtained on relatively poorly characterized sintered samples of questionable purity. More recent information on the properties of single crystals of the carbides indicates that conclusions regarding their usefulness, based on studies of sintered samples, may be pessimistic and this class of material may have considerably more potential.^{2,3,4}

The overall objective of this program was designed to examine the high temperature deformation mechanism of single crystals of zirconium carbide and zirconium diboride. Specifically, experiments were carried out on large, high purity, well characterized single crystals of high crystallographic quality to determine the slip direction, active slip planes, the critical resolved shear stress as a function of temperature and the steady state creep rate as a function of stress and temperature. An understanding of the mechanical behavior of these materials may point out specific directions for improvement in these properties through such techniques as alloying or microstructure control.

Zirconium carbide typifies the monocarbides of the transition metals of the fourth and fifth group metals and it is isomorphous with the other monocarbides having the NaCl face-centered cubic structures. ZrC is the only compound that exists in the Z-C system; however, it can exist over a wide range of carbon deficient compositions. ZrB₂ on the other hand, has the simple

hexagonal crystal structure (AlB_2 type) typical of the diborides of the transition metals and has a very small range of stoichiometry. The other two compounds reported in the Zr-B system, ZrB and ZrB_{12} , were not investigated.

II. SUMMARY

The objectives of this work were to examine and define the deformation mechanisms at high temperature of intermetallic compounds of the transition metal carbides and borides. The potential utility of this class of material may only be realized through an understanding of the deformation processes which control the mechanical behavior.

Specifically, large, high quality, high purity single crystals of ZrC and ZrB₂ were prepared from melts by the floating zone technique and characterized by chemical, X-ray and metallographic techniques. Some initial studies were carried out on polycrystalline zirconium carbide to examine the effect of grain boundaries on the deformation processes.

Total dislocation densities in the as-grown ZrC single crystals as determined from etch pit experiments were of the order of 10^5 - 10^6 dislocations per cm². Dislocation structures were verified by X-ray topographical and transmission microscopic techniques. Deformation in the temperature range of 1000-2000°C was found to occur in the $\langle 110 \rangle$ direction on three low index planes {100}, {110}, and {111}. The critical resolved shear stress was approximately identical on all three planes. This previously unobserved result indicates that potentially ten independent slip systems are operative in ZrC and polycrystalline material should accommodate large plastic deformation. Electron transmission photographs indicate that the density of dislocations is substantially increased as a result of deformation and that large numbers of loops are left behind moving dislocations.

The creep data on ZrC single crystals in the temperature range 1400-2000°C shows that the creep rate is proportional to the fifth power of the stress with an activation energy of ~ 110 Kcal/mole.

Dislocation structures show the presence of well defined cell walls, some of which are simple tilt boundaries and others are hexagonal networks. The absence of stacking fault fringes as well as extended and contracted nodes indicate that the apparent stacking fault energy is high since the dislocations do not dissociate into partials.

The lack of evidence for partials, the high stacking fault energy, and the formation of cell walls, coupled with the stress dependence of the creep rate and the observed activation energy are all consistent with the rate controlling mechanism for steady state creep of ZrC in this temperature range being a diffusion controlled process involving climbing of dislocation.

Single crystals of high purity (ZrB_2) were prepared and characterized. Their composition, as determined by chemical and microstructured analysis, was nearly stoichiometric ZrB_2 . A fine oriented precipitate of less than one volume percent that was present in the hexagonal single crystals was identified as fcc ZrB. Although precipitates on the basal and prismatic planes are structurally identical, they differed in their orientation with respect to the matrix.

Electron transmission microscopy techniques were used to determine that the Burgers vector in ZrB_2 is the "a" axis which is parallel to the $\langle 1120 \rangle$ poles, i.e., along the basal plane. At low temperatures the active slip planes around microhardness indentations are the three prismatic $\{10\bar{1}0\}$ of the simple hexagonal lattice; at high temperatures ($>2125^\circ\text{C}$) the basal plane was the active slip plane. Thus, there are only two independent slip systems in ZrB_2 and polycrystalline material cannot undergo large amounts of plastic deformation prior to fracture.

Single crystals of ZrB_2 exhibited no observable plastic deformation at temperatures up to 2000°C in uniaxial compression. At higher temperature crystals

deformed without fracture and exhibited a drop in the flow stress after initial yielding and prior to the onset of work hardening.

The absence of plastic deformation in ZrB_2 single crystals at temperatures below 2000°C is believed to be due to absence of mobile dislocation combined with the pinning effect in the dislocation by the observed precipitate. The high yield stress observed at 2125°C is attributed to the blocking of dislocations by the precipitate particles and the yield drop is a result of the penetration past the precipitated particles by large numbers of dislocations.

As predicted from the behavior observed for single crystals of zirconium carbide, polycrystalline material prepared by zone melting techniques exhibited homogeneous plastic deformation. No grain boundary sliding was observed in the studies of bicrystals, and the creep rate of an 0.5 mm grain size polycrystal sample was essentially identical to a single crystal of comparable purity and carbon content. The recovery mechanism postulated for single crystals apparently applies to the large grained polycrystalline material as well.

Substantial differences were observed between the deformation behavior of relatively high purity, high density, stoichiometric polycrystalline ZrC and commercially available hot pressed ZrC . Apparently grain boundaries are areas of weakness in the fine grained hot pressed material because intergranular fractures occurred at a stress equivalent to the yield stress in both single and polycrystalline material prepared in this study.

Fine grained polycrystalline material could conceivably be produced through a thermochemical cycle that would provide the deformation at one temperature and a recrystallization at subsequent temperature. We observed that recovery occurs by polyganization in ZrC over the temperature range studied. In a high stacking fault material such as ZrC , if recrystallization could be induced it should occur at still lower temperatures where diffusion controlled climb of dislocation is suppressed.

Several approaches to the improvement and alteration of the mechanical properties of ZrC , ZrB_2 , and related compounds are suggested in the observations and conclusions of this work. The high temperature mechanical properties of high purity ZrC do not make it attractive for structural applications. Substantial improvement in the high temperature properties could be made by techniques such as alloying to lower the stacking fault energy and by the formation of dispersed second phase or illustrated by the recent work on boron doped vanadium carbide.²¹ The result of the studies on ZrB_2 indicated that these materials have sufficient strength at temperatures up to 2000°C to be used as structural material. The high strength results from the presence of the finely divided precipitate particles and would be expected to persist until the second phase coarsened or went into solution above 2400°C . At higher temperatures, single crystals should be free of the precipitate and should be sufficiently ductile to be shaped. Polycrystals must have certain compositions and be deformed in a temperature range where they are both single phase and have a recovery process such as recrystallization occurring at a sufficiently high rate to avoid fracture. After deformation, shaped samples can be heat treated to precipitate the second phase to produce a good high temperature structural material.

III. SINGLE CRYSTAL ZIRCONIUM CARBIDE

A. Preparation of Single Crystals

Single crystals were prepared by a floating zone crystal synthesis technique that had been developed earlier in this laboratory.⁵ Examination of the plastic behavior of ZrC depended to a large extent on the ability to prepare and characterize good single crystals which were free of high angle boundaries, second phase and porosity.

