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Mechanical behaviour of polycrystalline TiC

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The mechanical behaviour of hot-pressed TiC was studied. Compacts were fabricated from commercially available TiC powders, which were found to contain impurities including iron, cobalt, silicon and free carbon. Those impurities segregated to the grain boundaries and formed low melting-point phases which degraded the high-temperature strength. Differences in the temperature at which strength began to fall sharply were correlated with differences in the impurity chemistry of the TiC starting powders. It was found that a high-temperature vacuum heat treatment of the as-hot-pressed TiC significantly reduced the levels of impurities at the grain boundaries. This, in turn, caused a dramatic improvement in high-temperature strength. The TiC, so treated, possessed a grain size of approximately 25 μm and exhibited a D–B transition in bending at about 1425° C.

1. Introduction

TiC is a material of scientific interest and practical utility. It is extremely hard and has a very high melting point along with a wide range of carbon substoichiometry. The crystal structure of TiC is the rock-salt (B1) type; but, unlike many other such materials, it slips at high temperature ($\simeq$ 800° C) on $\{111\}$ planes in $\langle 110\rangle$ directions [1, 2]. Recent work [3] on single-crystal TiC shows that the slip undergoes a change from $\{110\}\langle 110\rangle$ to $\{111\}\langle 110\rangle$ around 800° C. The importance of the $\{111\}\langle 110\rangle$ slip is the availability of five independent slip systems, the minimum number required for a polycrystalline aggregate to deform in a manner such that the deformation in one grain is compatible with that in neighbouring grains. The operation of $\{111\}$ $\langle 110\rangle$ slip in TiC around 800° C would account for the transition from brittle to ductile behaviour.

Few investigations have been conducted on the plastic behaviour of polycrystalline TiC. Creep of fused, large-grained (1.5 mm × 0.3 mm × 0.3 mm) polycrystalline TiC above 1600° C has been studied [4]; and the bending behaviour of a coarse-grained hot-pressed material has been examined up to 2070° C [5]. In addition, the mechanical behaviour in compression was reported for polycrystalline TiC prepared by arc melting, r.f. melting, and sintering [6]. However, these results were largely nonreproducible, due in part to the difficulties in obtaining near theoretically dense polycrystalline TiC. More recently, work in this laboratory [7] on well-characterized, dense TiC showed that a ductile-to-brittle (D–B) transition at 800° C could be demonstrated for polycrystalline material in compression. No plasticity was reported in the limited bend testing performed as part of this study.

The present research was undertaken to study in greater detail the mechanical behaviour of high-density TiC prepared by conventional hot pressing of commercially available powders from a number of powder sources. Four-point bend testing was utilized over the temperature range 20 to 1700° C. Limited compression testing was also undertaken. During the course of this study, it was found that powder impurities played a major role in determining mechanical behaviour. The effects of impurities and of heat treatments to remove those impurities were studied comprehensively, and the results were correlated with the D–B transition in polycrystalline TiC.

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TABLE I Impurity chemistry of as-received TiC powders

Impurity	Starck (wt ppm)	RMI (wt ppm)	Ventron (wt ppm)
W	6500	1600	3600
Co	1200	15	10
Fe	545	3300	2550
Cr	425	470	430
Ni	40	10	10
Al	15	30	200
Cu	15	50	15
Si	45	95	80
Mo	75	20	100
Zr	10	35	50
Ca	30	20	30
O	2400	4300	4100
Free C	250	2150	4500

2. Experimental procedure

2.1. Materials

Nominally stoichiometric TiC powders were purchased from three commercial vendors*. The impurity contents of the powders are indicated in Table I. Metallic constituent levels were determined by emission spectrographic analysis. The oxygen content was measured by neutron activation. The powders also contained free carbon as shown in Table I. These analyses were carried out by placing each powder in hot aqua regia, which dissolves TiC but not free carbon. The carbon residue was collected by filtration, and the content was determined by combustion.

Powder particle-size distributions were determined by the X-ray sedimentation technique. All three lots exhibited a wide distribution. The Starck material had a maximum particle size of about 30 μm, median size of about 7 μm and contained approximately 7% submicron fines. The RMI and Ventron powders were noticeably more coarse. The distributions ranged from about 40 to approximately 1 μm, with median sizes of about 10 and approximately 12 μm, respectively. In addition, submicron films were essentially absent in both powders and large particles of up to 100 μm were found in the RMI powder.

2.2. Sample preparation

As-received and as-sieved (–400 mesh) powders were conventionally hot pressed in 2 inch internal diameter graphite dies lined with graphite foil. Pressing temperatures ranged from 1700 to 1750° C, times from 30 to 60 min and pressures from 34 MN m^{-2} (5 ksi) to 59 MN m^{-2} (8.6 ksi). Consolidation was performed in vacuum (10^{-1} torr) or argon [35 kN m^{-2} (5 psi)].

Four-point-bending test specimens were diamond-saw cut from the TiC billets to the dimensions 4.5 mm x 2 mm x 26 mm. The tensile surface of each bar was polished to 6 μm and the edges were slightly rounded to eliminate chipping. The other surfaces were finished to 15 μm. Some of the bars were subjected to a vacuum heat treatment of 2150° C for 10 h. This was accomplished by placing the bars in tents of graphite foil located within a graphite crucible. The crucible was inductively heated to the temperature and maintained under a 10^{-1} torr vacuum. These bars were repolished prior to testing.