The preparation technique is schematically shown in Figure 1. High purity zirconium carbide powder was used as starting material.* It was necessary to add excess carbon to the ZrC starting powder to compensate for the excessive carbon losses during the growth process. The final stoichiometry of the single crystal can be controlled by adjusting the amount of carbon added. Powders were packed in a 3/8-inch inside diameter graphite tube which was rf induction heated. Pressure was maintained on the top and bottom plungers while the rod was sintered along its length. Other techniques were used to prepare the rods, such as isostatic pressing, followed by sintering; however, the procedure described above gave reproducible results and was the simplest to carry out.

The rods which were sintered to approximately 60-70% density were held in the top chuck of the vertical float zone apparatus. Melting was accomplished by coupling directly to the sample of ZrC with a four turn coil. The rf power supply was a 10KW, 450kc generator.

Growth directions were controlled by the use of seed crystals which proved particularly advantageous for the synthesis of single crystals to

* ZrC powder obtained from Wah Chang Corp.

be used in a deformation study. A seed crystal, which had been cut to the desired orientation was held by the graphite holder in the lower chuck. A crystal growth run was initiated by bringing the tip of the polycrystalline sintered bar into contact with the molten end of the single crystal. A molten zone was passed through the polycrystalline rod in the upward direction after a stable molten zone was established between them. Growth rates between 1 to 1 1/2 inches per hour have been found satisfactory.

The apparatus is operated in approximately 1 atmosphere of inert gas. A run usually yields 1 to 2 inches of good single crystal approximately 1/4 inch in diameter. Single crystals of ZrC have been grown along the (100), (110), and (111) crystallographic axes, as well as the 0.5 orientation for $\langle 110 \rangle$ {111} slip.

Metallographic examination has shown the crystals to be single phase and free of internal porosity. X-ray examination showed the samples to be free of large angle boundaries and no resolvable lattice rotation occurred along the length of the samples.

Chemical analyses indicate that no free carbon was present and that metallic impurities were less than 0.01%. The chemically combined carbon content of the single crystals used in this work was ≈ 48.5 atomic percent, which is approximately 1 atomic percent less than the carbon solubility limit in ZrC. Analysis of typical samples indicated the O_2 and N_2 contents to both be of the order of 100-600 ppm in solution. The chemical analyses data are summarized in Table 1.

B. Dislocation Structures of As-Grown Crystals

Prior to deformation, the structure of single crystals was characterized by etch pit, X-ray, and transmission electron microscopy techniques. It was found that boiling sulfuric acid which was reported to reveal dislocations on the {100} cleavage planes of TiC^2 was also a suitable etch for dislocations on the {100} planes of zirconium carbide. The composition of the acid during etching was critical and was difficult to control. Etch pit studies show that the dislocations in the as-grown crystals are concentrated in low angle boundaries and the 100 micron diameter cells between these boundaries are essentially free of dislocations. The total dislocation densities of the as-grown crystals are of the order of 10^5 - 10^6 dislocations per cm^2 .

To insure that these etch pits did in fact correspond to points where dislocations intersected the free surface, other techniques were employed which also revealed dislocations. If these boundaries indeed result from ordered arrays of dislocations, then X-ray topography should reveal a structure that is similar to those observed after etching.⁶ Figure 2 a is a photomicrograph of a cleaved and etched single crystal. The substructure is quite distinct. Figure 2 b is an X-ray image of the same sample. The X-ray image which was obtained by the Schulz⁷ method, which is a modified Berg-Barret technique, reveals a structure which is identical to that in Figure 2 a. In particular the predominant boundary which forks in the lower right hand corner of Figure 2 a and runs across the sample to the upper left hand corner can be clearly seen in Figure 2 b.

All the boundaries which run horizontally across the sample and intersect this forked boundary can be accounted for. This observation confirms that the pits revealed during etching result from the presence of dislocations which intersect the cleaved surface and that the substructure is due to arrays of dislocations in low angle boundaries. The dark straight lines in Figure 2 a are cleavage cracks which resulted from thermally shocking the sample during etching.

The degree of crystallographic misorientation across the boundaries, calculated from the X-ray image in Figure 2 a, is of the order of 0.01 degree. These very low angle boundaries appear to be nearly pure tilt boundaries from the split image.

Single crystals were cut into sections 0.010 inches thick with a high voltage spark discharge apparatus. These sections were subsequently electrochemically thinned in a solution of 4 parts methyl alcohol to 1 part perchloric acid at -35°C to a thickness of 500-1000Å for direct observation by transmission electron microscopy. A Hitachi HU-11A, 100KVA electron microscope equipped with a tilting stage was used for all transmission work.

Examination of large areas of the as-grown crystals with many different operating planes refracting revealed few dislocations. In a few instances rows of dislocations were observed running through the foils; one of which is shown in Figure 3. The spacing between these dislocations is approximately 1 micron which agrees with a spacing of 1.6 microns corresponding to the 0.01 degree tilt boundaries observed by X-ray topography. The electron microscopy observations of the as-grown material agree

quantitatively with those of the etch pit and X-ray studies. The majority of dislocations are in low angle boundaries and the areas within the boundaries are essentially free of dislocations.

C. Identification of the Burgers Vector and the Active Slip Planes

The shortest repeat distance in the NaCl structure is a $1/2$ [110] vector and would be the expected Burgers vector in ZrC from energetic considerations. This is the observed Burgers vector in the fcc metals and ionic compounds with the NaCl structure e.g. NaCl, LiF and MgO. The identity of the expected slip plane is not as predictable as the slip direction.

In ionically bonded compounds with the close packed NaCl structure, slip cannot occur easily on the close packed plane because of electrostatic repulsions caused by passing like charged ions near one another. Slip is observed to occur primarily on {110} planes at intermediate temperatures and secondarily on {100} planes at high temperatures. Near the melting points of these ionic compounds the {111} planes can become active. TiC which has both the same NaCl type crystal structure and mixed metallic-covalent bonding as ZrC has been observed to slip on {111} planes^{2,3} at all temperatures investigated. The nature of the bonding in ZrC is not completely understood which makes it difficult to anticipate a slip plane.

The Burgers vector of ZrC was identified using transmission electron microscopy diffraction techniques. Dislocations are not visible in transmission electron microscopy when the Burgers vector lies in the diffracting crystallographic plane.⁸ This corresponds to the condition

where the dot product $g \cdot b = 0$, where g is the reciprocal lattice vector of the operating plane and b is the Burgers vector. The determination of the Burgers vector of ZrC is illustrated in Figure 4 for a sample in which the plane of the foil is of a $\{111\}$ type. Figure 4 a is a bright field image with a $(1\bar{1}0)$ plane tilted into a diffracting condition. Figure 4 b is a bright field image of the same area after the specimen has been tilted to a position where the $(\bar{1}\bar{1}2)$ plane is diffracting. Dislocations at A, B, and C in Figure 4 a are not in contrast in 4 b indicating that their Burgers vector lies in the $(\bar{1}\bar{1}2)$ plane. The only low index directions meeting these conditions are the $(\bar{1}10)$ and $(1\bar{1}0)$ poles. If the Burgers vector of these dislocations is of a $\langle 110 \rangle$ type then on the average one-third of all the dislocations should go out of contrast with any given (112) plane in an operating position. Although it is not entirely clear from Figures 4 a and 4 b because their photographic quality, at least half of the dislocations in the boundary directly above B that are in contrast in 4 a cannot be seen in 4 b. These results indicate that slip in ZrC occurs with dislocations having the anticipated $1/2 \langle 110 \rangle$ Burgers vector.

The slip planes were identified from the slip traces on two adjacent sides of the sample. This technique⁹ is commonly used to identify the indices of the composition plane of a twinned crystal. Deformation was carried out in compression in a high temperature vacuum furnace attached to a standard Instron testing machine. Crystals were deformed at temperatures between 1050°C and 2000°C in a vacuum of 10^{-5} torr. The crystals were strained between 3-5% at a strain rate of approximately $2 \times 10^{-3} \text{ min}^{-1}$.

It was observed that the active slip plane varied with different orientations of the stress axis. Slip was found to occur on either the $\{100\}$, $\{110\}$, or $\{111\}$ planes depending on the orientation of the stress axis. The maximum resolved shear stress for each type of slip system and the observed slip plane are given in Table II for the three stress axes used. In all three orientations the resolved shear stress on one type of slip plane is higher than the other two; in every case slip was observed only on the plane of highest resolved shear stress. Slip on these three planes is possible with the observed Burgers vector since a $[110]$ direction is found in all of them. The potential operation of 10 independent slip systems ($\langle 110 \rangle \{100\}$ 3, $\langle 110 \rangle \{110\}$ 2, and $\langle 110 \rangle \{111\}$ 5) suggests that the grains of polycrystalline samples should geometrically accommodate large deformation.

D. Critical Resolved Shear Stress as a Function of Temperature

The yield stress that was used throughout was that defined by the intersection of the elastic and plastic regions of a stress-strain curve. The crosshead rate was 0.002 cm/min in every case; however, the specific crosshead rate or nominal strain rate varied approximately 20% due to variations in sample length. It is probable that this variation in strain rate does not cause more than a 10% change in the observed yield stresses.¹⁰ The slip planes of all samples were identified from the slip traces and the yield stresses were resolved on the operating slip system. The critical resolved shear stresses that were observed on the three operating slip planes are plotted as a function of temperature in Figure 5 with stress axis indicated in the stereographic triangle.

In no case was a yield drop observed with these ZrC single crystals. An excessive dislocation count, insufficient purity and/or the use of a soft machine may be responsible for its absence. In LiF¹¹ a yield drop is not apparent with dislocation densities in excess of 10^5 per cm². All of the ZrC single crystals examined by etch pit counts had initial dislocation densities in the range of 10^5 to 10^6 . Pyrolytic graphite caps were used between the specimen and the tungsten push rods which made the deformation apparatus soft. The occurrence of a yield drop does not depend critically on the use of a hard machine, but it is less precipitous with a soft machine. It has been experimentally observed that harder LiF crystals¹¹ show smaller yield drops than the softer, higher purity crystals. While the dislocation-impurity interactions which cause this effect are not completely understood it seems reasonable to consider the impurities as being responsible for the absence of a yield drop in ZrC since the impurity levels in these single crystals were in the range where these effects are observed in ionic crystals.

The difference between the critical resolved shear stresses on the different slip planes are unusually small. The $\tau(T)$'s for the {110} and {111} slip planes are essentially equal over the temperature range where the experiments overlap. A similar plot of the critical resolved shear stresses for MgO¹² shows that while the τ 's for the {110} and {100} slip planes nearly are of the same magnitude at approximately 1200°C ($T_m/2 = 1263^\circ\text{C}$), they differ by a factor of ten 800°C lower. At present we can offer no explanation to resolve this small difference in critical resolved shear stresses in ZrC.

A second anomalous feature of these results is that when slip occurred on either {100} or {110} planes, the yield stress resolved in shear on the most favorably oriented {111} plane exceeded the critical value for slip without any evidence of yielding on that system. Considerable effort was made to insure the accuracy of the slip plane identifications. In the cases where {110} planes were identified as the active planes the samples were cut so that all faces were {100} planes. Only {110} planes could account for the slip traces (on one face traces intersected at 90° to each other, both inclined 45° to the $\langle 100 \rangle$ stress axis and on the adjacent face only one set of traces which was perpendicular to stress axis) and the shape of the sample after deformation (two opposing faces barreled and the other two remaining planar). This specific observation is similar to the behavior of MgO at temperatures just above $T_m/2$.¹³ When stressed along a $\langle 100 \rangle$ axis in the lower intermediate temperature range MgO deforms on two of the four equally loaded slip systems. Like ZrC these were one conjugate pair which intersect at 90° . The reason for the inactivity of the {111} planes under conditions when their critical resolved shear stress had been exceeded remains unexplained.

These $\tau(T)$ results can be plotted as $\ln(\tau)$ against $1/T$ and represented reasonably well by a straight line. If the shapes are to be interpreted correctly in terms of activation energies the dislocation motions occurring during yielding must be controlled by a stress biased activated process such as overcoming the Peierls force. At this time there is not sufficient evidence to associate the apparent activation energies of approximately 20kcal/mole for {111} slip and 30kcal/mole

for {100} slip with a specific molecular process and thus we present them only as the slopes on these lines.

Electron transmission photographs indicate that there are large numbers of loops left behind as dislocation moves. The large increase in the density of dislocations is evident from the comparison of Figure 3 and Figure 6 which shows the dislocation structure in a single crystal after 3 percent deformation at 1400°C.

E. Creep and Recovery

Dynamic creep measurements were made at temperatures of 1400, 1600 and 2000°C on single crystals loaded along a $\langle 111 \rangle$ stress axis. The temperature and strain rate were held constant until the load stabilized; the strain rate was then increased to higher values to determine subsequent steady state creep stresses. Creep rates and creep stresses were calculated from corrected cross-sections and lengths. Total strains calculated from the final dimensions agreed well with measurements calculated from the crosshead movement.

Figure 7 shows the logarithms of the creep rates and stresses observed at the three temperatures studied. The data is represented by:

$$\dot{\epsilon} = A \sigma^n e^{-Q/RT}$$

with $n = 5$ and $Q = 110$ kcal/mole. This dependence of creep rate on stress, was predicted by Weertman¹⁴ for the case where dislocations climbing out of their glide planes to bypass obstacles was assumed to be the rate controlling recovery process.

In most materials, the activation energy for creep above $1/2 T_m$ is found to be approximately equal to the activation energy for self-

diffusion since dislocations climb by vacancies diffusing through the bulk of the material either to or from jogs where they were given off or absorbed. If the number of jogs were just those found in thermal equilibrium, then the activation energy for creep would contain an additional term corresponding to the energy of jog formation. However, the number formed by intersecting dislocations in a deformed sample greatly exceeds those formed by thermal vibrations alone; hence, the concentration of jogs is independent of temperature to a first approximation and the activation for creep is equal to the energy for self-diffusion.¹⁵

In binary systems the diffusion rate of the lower mobility species is the rate determining step of a creep process. It would be anticipated that carbon should have a relatively high diffusion rate and low activation energy because of its size, lattice position and large number of carbon vacancies which exist in carbon deficient fcc carbides. In agreement with this anticipated behavior, Hollox¹⁶ concluded that the creep rate of titanium carbide near $1/2 T_m$ was controlled by the mobility of titanium based on the approximate equality of the activation energies for creep of TiC and of the volume diffusion coefficient of Ti in TiC. Sarian and Criscione¹⁷ have studied carbon diffusion in ZrC single crystals by radioactive tracer techniques and reported an activation energy of 113 kcal/mole. We are not aware of any experimental studies of zirconium diffusion in ZrC. It has been estimated from an empirical relationship ($Q = 38 T_m$)¹⁸ that the activation energy for the diffusion of Zr in ZrC is between 120 and 140 kcal/mole depending on composition.