A few compression tests were conducted with heat-treated material. Specimen dimensions were 2.3 mm x 2.3 mm x 5 mm.

2.3. Test procedure

Four-point-bending tests were performed using an Instron universal test machine at a crosshead speed of 5.08×10^{-2} cm min^{-1} (0.002 in min^{-1}). Specimens were mounted in a SiC bending jig having an outer span of 19.05 mm (3/4 in) and an inner span of 9.53 mm (3/8 in). Compression tests were conducted in the Instron at the same crosshead speed. The specimens were placed between two SiC platens during those tests.

The Instron was equipped with a vacuum furnace utilizing a tungsten mesh heating element for high-temperature testing in vacuum ($\simeq 10^{-4}$ torr) or inert atmosphere. Specimens were held at temperature for about 15 min prior to testing.

3. Results and discussion

Fig. 1 is an optical micrograph of a hot-pressed compact consolidated from unsieved Starck powder. This billet (designation STC-19) was pressed at 1750° C for 30 min in vacuum with a ram pressure of 55 MN m^{-2} (8 ksi). The average grain size was 12 μm; and the density, as determined by water immersion, was 4.81 g cc^{-1} (98% of theoretical based on stoichiometric TiC with lattice parameter $a = 0.43285$ nm). The unseived RMI and Ventron powders did not consolidate so well as the unsieved Starck powder, with final

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*(a) Hermann C. Starck, Inc., 280 Park Avenue, New York, NY 10017, USA, (b) Refractory Metals Inc. (RMI), 8450 Lockheed, Houston, TX 77034, USA and (c) Alpha Products Ventron Division, 152 Andover St., Danvers, MA 01923, USA.

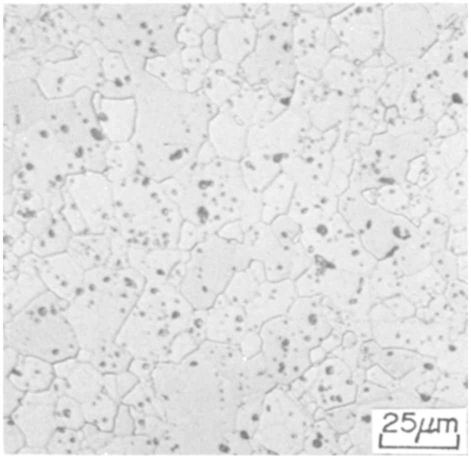


Figure 1 Optical micrograph of TiC hot pressed from unsieved Starck powder (etched in boiling H_2SO_4).

densities in the range 93 to 96% of theoretical. This is presumed to be a result of the coarser powder-size distribution and the lack of sub-micron fines in these starting materials. It was found that the density increased with increasing ram pressure, temperature and time over the ranges reported. There were no apparent differences in microstructures or properties when specimens pressed in vacuum were compared with those pressed in argon.

The densities of the powder compacts could be improved by sieving the as-received powders to −400 mesh with copper sieves. However, this introduced about 300 ppm Cu from the sieves which proved to be extremely detrimental to the high-temperature mechanical properties, as will be discussed later.

Fig. 2 shows the bending strength as a function of temperature for specimens cut from Starck billet STC-19. The room-temperature strength was maintained up to 1000° C, but a drastic drop in strength occurred at higher temperatures. For the RMI and Ventron billets pressed from unsieved powders, the low-temperature bending strength