The activation energy observed for our creep experiments agrees better with that reported for volume diffusion of carbon in ZrC than that estimated for zirconium and appears to indicate that carbon is the lower mobility species. The specific mechanism by which the diffusive process occurs in the transition metal carbides is poorly defined at present. There is considerable evidence that the vacancies in the carbon sublattice can be ordered in specific temperature and composition domains¹⁹ which would require a more complex, cooperative diffusion process than simple analyses describe. More complete understanding of the diffusion process is required to resolve the apparently low diffusion rate of carbon; however, the data are consistent with the hypothesis that diffusion controlled climb of dislocations is the rate controlling recovery process in the creep of ZrC single crystals over the temperature range studied.

F. Dislocation Structure in Deformed Samples

An electron transmission photograph of the dislocation structure of a single crystal used in a creep experiment is shown in Figure 8. It is evident that a major change in the concentration of dislocations has occurred with deformation; however, they are concentrated in well-defined cell walls as was the case with the as-grown crystals. Also, the interior of the cells have low dislocation densities. Some of the cell walls are simple tilt boundaries (Figure 9) or hexagonal networks (Figure 10). The formation of cell walls is a further indication of dislocations climbing. When dislocations became blocked from moving in their slip plane by intersecting with other dislocations, sub-boundaries, etc., the strain energy can be lowered by the dislocations

climbing out of their slip planes where they can arrange in low energy configurations, e.g., cell walls. Similar observations have been observed in aluminum. The formation of cell walls is a process analogous to polygonization and is essentially a recovery process limited by the rate of climb of dislocations.

In all of the observations of the dislocation structures, no evidence has been found for the dissociation of dislocation into partials. The absence of stacking fault fringes and extended and contracted nodes indicates that partials are not widely separated and that the stacking fault energy is high. Estimates of the stacking fault energy from the radius of curvature of nodes indicates that energy is at least of the order of 200 ergs/cm^2 . In high stacking fault energy materials partials are not widely separated, and they may combine quite easily before climbing.

The lack of evidence of partials, the high stacking fault energy, and the formation of cell walls are all consistent with climbing the controlling mechanism as observed from the creep rate dependence on stress. It should also be noted that the observed operation of three slip planes would not be possible if the dislocations extended into partials since the two partials must lie in the slip plane and thus define a single plane.

G. Summary

Studies of the high temperature deformation behavior of ZrC single crystals revealed that slip occurred in the anticipated $\langle 110 \rangle$ direction. The observation of three low index active slip planes with approximately equal critical resolved shear stresses over a wide range of temperature is unusual. The potential operation of ten independent slip systems would suggest that polycrystalline ZrC bodies should have no problem in geometrically accommodating large amounts of plastic deformation. However, this anticipated behavior has not been observed in hot pressed ZrC samples²⁰; intergranular cracks were in evidence from first irreversible deformation.

The high temperature mechanical properties of high purity ZrC do not make it an exceptionally attractive high temperature structural material. Plastic deformation occurred at stresses of approximately 24 kg/mm^2 (48,000 psi) at temperatures as low as 1080°C . Creep rates at temperatures as low as 1400°C are excessive for most applications.

An understanding of the fundamental mechanism of deformation in function metal carbides suggests that substantial improvement in high temperature mechanical properties could be made by techniques such as the lowering of the stacking fault energy and by the formation of a dispersed second phase illustrated by the recent work of boron doped VC²¹.

IV. SINGLE CRYSTAL ZIRCONIUM DIBORIDE

A. Preparation of Single Crystals

Single crystals of ZrB_2 were prepared by the floating zone technique described in the previous section. The parameters of powder preparation, growth condition, etc., have been the subject of other programs in this laboratory.²² Feed powder of ZrB_2 and boron were obtained from Wah Chang Corp. and were approximately 99% pure. ZrB_2 powder, with the addition of boron to maintain stoichiometry due to loss of boron during the growth runs, was packed into graphite dies containing boron nitride liners. Boron nitride was used to prevent carbon contamination of the diboride rods and split dies and liners were used to facilitate removal of the pressed and sintered rod.

Powders were hot pressed at 2000°C and 500 psi under an argon - 5% hydrogen atmosphere. Densities of the order of 60-70% theoretical were obtained. Pressed and sintered rods of ZrB_2 with excess boron were zone melted by techniques described earlier for ZrC ; typically 1-2" single crystals approximately 1/4" in diameter were produced in this manner.

Single crystals were characterized by chemical, X-ray and microstructural techniques. Table III summarizes the analytic data for ZrB_2 . Because the composition range over which ZrB_2 exists is narrow and the distribution coefficients are very small, control over the growth process is difficult; however, the crystals were nearly stoichiometric.

Single crystals analyzed 99.85% pure, with carbon the principal impurity. Over 90% of the residual impurities in the powders were removed during the crystal synthesis.

Our experience has been that microstructural analysis is the most sensitive measure of the Zr:B ratio, since the single phase field is very narrow.

Microstructurally, we observed a fine oriented Widmanstätten-like precipitate in concentration of less than are present in all ZrB_2 single crystals. The nature of these precipitates will be discussed later.

X-ray topographical photographs of the ZrB_2 single crystals showed growth striations with misorientations of approximately 0.25° across their boundaries. It also appears from back reflection Laue X-ray photographs that some crystals contained boundaries with orientations as high as $2-3^\circ$.

B. Identification of Burgers Vector in As-Grown Crystals

The Burgers vector of dislocations in ZrB_2 were identified using electron microscopy techniques. The samples were thinned by electro-polishing sections of crystals in a solution of 4 parts Methanol, 1 part perchloric acid at -40°C . Figures 11a and 11b show the dislocations that are visible in dark field when the thin foil sample is tilted to bring $(01\bar{1}0)$ and $(10\bar{1}0)$ planes into diffracting conditions. Dislocations at A, B, C, D, and E are in contrast when the $(01\bar{1}0)$ plane is imaged and go out of contrast when the $(10\bar{1}0)$ plane is imaged. Dislocations at F, G, H, K, and J do the opposite. Roughly an equal number of dislocations remain in contrast in both diffracting conditions.

It can be seen from the pole figure in Figure 12 that the only low index directions found along the traces 90° from the $(10\bar{1}0)$ and $(01\bar{1}0)$ poles are the close packed "a" axis parallel to the $\langle 1120 \rangle$ type poles and the $[0001]$, c axis. The c axis is excluded as a possible Burgers vector for the dislocations shown in Figures 11a and 11b because this pole is 90° from both diffracting poles and thus dislocations having this Burgers vector would not have been in contrast in either of the two dark field photographs. Approximately two-thirds of the dislocations changed contrast and approximately

one-third remained unaffected in these two diffracting conditions. These observations indicate that the Burgers vector in ZrB_2 is the "a" axes which are parallel to the $\langle 1120 \rangle$ poles. This is the most commonly observed Burgers vector in hexagonal crystal lattices.

Dislocations K and L which join dislocation M at a 3 point node are both out of contrast when the $(01\bar{1}0)$ plane is diffracting and both are in contrast when the $(10\bar{1}0)$ plane is diffracting. Dislocation M is in contrast in both diffracting conditions. Dislocation K must have a Burgers vector that is parallel to either a $[2\bar{1}\bar{1}0]$ or $[\bar{2}110]$ pole and dislocation L the other, while dislocation M must have a Burgers vector that is parallel to either a $[11\bar{2}0]$ or a $[\bar{1}\bar{1}20]$ pole to satisfy these electron microscopy observations as well as the rule that the sum of the Burgers vectors of the dislocations meeting at a node is zero.

There was no evidence that the dislocations were split into partials.

C. Slip System in ZrB_2

Slip was induced in ZrB_2 single crystals at room temperature with microhardness indentations and at elevated temperatures in uniaxial compression. The slip planes were identified by plotting the poles of slip traces on stereographic projections of oriented crystals.

Microhardness indentations with a 600 gram loading were made on several crystallographic planes. At least 18 indentations were made on each plane with the long axis of the pyramid rotated 10° between successive indentations. One or two sets of slip traces were observed at each indentation. During the 90° rotation a total of three planes were observed to operate; however, no more than two were observed at any single indentation. The traces indexed

to be the three prismatic, $\{10\bar{1}0\}$ planes of the simple hexagonal lattice. A microhardness indentation and two sets of slip traces are shown in Figure 13.

One centimeter long ZrB_2 single crystals, with the stress axis oriented as indicated in the pole figure (Figure 12) were loaded in compression at 1490, 2000, and 2125°C at a crosshead rate of 0.002 cm per minute. The samples loaded at the two lower temperatures fractured prior to yielding. Slip lines were evident on the 2125°C sample after 4.5% deformation. The slip lines on two adjacent faces of the crystal are shown in Figures 14a and 14b. This slip plane indexed to be the basal, (0001) plane of the simple hexagonal lattice.

The observation that basal plane is the active slip plane at high temperatures is particularly significant for the anticipated high temperature deformation of polycrystalline ZrB_2 . There are only two possible independent slip systems²³ when the slip is confined to this plane and deformation parallel to the c axis cannot take place. If this remains the only active slip plane, grains in polycrystalline bodies cannot accommodate homogeneous plastic deformation and would be expected to fail with limited deformation. With slip occurring in the close packed "a" directions, an arbitrary strain cannot be accommodated even if the prismatic planes also operate since possible Burgers vectors have no component parallel to the c axis.

The two lower temperature samples cleaved along the basal plane of the crystal lattice. The cleavage plane was identified by back reflection diffraction patterns of the fracture plane.

D. Yield Stress in ZrB_2

Single crystal samples loaded at 1490 and 2000°C fractured at axial stresses of 15.8 and 8.9 kg/mm² respectively with no evidence of microscopic

plastic deformation. The sample loaded at 2125°C was plastically deformed at 4.5% without introducing any cracks.

The stress-crosshead displacement behavior observed for the 2125°C sample is shown in Figure 15. After initial yielding at an axial stress of 10.65 kg/mm² the flow stress dropped to 6.72 kg/mm². The crystal flowed approximately 1.2% at this stress level before beginning to work harden. Approximately half of the irreversible deformation took place during the yield drop.

In these experiments the pole of the basal slip plane was 69° from the stress axis. The most favorably oriented slip direction is 25° from the stress axis which gives a Schmidt factor (τ/σ) of 0.324 for the active slip system. The resolved shear stress at the yield point on the most favorably oriented slip system is 3.45 kg/mm² (4900 psi).

This combination of a yield drop with a high yield stress is unusual in single crystals of this purity (99.85% pure on a weight basis with carbon being the principal impurity). A yield stop is frequently observed at low and moderate temperatures in very high purity crystals containing few dislocations, but at much lower stress levels. These ZrB₂ crystals contained in excess of 10⁷ dislocations per cm² and the yield drop was observed 640°C above half the absolute melting point of ZrB₂. This suggests that dislocation motion was blocked or restricted by stronger barriers than inter-dislocation forces or impurity atoms. The behavior is more typical of that observed with a dispersion hardened alloy with a few mobile dislocations.²⁴

After etching for 45 seconds in a solution of 7 ml HF in 100 ml HNO₃ these ZrB₂ single crystals exhibited the microstructural features shown in Figure 16. It was found from analyses of the traces of the markings that

there were two kinds of plate-like precipitates; one with a habit plane parallel to the prismatic planes of the matrix and the other parallel to its basal plane. The three sets of prismatic precipitates can be seen in Figure 16, which is a photomicrograph of a basal plane. The finer set of markings results either from the basal plane precipitate or dislocations. Traces resulting from the basal set were only clearly seen on polished and etched faces with different orientations.

To identify the precipitate, the crystals were thinned and examined by transmission electron microscopy. Both precipitates gave sharp diffraction patterns from which their relative orientation to the matrix and their crystal structures were determined. The structures and lattice parameters of the two types of precipitates were identical and found to be face centered cubic with a lattice parameter of $4.71\text{\AA}$. Although the basal and prismatic plane precipitates are structurally identical, they differ in their orientation relation with respect to the matrix. These relations are:

(a) Basal Plane Precipitate

$$(111)_{\text{ZrX}} // (0001)_{\text{ZrB}_2}^*$$

$$[110]_{\text{ZrX}} // [100]_{\text{ZrB}_2}$$

(b) Prismatic Plane Precipitate

$$(100)_{\text{ZrX}} // (10\bar{1}0)_{\text{ZrB}_2}$$

$$[010]_{\text{ZrX}} // [0\bar{1}1]_{\text{ZrB}_2}$$

* For the hexagonal lattice, the four index system specified planes, and three specifies directions.

A more detailed discussion of the characterization of these precipitate particles has been published.²⁵ It was concluded from these studies that the precipitate is the face centered cubic zirconium monoboride, possibly stabilized by an impurity since the monoboride may not exist in the pure Zr-B binary system.²⁶

If dislocations were not blocked by these precipitate particles, the resolved yield stress at 2125°C would be expected to be negligible compared to the 3.45 and 2.18 kg/mm² observed at the upper and lower yield points. When dislocations are blocked by particles, the resolved shear stress, τ , at which dislocations pass by pinning particles is given by:²⁷

$$\tau = \frac{Gb}{d}$$

where G is the shear modulus, b is the Burgers vector and d is the interparticle spacing. The shear stress determined by this criteria corresponds to the plateau region in the stress-strain curve, after the yield drop and before work hardening, where large numbers of dislocations are penetrating the precipitate particle pins.

It is difficult to rigorously assign a value to the interparticle spacing from photomicrographs such as that shown in Figure 16, since the interparticle spacing between prismatic precipitate particles is not uniform. Also, it was not possible to adequately resolve the basal precipitate particles to reliably measure their interparticle spacing.

The basal particles are only approximately 100Å thick in the direction parallel to the c axis of the ZrB₂ lattice compared with the 1 to 2 micron dimensions of the prismatic particles in this direction. Therefore, it is probable that the basal precipitate particles would have substantially less effect on the motion of dislocations in the basal slip plane than the

prismatic particles. The interparticle spacing between the prismatic particles shown in Figure 16 is approximately 5 microns. The variation in this dimension is such that it is of little value to attempt a more accurate determination. Substitution of this interparticle spacing, a Burgers vector of $3.17\text{\AA}$ and a shear modulus of $1.9 \times 10^4 \text{ kg/mm}^2$ into this expression, results in a value of 1.20 kg/mm^2 for the critical resolved shear stress for penetration of dislocations between the pinning particles. We believe that this is in sufficient agreement with the observed value of 2.18 kg/mm^2 to demonstrate that the yield stress of these ZrB_2 single crystals at a temperature of 2125°C is in fact determined by the prismatic precipitate particles.