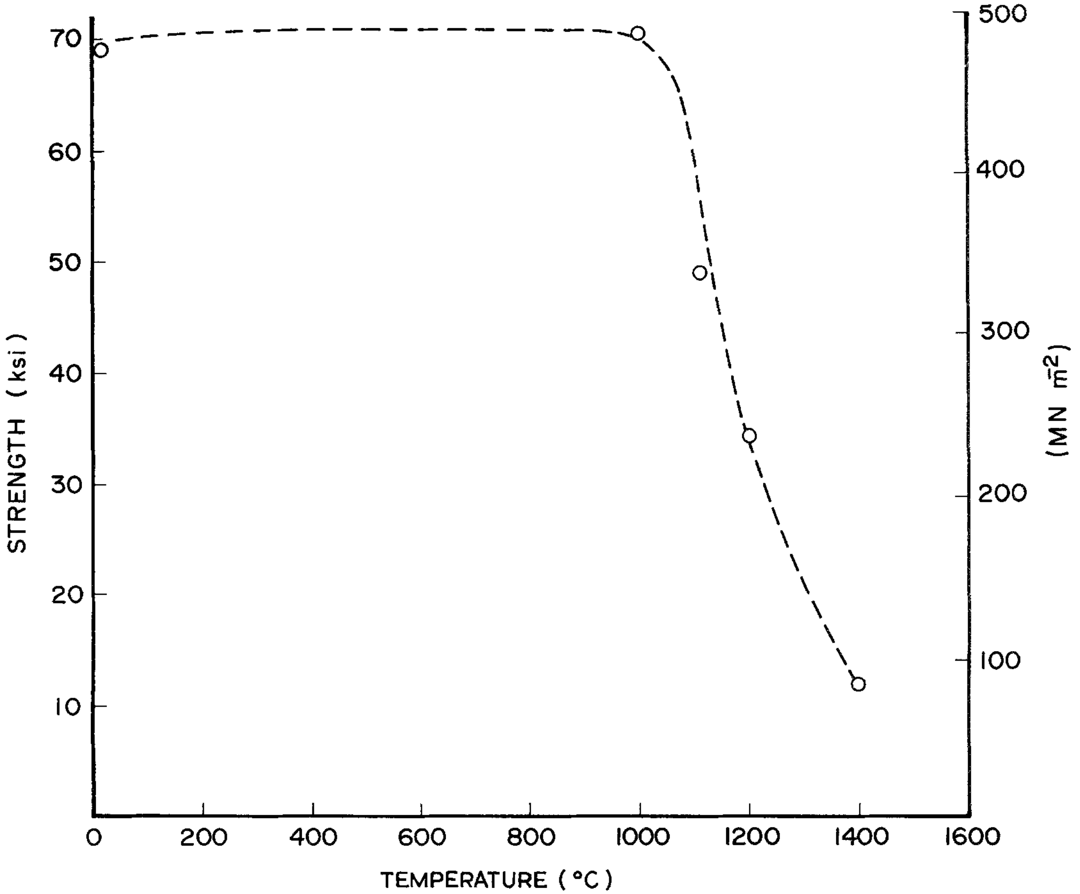


Figure 2 Fracture strength as a function of temperature for TiC hot pressed from unsieved Starck powder and tested in four-point-bending.

was reduced to the range 275 to 345 MN m^{-2} (40 to 50 ksi) as a result of the extensive porosity in these billets (including pore coalescence). However, similar to the Starck billet, room-temperature strength was initially maintained as the test temperature was raised, but dropped sharply at high temperatures. Unlike the Starck material, the strength degradation began above 800° C.

As reported, higher densities could be achieved by sieving the powders before hot pressing. This led to some increases in low-temperature strength, especially for the RMI and Ventron materials [380 to 450 MN m^{-2} (55 to 65 ksi)]. However, the high-temperature strength degradation for specimens fabricated from sieved powders from all three vendors began above 600° C.

Fig. 3a is an SEM micrograph of the fracture surface of an STC-19 specimen tested at room temperature. The fracture mode is predominantly transgranular cleavage. Fig. 3b is the corresponding fractograph for a specimen tested at 1100° C. Here the fracture is much more intergranular, and the extent of intergranular fracture continues to increase as the test temperature is raised. At 1400° C the fracture is almost exclusively intergranular. In all cases the load against deflection behaviour is linear and the specimens fail in a brittle manner.

The fracture behaviour with temperature just described holds equally well for the other materials fabricated and tested, the only difference being the temperature at which the failure mode begins to change and the strength begins concurrently to degrade.

These fracture characteristics indicate that the grain boundaries are weak at high temperatures (above 600° C for the sieved powders, above 800° C for the unsieved RMI and Ventron powders, and above 1000° C for the unsieved Starck powder). The reason for this becomes apparent when the fracture surfaces are examined more closely. Fig. 3c is a higher-magnification fractograph of the 1100° C STC-19 specimen. A grain-boundary segregant can clearly be seen on

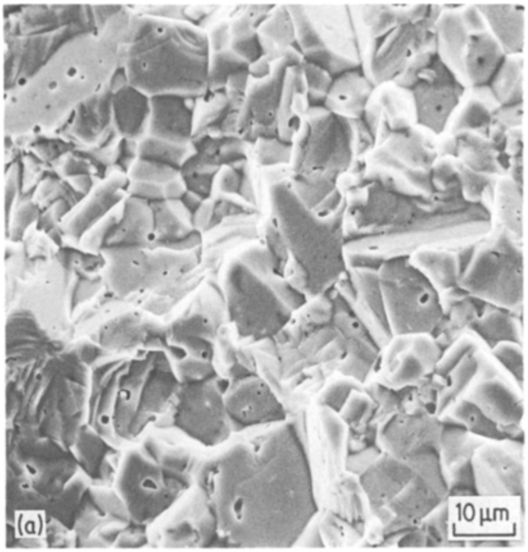
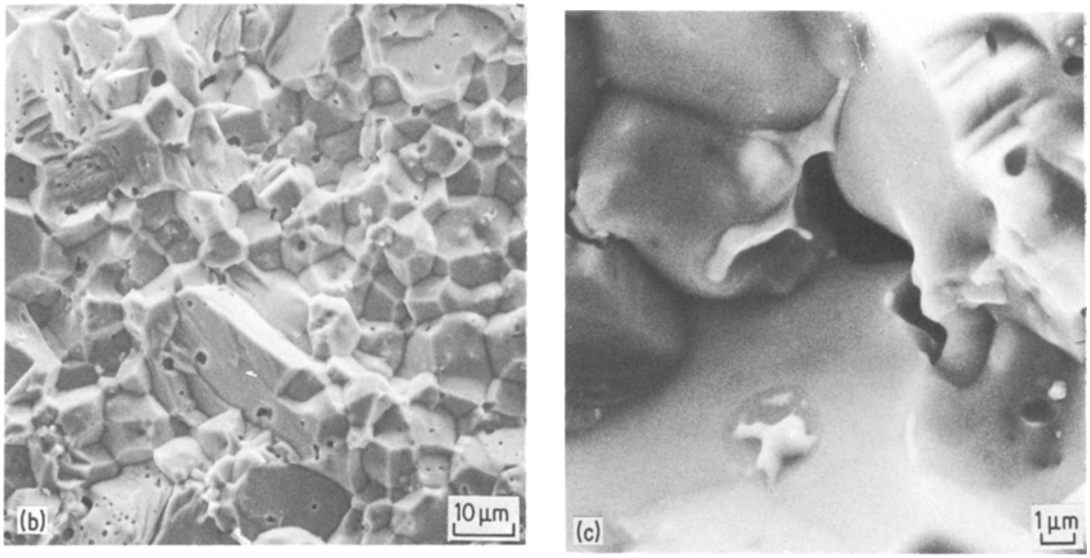


Figure 3 SEM fractographs of TiC specimens hot pressed from unsieved Starck powder. Bend testing performed at (a) room temperature, (b) 1100° C, and (c) 1100° C (higher magnification).



the boundary facets. Veins of this segregant also line the multigrain junctions. Some of this material has melted or softened at 1100° C and "balled up" upon exposure of this free surface at fracture. The presence of a grain-boundary segregant is confirmed in the TEM (transmission electron microscope). Fig. 4 shows a film of the segregant separating two TiC grains.

Spot-mode energy-dispersive X-ray spectrometry (EDX) data obtained in both the STEM (scanning transmission electron microscope) and SEM (scanning electron microscope) indicate that the segregant contains cobalt, iron and silicon in the case of Starck powder compacts. A typical spectrum is shown in Fig. 5. The titanium peaks are the result of the beam-activation volume encompassing some of the TiC matrix. For RMI and Ventron powder compacts, the EDX analyses indicate the presence of iron and silicon in the segregant. When the powders are sieved, copper joins the other elements at the grain boundaries.

In situ Auger fracture-surface analyses confirm these results. Fig. 6a is a spot-mode grain-boundary-segregant Auger spectrum from a compact fabricated from sieved RMI powder. The elemental distribution is non uniform, since changing the Auger spot location – sometimes even within the segregant on the same boundary – will cause a change in the relative peak intensities. The presence in the spectrum of titanium and carbon peaks, whose shapes and relative intensities are characteristic of TiC, was typical and resulted from beam spreading beyond the edges of the segregant patches examined and/or holes in the patches. These patches were about 1 to 4 μm in diameter. At the beam currents utilized to obtain good Auger signal-to-noise ratios, the effective beam diameter may have been as large as 2 to 5 μm. Furthermore, exact centering of the beam on the patch was difficult. In addition, although these layers appear to be largely continuous, the possibility of holes or discontinuities extending to the underlying grain cannot be ruled out. The conclusion that the TiC Auger peaks originated from the surface of the exposed matrix is further supported by TEM microdiffraction analyses of the grain-boundary films. No evidence was found of any TiC in the segregant.

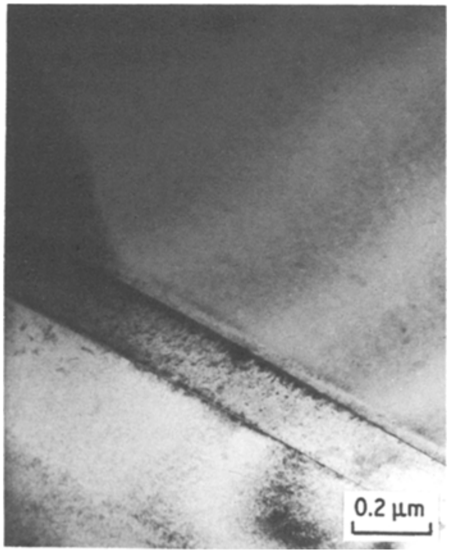


Figure 4 TEM micrograph of the grain-boundary film in TiC hot pressed from sieved RMI powder.

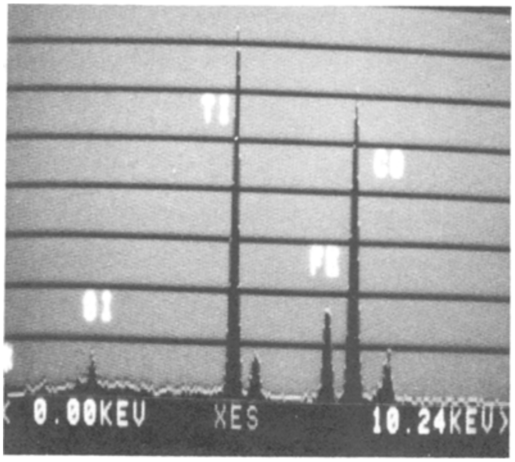


Figure 5 Typical EDX spectrum of the grain-boundary phase in TiC hot pressed from unsieved Starck powder.

The metallic impurities at the boundaries are not soluble in the TiC matrix. This was demonstrated by sputtering the fracture surface in the Auger, as seen in Fig. 6b. Peak intensities for the major impurities change little until the interface with the underlying TiC grain is reached. At this point the peaks drop precipitously to undetectable levels. Unsputtered cleavage facets show no iron, cobalt, copper or silicon.