The level of the flow stress at the upper yield point and the percentage drop to the plateau are determined principally by the number of mobile dislocations present in the crystal prior to loading.²⁸ The 37% drop observed for the 2125°C sample suggests that there were essentially no unpinned dislocations in the as grown crystals. This absence of mobile dislocations combined with pinning action of the precipitate particles presumably lead to the failure by fracture of the two lower temperature samples prior to their yielding.

E. Summary

The slip systems observed in ZrB_2 are typical of those observed in materials having hexagonal crystal structures. With slip confined to the "a" direction along the basal plane, there are only 2 independent slip systems in ZrB_2 and polycrystalline specimens cannot undergo large amounts of plastic deformation prior to failure without a recovery process, such as recrystallization, occurring at a high rate.

The oriented Widmanstätten precipitate that was observed in these ZrB_2 single crystals strongly influenced yielding at elevated temperatures. Ductility at temperatures below 2125°C can be achieved only if they are eliminated. Previous work indicated that they were the fcc-ZrB phase, hence the overall boron/metal ratio of the single crystals must be increased to eliminate them at low temperatures.

The presence of these particles does suggest that ZrB_2 has the same composition as these crystals and should have interesting thermomechanical properties. The samples studied in this program had sufficient strength at temperatures in excess of 600°C above half their absolute melting point to be used as structural materials. This unusual behavior was demonstrated to result from the presence of the finely dispersed precipitate particles and would be expected to persist until they either coarsened or went into solution above 2400°C .²⁹ At temperatures in excess of 2400°C single crystals which would be free of the fine precipitate should be sufficiently ductile to be easily shaped. For polycrystalline bodies to be shaped extensively, they must have certain compositions and be deformed in a temperature range where they are both single phase and have a recovery process such as recrystallization, occurring at a sufficiently high rate to avoid fracturing. When the 2125°C sample discussed above was deformed further at 2125°C , it recrystallized to a point that the back reflection Laue pattern produced complete rings with no evidence of intergranular cracks. After high temperature deformation the monoboride can be precipitated by heat treating at temperatures between 2400 and 2125°C to produce a high temperature structural material with a high strength and good creep resistance within 200°C of forming temperatures.

V. POLYCRYSTALLINE ZIRCONIUM CARBIDE

A. Introduction

Determination of the slip systems and measurements of the critical resolved shear stress for high purity single crystals of ZrC indicated that slip occurred in the $\langle 110 \rangle$ direction on $\{100\}$, $\{110\}$ and/or $\{111\}$ planes. Furthermore, high temperature creep experiments on single crystals indicated that the rate controlling step was a diffusion controlled process involving the climbing of dislocations.

On the basis of the deformation experiments we would anticipate that polycrystalline ZrC should accommodate large amounts of plastic deformation since the slip systems included 10 independent cases. However, results reported in the literature for hot pressed ZrC samples²⁰ indicated that this was not the case. Intergranular cracks were formed with little plastic deformation and all the irreversible deformation could be accounted for by grain boundary sliding.

A series of experiments were undertaken with high purity, well characterized polycrystalline zirconium carbide samples to first resolve these differences in behavior between the single crystals and hot pressed polycrystalline materials and to determine if the creep mechanism of polycrystalline material was similar to that observed for single crystals.

B. Preparation of Dense Polycrystalline ZrC

Polycrystalline rods of ZrC were grown directly from the melt by an rf induction heated floating zone process.⁵ The molten zone was formed between polycrystalline hot pressed rods. Unmelted grains in the polycrystalline rod at the solid-liquid interface act as seeds and the initial material to solidify as the zone traverses the feed rod is fine grained polycrystalline. Typically,

the grain size increases with progressive solidification until the solidified rod is tri-, bi- or in some cases monocrystalline. The grains are columnar rather than equiaxed.

The fine grained regions were not suitable for deformation studies since the grains in the as grown boules were high asymmetrical. However, bi- and tri-crystalline samples could be cut from oriented boules. Characteristics of samples are summarized in Table IV.

C. Plastic Deformation of Polycrystalline ZrC

A bicrystal sample was cut from a float zone boule such that the normal to the planar grain boundary was 70° from the stress axis. Geometrically this leads to the following stress pattern at the grain boundary in the plane defined by the stress axis and the normal to the grain boundary:

$$\tau = 0.32 \sigma$$

$$\sigma_1 = 0.12 \sigma$$

$$\sigma_{11} = 0.89 \sigma$$

where

τ is the shear stress across the grain boundary

σ_1 is the stress normal to the grain boundary, and

σ_{11} is parallel to the grain boundary

Lines were scribed across the grain boundary with a microhardness indenter to quantitatively account for the fraction of irreversible strain resulting from grain boundary sliding.

This sample was deformed in compression between 1 and 3% at 1200, 1785, and 2000°C. In every case the observed yield stresses corresponded closely to those expected from the single crystal experiments. At the two higher temperatures some grain boundary sliding was observed; however, it accounted for less than

one percent of the total plastic deformation at each temperature. No displacement between the grains was observed at 1200°C.

A polycrystalline ZrC sample with a grain size of approximately 0.5 mm was deformed 20% in compression at 2000°C. The three and four grain junctions (Figures 17a-17b) showed no indication of intergranular cracking after extensive plastic deformation. Thus, the ability of the active slip systems in ZrC to accommodate homogeneous plastic deformation that was anticipated from the results of the single crystal deformation experiments was confirmed in large grained polycrystalline material.

A sample from a hot pressed ZrC rod purchased from the Carborundum Co. was deformed in compression at 1950°C. Unlike the polycrystalline samples taken from float zone boules, this sample fractured at an axial stress of 3.8 Kg/mm^2 prior to undergoing any macroscopic plastic deformation. The microscopic section of the load sample (Figure 18) shows that, like the previously reported results, the crack path was intergranular. At higher magnification (Figure 19) slip lines in the grains can be resolved, indicating that limited plastic flow had occurred prior to fracturing. The stress at which fracture occurred is within 10% of the yield stress expected from the single crystal experiments.

The results of these experiments may be summarized as follows:

1. That as expected from the work on single crystals, the number of active slip systems in ZrC are sufficient to allow homogeneous plastic deformation in polycrystalline ZrC without fractures.

2. Yield stress for bicrystals, large grain polycrystalline and hot pressed material were substantially the same as single crystals at the same temperature. The grain size, higher carbon content and higher impurity levels in hot pressed ZrC did not cause the microscopic yield stress to differ substantially from that observed with high purity single crystals.

3. Below 2000°C grain boundary sliding does not contribute extensively to plastic deformation in polycrystalline ZrC.

4. Grain boundaries appear to be a source of weakness and contribute to fracture in hot pressed ZrC. In high purity, high density material grain boundaries have little effect on the deformation process.

D. Creep and Recrystallization

Dynamic creep measurements were made at 2000°C at several strain rates with a polycrystalline sample with a grain size of approximately 0.5 mm cut from a float zone boule. The experimental procedures were the same as used for the single crystal studies. The results are shown in Figure 20 along with the data on single crystals reported previously. At 2000°C the polycrystalline sample showed the same stress dependence of the creep rate that was observed for single crystals. In both cases the proportionality between the steady state creep rate and the applied stress, was:

$$\dot{\epsilon} \propto \sigma^5.$$

Furthermore, the activation energy for the single crystal was 111 Kcal/mole. The observed stress dependence and activation energy are consistent with a recovery mechanism which occurs by the climb of dislocation out of these slip planes. For large grained polycrystalline zirconium carbide, the rate controlling process is apparently the same as for single crystals. It is possible however that the creep behavior of fine grained polycrystalline zirconium carbide might be controlled by diffusional mechanisms other than involving dislocations, i.e., vacancy diffusion.