There is no evidence of oxygen segregation in the as-hot-pressed materials. Auger oxygen peaks of relatively low intensity were detected on the grain boundaries and cleavage facets of the *in situ* fractured specimens. They were of equal intensity for all topographical areas and, since they were rapidly reduced by sputtering, were likely the result of adsorbed oxygen. These results indicate

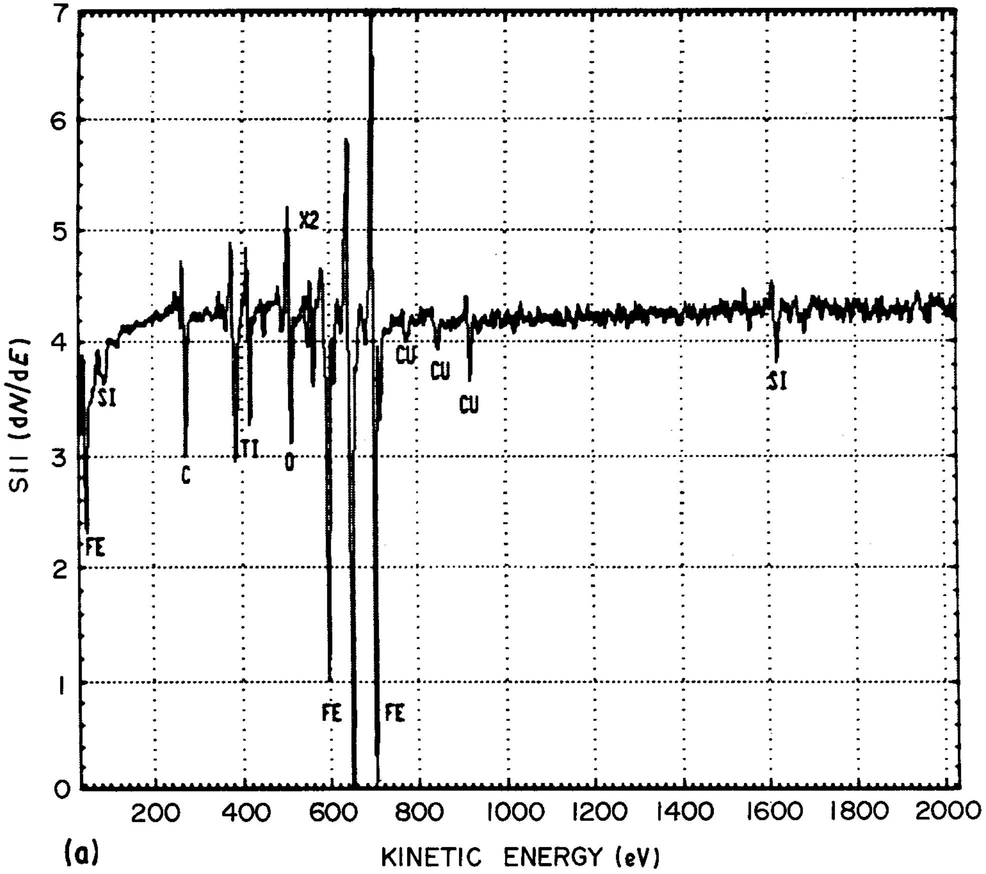


Figure 6 Auger data for TiC pressed from sieved RMI powder. (a) Spot-mode spectrum from the grain-boundary segregant and (b) spot-mode sputter profile from the same location.

that the oxygen is uniformly dissolved in the material.

The high-temperature mechanical behaviour of the hot-pressed materials can be explained by the softening and/or melting of regions of the grain-boundary segregant at elevated temperatures. If this be the case, the chemistries at the boundaries must be such that phases are formed which soften near the temperature at which the strengths decrease. In the case of the sieved-powder compacts, this temperature was about 600° C. The metallic impurities were iron, copper and silicon for the RMI and Ventron billets, and cobalt, iron, copper and silicon for the Starck billet. Examination of the Fe–Co phase diagram reveals no low melting-point phases. However, the contrary is true for the Co–Si and Fe–Si binaries. For Co–Si, liquid phases at temperatures ranging from 1195 to 1310° C extend across the diagram above 14 at% Si. For Fe–Si above 32 at% Si, liquid phases exist at 1200° C. Lower eutectic temperatures would be expected when copper is also present with the above elements. The Co–Cu and Fe–Cu phase diagrams show broad solid solubility with the appearance of a liquid phase at about 1100° C for most compositions. Furthermore, in the Cu–Si system, liquid phases exist at 800 to 850° C for most compositions above about 12 at% Si. Based upon this information, it is very reasonable to assume that the Fe–Cu–Si and Co–Fe–Cu–Si chemistries present at the grain boundaries would indeed result in considerable softening of regions of the segregant above 600° C, since there may exist a complex eutectic at a temperature lower than that of any of the constituent binary eutectics. The presence of carbon in the segregant, as will be discussed later, further supports this argument. It should be mentioned that chemical analyses of hot-pressed specimens showed iron, cobalt, copper and silicon levels which closely matched those in the starting powders. However, since the elemental distribution is non-homogeneous in the segregants, there is no single grain-boundary composition that can be identified.