As pointed out previously, fine grained material fabricated by the floating zone process was not suitable for deformation studies because the grains were highly asymmetrical. In an attempt to produce fine grained material by recrystallization, a columnar grained, polycrystalline sample was deformed at 2000°C, 25-30%, rotated 90° and again deformed 25-30%. This deformation cycle did not result in recrystallization and the original, highly deformed grains were still present.

Fine grained polycrystalline MgO has been produced¹³ for deformation studies by deforming samples at a temperature corresponding to $2/3 T_m$ and then raising the temperature to $3/4 T_m$ where the samples recrystallized. The equivalent temperatures for ZrC were beyond the 2200°C limit of our apparatus; however, it appears that the lower temperatures used cannot explain the failures to recrystallize ZrC. It had been shown from the previous crystal work that ZrC had a very high stacking fault energy and in a material having a high stacking fault energy, recovery occurs by polygonization at high temperatures and if recrystallization can be induced it will only occur at low temperatures where diffusion controlled climb of dislocations is suppressed. We observed only polygonization at 2000°C and we conclude that if a thermomechanical cycle could be found that leads to recrystallization in ZrC the process would take place at still lower temperatures. Although single crystals have been plastically deformed at temperatures as low as 1080°C without recrystallization, the amount of plastic flow induced was not large.

E. Summary

Substantial differences in the deformation behavior between relatively high purity, high density, stoichiometric zirconium carbide and commercially available hot pressed ZrC were encountered in these limited

observations. Apparently the grain boundaries are areas of weakness in the fine grained hot pressed material containing excess carbon and intergranular fracture occurred at substantially the same stress as the yield stress in single crystals and high purity, high density polycrystals. It is significant that the small grain size, higher impurity content and excess carbon content did not substantially effect the yield stress where plastic flow was observed in ZrC.

As predicted from single crystal behavior, the polycrystalline material prepared by zone leveling techniques exhibited homogeneous plastic deformation not unlike that observed in single crystals. We found that the presence of grain boundaries appears to contribute little to the overall deformation process. No grain boundary sliding was observed in the bicrystals and the creep rate of polycrystals and single crystals of comparable purity and carbon content was essentially the same. It would appear that the recovery mechanism postulated for single crystals probably applies to the large grained polycrystalline ZrC as well.

Although the observations on the behavior of polycrystalline zirconium carbide are very limited they do indicate that information on single crystal deformation can be utilized to guide and understand the behavior of the polycrystalline ZrC of comparable purity and composition. Further details of the behavior of polycrystalline materials of controlled microstructure and composition might uncover some interesting aspects relating to the improvement in strength by hot working of polycrystalline material and subsequent heat treatment.

REFERENCES

1. E. K. Storms, The Refractory Carbides, Academic Press, New York (1967).
2. W. S. Williams, "Influence of Temperature, Strain Rate, Surface Condition, and Composition on the Plasticity of Transition-Metal Carbide Crystals," J. Appl. Phys. 35 No. 4, 1329-1338 (1964).
3. G. E. Hollox and R. E. Smallman, "Plastic Behavior of Titanium Carbide," J. Appl. Phys. 37 No. 2, 818-823 (1966).
4. R. Chang, "Flow and Recovery Properties of Nearly Stoichiometric Polycrystalline Uranium Carbide and the Mechanism of Work Hardening of Crystalline Solids," J. Appl. Phys. 33 No. 3, 858-863 (1962).
5. G. Feick, "Thermodynamic and Kinetic Studies for a Refractory Materials Program," ASD-TDR-62-204 Part 1, April 1962, AF 33(616)7472, Arthur D. Little, Inc.
6. C. S. Barrett, Structure of Metals, McGraw-Hill, New York (1952).
7. L. G. Schulz, "Method of Using a Fine Focus X-Ray Tube for Examining the Surface of Single Crystals," J. of Metals 6 No. 9, 1082-1083 (1964).
8. G. Thomas, Transmission Electron Microscopy of Metals, John Wiley & Sons, Inc., New York and London, p. 234, 1962.
9. B. D. Cullity, Elements of X-ray Diffraction, Addison-Wesley Publishing Co., Reading, Mass., p. 250, 1956.
10. P. P. Gillis and J. J. Gilman, "Dynamical Dislocation Theory of Crystal Plasticity," J. Appl. Phys. 36, No. 11, 3370-3386 (1965).
11. W. G. Johnston, "Yield Points and Delay Times in Single Crystals," J. Appl. Phys. 33 No. 9, 2716-2730 (1962).
12. C. O. Hulse, S. M. Copley and J. A. Pask, "Effect of Crystal Orientation on Plastic Deformation of Magnesium Oxide," J. Amer. Ceram. Soc. 46 No. 7, 317-323 (1963).

13. R. B. Day and R. J. Stokes, "Mechanical Behavior of Magnesium Oxide at High Temperatures," J. Amer. Ceram. Soc. 47 No. 10, 493-503 (1964).
14. T. Weertman, "Steady-State Creep through Dislocation Climb," J. Appl. Phys. 28 No. 3, 362-364 (1957).
15. G. Schoeck, Mechanical Behavior of Materials at Elevated Temperatures, J. E. Dorn, Ed., McGraw-Hill, New York, p. 92, 1961.
16. G. E. Hollox, Tech. Report 68-10C, RIAS, May 1968.
17. S. Sarian and J. M. Criscione, "Diffusion of Carbon through Zirconium Monocarbide," J. Appl. Phys. 38 No. 4, 1794-1798 (1967).
18. D. L. Harrod and L. R. Fleischer, Intl. Symposium, "Anisotropy in Single-Crystal Refractory Compounds," Dayton, Ohio, 13-15 June 1967.
19. R. G. Lye, G. E. Hollox, and J. D. Venables, Bonding Structure and Mechanical Behavior of Vanadium Carbide Single Crystals, Fourth Technical Report to NASA (Contract NASw-1290), First Technical Report to ARO(D), RIAS, Baltimore, Maryland, June 1967.
20. M. H. Leipold and T. H. Nielsen, "Mechanical Properties of Hot-Pressed Zirconium Carbide Tested to 2600°C," J. Amer. Ceram. Soc. 47 No. 9, 419-424 (1964).
21. G. E. Hollox and J. D. Venables, "The Microstructure and Mechanical Properties of Pure and Boron-doped VC_{0.85}," presented at the Intl. Conf. on the Strength of Metals and Alloys," Tokyo, Japan, 4-8 Sept. 1967.
22. J. S. Haggerty, D. W. Lee, and J. F. Wenckus, "Preparation and Characterization of High Quality Single Crystal Refractory Metal Borides and Carbides," AFML-TR-68-228, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, September 1968.
23. G. W. Groves and A. Kelly, "Independent Slip Systems in Crystals," Phil. Mag. 8, 877 (1963).

24. J. B. Newkirk, "Precipitation from Solid Solution," Amer. Soc. for Metals, Cleveland, Ohio, 1959, p.99.
25. W. J. Leombruno, J. S. Haggerty, and J. L. O'Brien, "Structure and Orientation of the Second Phase in ZrB_2 Crystals," Mat. Res. Bull. 3, 361 (1968).
26. E. Rudy and S. T. Windisch, "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems," Part 1, Related Binary Systems, Vol. VIII Zr-B System, AFML-TR-65-2, AFML, Wright-Patterson AFB, Ohio, January 1966.
27. E. Orowan, "Classification and Nomenclature of Internal Stress," Institute of Metals, Symposium on Internal Stresses in Metals and Alloys," pp. 47-59 (1948).
28. W. G. Johnston, "Yield Points and Delay Times in Single Crystals," J. Appl. Phys. 33, 2716 (1962).
29. B. Post and F. W. Glaser, "Borides of Some Transition Metals," Chem. Phys. 20, 1050 (1962).

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PAPERS FOR PUBLICATION UNDER CONTRACT AT(30-1)-3411

D. W. Lee and J. S. Haggerty, "Plasticity and Creep of Single Crystals of Zirconium Carbide," to be published in J. of Am. Ceram. Soc. (1969).

J. S. Haggerty, J. L. O'Brien and D. W. Lee, "High Temperature Deformation of ZrB_2 Single Crystals," to be published in J. of Am. Ceram. Soc. (1969).

TALKS AND PRESENTATIONS

D. W. Lee and J. S. Haggerty, "Deformation in ZrC Single Crystals," Am. Ceram. Soc. Meeting, Washington, D.C., April 1966.

J. S. Haggerty and D. W. Lee, "Mechanism of Plastic Deformation in Single Crystals and Polycrystalline ZrC," Basic Sciences Meeting, Am. Ceram. Soc., State College, Pa., October 1966.

J. S. Haggerty and D. W. Lee, Symposium on Materials Research, New England Section, Am. Ceram. Soc., Boston, Mass., May 1968.

FIGURE 1 SCHEMATIC DIAGRAM OF CRYSTAL GROWTH PROCESS

a

b

FIGURE 2 a. Single crystal of ZrC etched on a (100) plane in 1 : 1 boiling H_2SO_4 to show both individual dislocations and dislocation sub-boundaries, 22X

b. X-ray image of same area as in a. showing the boundaries to be of a tilt character, 12X

FIGURE 3 A ROW OF DISLOCATIONS WHICH
FORM A LOW ANGLE BOUNDARY IN
AN UNDEFORMED ZrC SINGLE CRYSTAL.

4a

4b

FIGURE 4. Dislocation structure revealed in dark field transmission electron microscopy under two diffracting conditions. Dislocations A, B and C are in contrast when a (110) reflection is imaged, Figure 4a, and are out of contrast when a (112) reflection is imaged, Figure 4b, indicating a [110] Burgers vector.

FIGURE 5

The critical resolved shear stress as a function of temperature for the {111}, {110}, and {100} planes. The orientation of the stress axis for the three samples are given in the stereographic triangle.

FIGURE 6 DISLOCATION STRUCTURE IN A $\{111\}$ SECTION OF A ZrC SINGLE CRYSTAL DEFORMED 3 PERCENT AT 1400°C . NUMEROUS EDGE DISLOCATION LOOPS ARE EVIDENT WHOSE PROJECTIONS ARE PARALLEL TO THE $[\bar{1}\bar{1}2]$ DIRECTION. THE BANDS OF DISLOCATIONS ARE GLIDE BANDS WHICH BELONG TO ANOTHER ACTIVE (111) SLIP PLANE

FIGURE 7 CREEP RATE VS. CREEP STRESS FOR ZrC SINGLE CRYSTALS AT THREE TEMPERATURES. THE LINE DRAWN THROUGH THE POINTS HAS A SLOPE OF 5.

FIGURE 8 CELL STRUCTURE IN SINGLE CRYSTAL ZrC AFTER 20% CREEP DEFORMATION AT 2000°C.

FIGURE 9--A PURE TILT BOUNDARY IN ZrC SINGLE CRYSTAL DEFORMED AT 2000°C.

FIGURE 10--HEXAGONAL NETWORK OF DISLOCATIONS IN SINGLE
CRYSTAL OF ZrC DEFORMED AT 2000°C.

11a

11b

FIGURE 11 Dark Field transmission electron photomicrographs of ZrB_2 . Figure 11a is taken with the $(01\bar{1}0)$ plane diffracting and 11b with the $(10\bar{1}0)$ plane diffracting. Magnification 35,000 X.

FIGURE 13 Slip lines in ZrB_2 resulting from a room temperature microhardness indentation. Magnification 500X.

14a

14b

FIGURE 14

Slip lines on adjacent faces of a ZrB_2 single crystal deformed 4.5% at 2125°C . The stress axis and the poles of the a and b faces are indicated in Figure 2. Magnification 125 X.

FIGURE 15 Stress-crosshead displacement behavior observed for a ZrB_2 single crystal deformed at 2125°C .

FIGURE 16

Photomicrograph of a ZrB_2 single crystal showing the characteristic oriented platey precipitate. Etched 45 seconds in 5% HF: HNO_3 solution. Magnification 500 X.

17a

17b

FIGURE 17 a. Three grain junction in polycrystalline ZrC sample deformed 20% in compression at 2000°C.
 b. Polycrystalline ZrC deformed at 2000°C in compression showing slip in four grains.

FIGURE 18 Hot pressed Polycrystalline ZrC sample deformed at
1950°C in compression.

FIGURE 19 Slip lines in fine grained hot pressed poly-
crystalline ZrC deformed at 1950°C

FIGURE 20 Creep rate versus creep stress at 2000°C for zone leveled ZrC

TABLE I

CHARACTERIZATION OF SINGLE CRYSTAL OF ZrC (RESULTS IN WT %)

Chemical Analysis

Carbon	11.20%
Zirconium	<u>89.27%</u>
	100.47%
Oxygen =	0.005%
Nitrogen =	0.067%

Spectrographic Analysis

B	0.07%
Fe	0.07%
Ti	0.12%
Si	0.001%
Al, Sn	0.01%
Mg	0.001 - 0.01%
Ca, Mn, Cu,	
Mo, Hf, Pb,	0.001%

TABLE II

RATIO OF THE RESOLVED SHEAR STRESS TO NORMAL APPLIED STRESS
ON VARIOUS PLANES WITH A [110] SLIP DIRECTION

<u>Load Direction</u>	<u>Slip Plane</u>	<u>τ / σ</u>
[100]	100	0
	110*	0.5
	111	0.415
[111]	100*	0.469
	110	0
	111	0.28
0.5 orientations	100	0.310
for $\langle 110 \rangle$ {111}	110	0.405
slip systems	111*	0.5

* Observed slip plane

TABLE III

CHARACTERIZATION OF ZrB₂ SINGLE CRYSTALS

(Wgt. %)

Chemical Analysis

Zirconium	81.0%
Boron	<u>18.3%</u>
	99.3%
Oxygen	0.009%
Carbon	0.130%
Nitrogen	0.011%

Spectrographic Analysis

Cr	< 0.0001%
Cu	0.001-0.01%
Fe	< 0.0001%
Mg	0.0001-0.001%
Na	0.0001-0.001%
Ni	< 0.0001%
Si	0.0001-0.001%
Sn	< 0.001%
Ti	0.0001-0.001%

TABLE IV

CHARACTERIZATION OF SAMPLES

(Wgt. %)

	<u>Float Zone</u> <u>Polycrystal</u>	<u>Hot Pressed</u> <u>Polycrystal</u>
Carbon	11.09%	10.85%
Free Carbon	0	2.07%
Nitrogen	0.16%	1.65%
Oxygen	0.0038%	0.0075%
Total Metallic	0.0100%	0.1470%