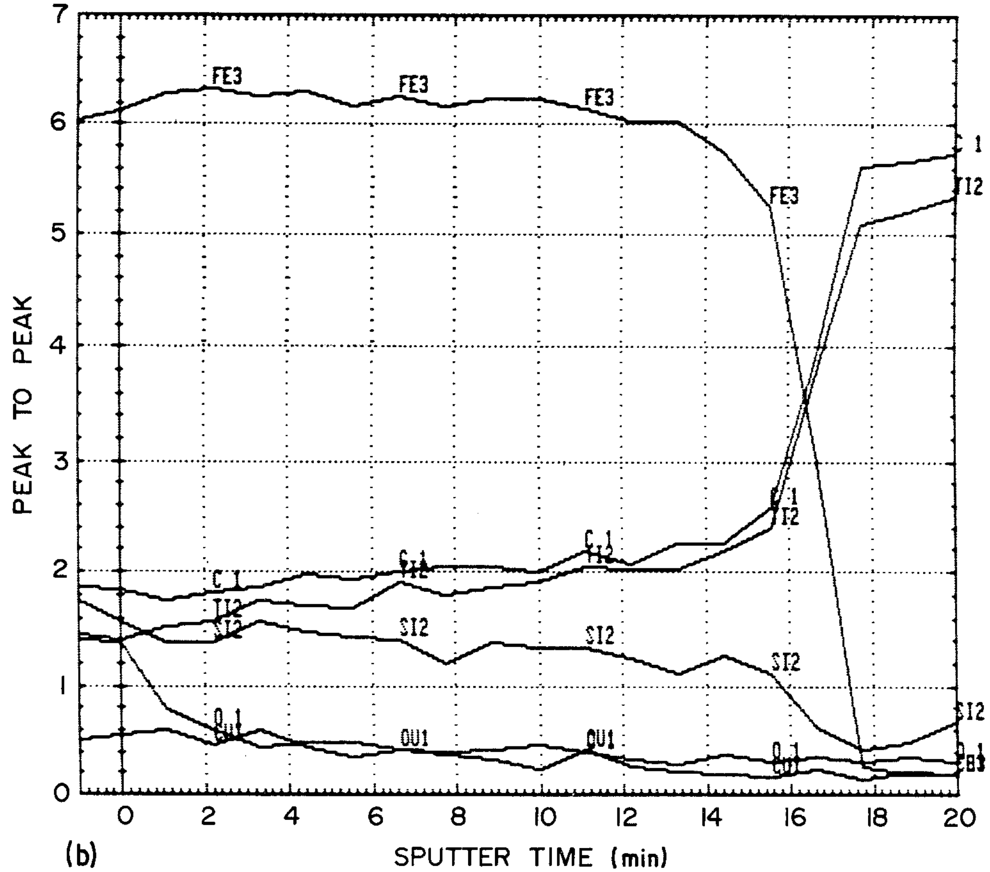


Figure 6 Continued

As a result, the volume fraction of the segregant that is soft or molten is very much dependent upon temperature. This accounts for the progressive decrease in the bending strength and increase in intergranular fracture as the temperature is raised above 600° C.

The temperatures above which the strengths degraded for the unsieved-powder compacts were 800° C for the RMI and Ventron specimens and 1000° C for the Starck samples. It is clear that these temperatures are higher than those for the sieved materials because copper is not present in the grain boundaries. However, the 200° C difference in degradation points must be explained. If only cobalt, iron and silicon were present in the boundaries of the Starck TiC and only iron and silicon in the RMI and Ventron TiC, the Starck material would degrade at a lower temperature than the other two. However, the opposite occurs, and this can be explained by the presence of carbon in the grain-boundary segregants. The Co–C system shows a eutectic at 1309° C above 5 at% C, but the Fe–C system exhibits a eutectic at 1147° C above about 8 at% C. Thus, a Fe–C–Si system would be expected to show low melting-point phases at lower temperatures than a Co-dominated Co–Fe–C–Si system. This would be especially true if there were insufficient carbon to reach the eutectic composition in the latter system. The most likely source of carbon would be free carbon present in the starting powders. The as-received powders do contain free carbon, but the Starck powder contains very much less free carbon than the RMI and Ventron powders. Hence the likihood that sufficient carbon is present to cause a significant drop in the temperature at which some softening begins is much greater for the RMI and Ventron materials. That circumstance and the low iron content of the Starck TiC are the factors which account for the approximate 200° C difference in degradation temperatures.

Recognizing the severity of the grain-boundary problem, experiments were undertaken for its

TABLE II Impurity chemistry of TiC specimens hot pressed from unsieved Starck powder

Impurity	As-hot-pressed (wt ppm)	As-hot pressed and vacuum heat treated (2150° C, 10 h, 10^{-1} torr) (wt ppm)
W	6800	7100
Co	1300	200
Fe	515	280
Cr	450	420
Si	75	40
O	2800	1100

alleviation. It was noted that for bending tests conducted at 1200° C and higher, a substantial fraction of the molten grain-boundary material exposed to vacuum upon fracture vaporized from the fracture surface. More of the segregant could be retained if the tests were conducted in argon. These results raised the hope that the grain-boundary segregant could be removed from the as-hot-pressed TiC via grain-boundary diffusion to the surface and vaporization during a high-temperature vacuum heat treatment of the test bars. Only unsieved Starck powder compact specimens were so treated because of their better initial properties and their lower overall impurity content.

Table II shows the quantities of the major impurities present both before and after a vacuum (10^{-1} torr) heat treatment of 10h at 2150° C. Significant reductions in the cobalt, iron, silicon and oxygen levels have been effected. The tungsten and chromium levels have not really changed, which is not surprising, since both form stable carbides. Discrete, small (2 to 3 μm diameter) WC grains appear in the microstructure, and regions of segregated WC within the TiC grains and at triple points were detected in the STEM. The chromium was never microscopically located and was assumed to be more homogeneously dissolved in the TiC. The free carbon content could not be determined. It is presumed that the cobalt, iron and silicon levels were reduced during the heat treatment by grain-boundary diffusion and vaporisation. The change in oxygen content will be discussed later.

The microstructure and mechanical properties of the heat-treated TiC were consistent with the significant reductions in the grain-boundary constituents of the segregant. The grain-boundary films, so apparent before heat treatment, could not be observed in the SEM or TEM after heat treatment. Fig. 7 shows the results of bending tests conducted on heat-treated specimens. Although low-temperature strength is degraded, mechanical integrity is maintained to temperatures much higher than those at which the as-hot-pressed material weakened. Further, the speci-

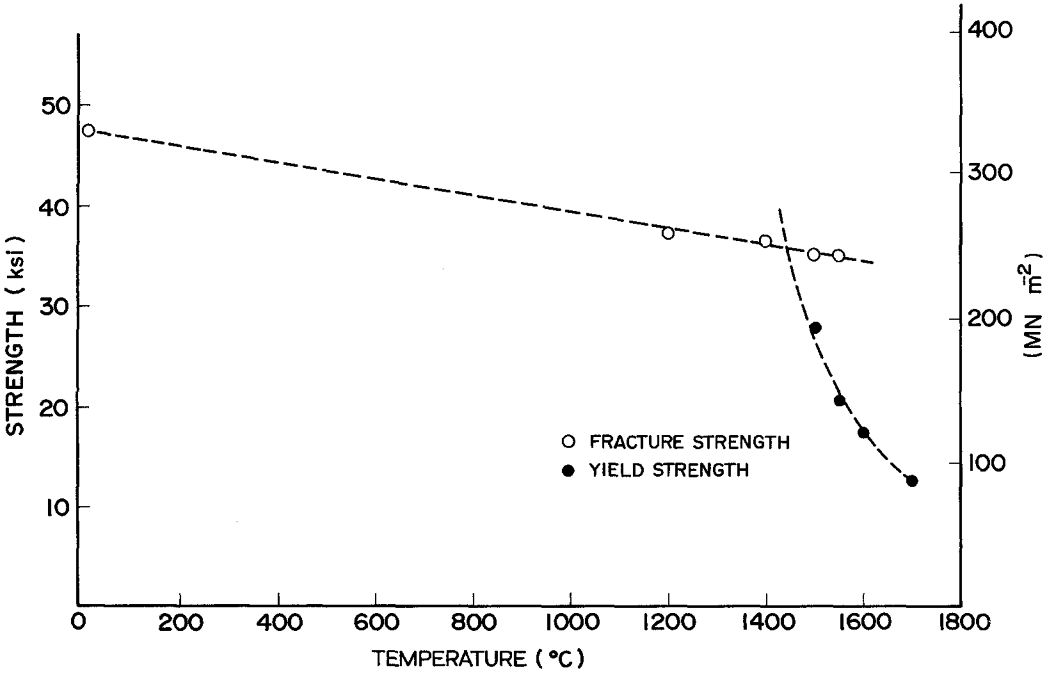


Figure 7 Fracture and yield strengths as a function of temperature for vacuum heat-treated TiC hot pressed from unsieved Starck powder and tested in four-point bending.

mens exhibit plastic yielding above 1400° C. The yield–stress data of Fig. 7 represent the points at which the load–deflection curves deviated from linearity. Above 1400° C the yield stress is lower than the cleavage and/or grain boundary strength and, therefore, the specimens exhibit plastic deformation. Obviously, the near removal of the grain-boundary segregant significantly increased the high-temperature strength of the grain boundaries.

The bars which yielded were macroscopically bent and TEM foils made from these specimens exhibited evidence of prior dislocation activity.

Figs. 8a and b show the fracture surfaces of heat-treated specimens tested at room temperature and 1550° C, respectively. It is apparent that grain growth has occurred during the heat treatment The average grain size near the centre of the specimens, where these photographs were taken, was about 30 μm. However, the grain size decreases to about 20 μm, moving from the mid-line of the bending specimen to the surface. Apparently, the grain-boundary segregant, which is a liquid during the heat treatment, aids transport across the boundary and thus promotes grain growth. Since its concentration is highest along the mid-line of the bar during heat treatment, the final grain size is greatest there.

Two other salient features of Fig. 8a and b merit discussion. These are the extent of intergranular fracture and the appearance of significant grain-boundary porosity. Unlike the non-heat-treated material (see Fig. 3), the heat-treated specimens show about 50% intergranular fracture at room temperature. This indicates that although the high-temperature strength of the boundaries has been dramatically increased, their room-temperature strength has been somewhat reduced. From Fig. 8b it is apparent that the failure mode is almost totally intergranular at 1550° C. The heat treatment, therefore, raised the grain-boundary strength above the yield strength at 1500° C, but did not raise it above the cleavage strength.

The appearance of grain-boundary porosity in the heat-treated specimens is not fully understood. Quantitative metallography of as-hot-pressed and as-heat-treated specimens revealed that the heat-treated material contains approximately an additional 1% total porosity. Concentration of large pores at the grain boundaries of the heat-treated samples was evident in the cross-sections examined. Although the sweeping of pre-existing pores to the boundaries during heat treatment can contribute to enhanced boundary porosity, it cannot account for the additional total porosity. Two other possible phenomena would, however, increase the bulk porosity. First, the grain-boundary segregant which diffuses out of the material during heat treatment leaves behind the spaces it formerly occupied. These voids could spherodize to the pore geometries observed. However, the volume fraction of segregant present could account for

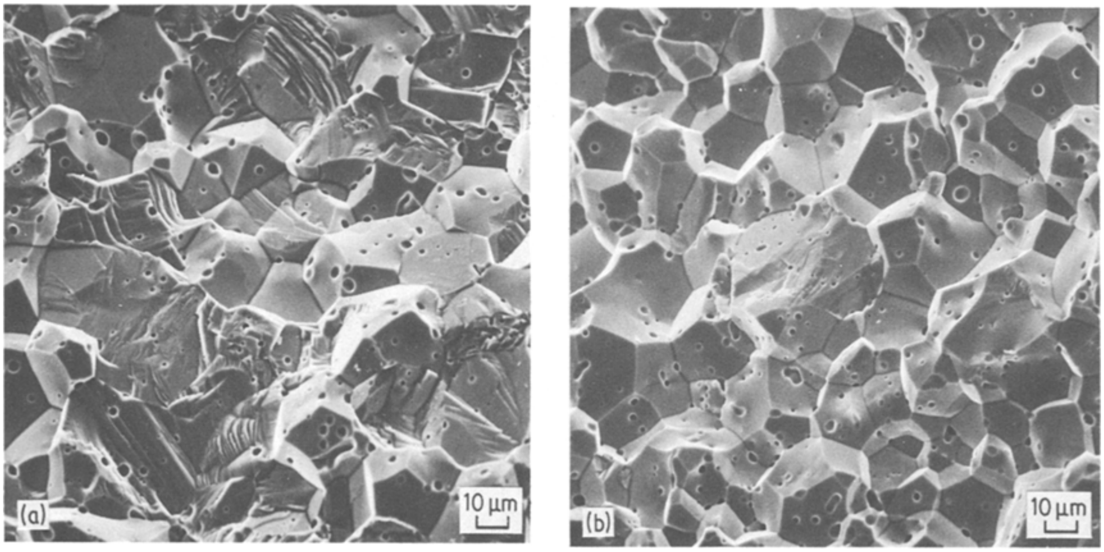


Figure 8 SEM fractographs of vacuum heat-treated TiC specimens hot pressed from unsieved Starck powder. Bend testing performed at (a) room temperature and (b) 1550° C.

only a small fraction of the approximate additional 1% porosity. Given these circumstances, it is most reasonable to speculate that the grain-boundary porosity was caused by the evolution of a gas. The most likely candidate is CO/CO_2, formed by the reaction of dissolved oxygen with carbon in the grain-boundary segregant or with the TiC itself. As indicated in Table II, oxygen content is significantly reduced during heat treatment. Hence, some of the gas evolved leaves the system via the grain boundaries. Gas which is entrapped would cause the spherical grain-boundary voids. Should CO/CO_2 be the culprit, its evolution would reduce the carbon content of the segregant and thus facilitate the increase in high-temperature boundary strength as previously discussed.

Regardless of its cause, the grain-boundary porosity is real. Furthermore, there is evidence of pore coalescence along the boundaries (see Fig. 8b). These larger pores and/or larger grains in the heat-treated microstructure may act as strength-limiting flaws, which would account for the reduction in low-temperature strength of the heat-treated material.

The grain-boundary strength is not so critical when specimens are tested in compression. For this reason, a few compression tests were performed on heat-treated material. The results agreed well with the data shown in Fig. 7. The yield strengths at 1200, 1400 and 1550° C were 370, 262 and 172 MPa (54, 38 and 25 ksi), respectively. These data are consistent with those obtained by Das *et al.* [7], for TiC of this grain size. It is thus apparent that when the yield strength exceeds or equals the fracture strength in bending (1200 and 1400° C), no plastic deformation is observed in bending. However, when the bending strength exceeds the yield strength, plastic deformation is observed at about the same stress level in bending as in compression. Thus, the heat treatment to remove the grain-boundary segregant increased the high-temperature strength of the boundaries sufficiently that yielding was observed above 1400° C in four-point bending.

4. Conclusions

1. Commercially available TiC powders contain impurities which segregate to the grain boundaries when the powders are hot pressed. These impurities, which include iron, cobalt, silicon and free carbon, form low-melting-point phases which degrade the high-temperature strength.

2. Sieving the as-received powders in copper sieves causes copper transfer to the powder. This element also segregates to the grain boundaries and reduces the temperature at which the strength degradation begins.

3. High-temperature vacuum heat treatment of as-hot-pressed material significantly reduces the level of impurities at the grain boundaries. This, in turn, causes a dramatic improvement in high-temperature strength.

4. When the grain boundary and cleavage strengths exceed the yield strength, plastic deformation is observed at about the same stress level in bending as in compression.

5. Heat-treated polycrystalline Starck TiC of average grain size about 25 μm possesses a D–B transition in bending at about 1425° C.

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