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Improved Thermal-Shock-Resistant Carbides

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ABSTRACT

The thermal-stress resistance of refractory-metal carbides is substantially improved by addition of chopped metal fibers. The thermal-stress resistance of a composite consisting of 50 vol% TaC-50 vol% chopped Ta wire is approximately 40% greater than that of pure TaC. At temperatures above 2500°C, a composite material of this type will still crack, but the presence of the fibers inhibits the propagation of the cracks completely through the structure so that fracturing is prevented or substantially reduced.

I. INTRODUCTION

It is known in the art that structural materials exposed to temperatures above 2500°C for any substantial period, i.e., for more than 60 min, rapidly degrade. Refractory-metal carbides are obvious candidates for such structural materials, but they are brittle and crack readily when cycled through such temperature regimes. This cracking, in turn, rapidly leads to complete fracturing that may cause catastrophic failure of the structure. Fracturing as used herein means the separation of a massive structural body into two or more smaller bodies and loss of its structural integrity. This inherent property of the refractory carbides has limited their use as a structural material for very-high-temperature service.

The addition of carbon to carbides in the form of hot-pressed or extruded carbide-graphite composites greatly improves their thermal-fracture resistance. The Materials Technology Group of the Los Alamos Scientific Laboratory (LASL) has done an enormous amount of work on the carbide-graphite composite systems.[1-5] Given this background and the limitations imposed by the compatibility of the composites in a H_2 atmosphere, we decided to investigate the addition of chopped refractory-metal fibers to the hot-pressed carbides.

II. FABRICATION

Chopped tantalum-wire fibers, 0.020 in. in diam by ~0.25 in. long, purchased from the Rembar Company, Inc., were blended in the desired proportions with TaC powder of nominal 1.5-μm average particle size. Such carbides are available from many sources. The dry-blended mixtures were spoon loaded into a graphite die and hot pressed at 1800°C and 3000 psi to ~85% of theoretical density. Typically, this took about 1/2 h.

III. STEADY-STATE THERMAL-STRESS TEST

Steady-state thermal-stress specimens were machined from 10, 50, 60, and 70 vol% tantalum-wire-containing billets in both the parallel and the perpendicular to the pressing direction. These specimens were made by cutting wafers with a diamond band saw, electrical-discharge machining the center hole, and diamond grinding the outside diameter and parallel flat surfaces. We do not know why as yet, but 30 vol% tantalum wire-TaC billets could not be cut with the diamond band saw.

The machined specimens were tested for thermal-stress ranking. The test apparatus and procedures are described in Ref. 6. Figure 1 shows the results of these tests compared with 100% TaC hot-pressed to ~98% of theoretical density. There is clearly a significant increase in thermal-stress resistance associated with certain contents of tantalum fiber.

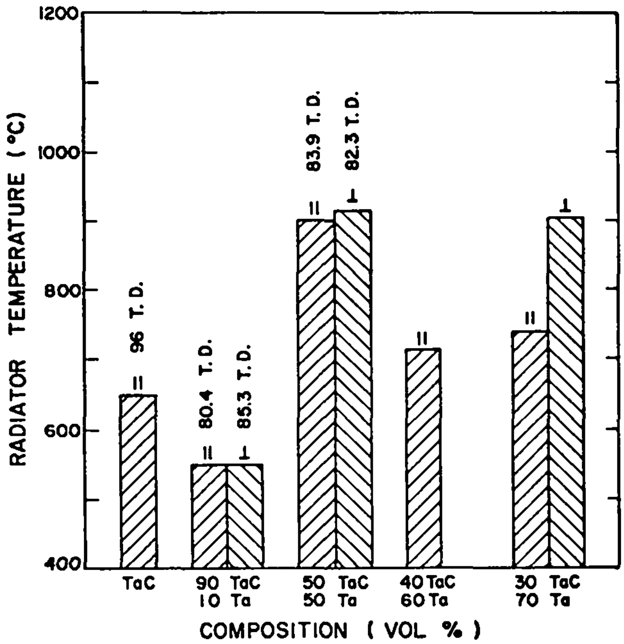


Fig. 1. Steady-state thermal-stress ranking of selected carbides.

Except for the 30 vol% TaC-70 vol% Ta specimens, the material was isotropic. Whereas the pure refractory-metal carbide shows steady-state thermal-stress resistance at 500 to 650°C radiator temperature, the 50 vol% TaC-50 vol% chopped Ta wire composite shows steady-state thermal-stress resistance at about 900°C radiator temperature. This is an improvement of about 40% over TaC, and it is believed to be significant.

IV. THERMAL-SHOCK-TEST RESULTS

Specimens, 1 in. o.d. by 1/4 in. i.d. by 1/16 in. thick, of TaC reinforced with 60 and 70 vol% chopped tantalum wire were thermally shock tested. The thermal-shock test is described in detail in Ref. 7, and the data for these materials are summarized in Table I. Two thermal-shock indices are given, one pertaining to crack initiation and the other to fracture. The latter is the most important in terms of the ultimate capability of these materials. Included in Table I, for comparison, are the results for with-grain RVC graphite which is reported to have good thermal-shock resistance. As can be seen, RVC did not crack; rather, fractures occurred through the washer.

TABLE I

THERMAL SHOCK DATA FOR TANTALUM-WIRE-REINFORCED TaC COMPOSITES

Material	Grain Orientation	Thermal-Shock Index	
		For Crack Initiation	For Fracture
RVC Graphite	WG	--	252/255
60 vol% Ta Wire + 40 vol% TaC	WG	80/100	Can't fracture[a]
60 vol% Ta Wire + 40 vol% TaC	AG	70/80	~ 225
70 vol% Ta Wire + 30 vol% TaC	WG	80/100	Can't fracture[a]
70 vol% Ta Wire + 30 vol% TaC	AG	60/80	~ 200

[a]Tantalum fibers melt before fracture.

The power setting required to initiate a crack and that required to completely fracture the materials differed greatly. Typically, a crack could be made to initiate at a power setting of ~80 to 100, and then to propagate (sometimes across the entire specimen). However, these cracks are very tight and did not significantly degrade the strength of the specimen. Apparently the tantalum wires bridging the cracks act as tiny reinforcing bars. With the thermal-shock instrumentation used, pure refractory-metal carbides require power settings of 60 to 80 for crack initiation. In such carbides, only a slight increase in the power setting leads to rapid fracture.

It was only at power settings greater than 200 that these materials could be fractured. In fact, the with-grain specimens could not be fractured at all, even though, at these power settings, they were so cracked that they resembled cracked safety glass. Several specimens were finally forced to part (fracture) into two pieces after melting the tantalum wires holding the cracked segments together. This suggests that fracture did not occur until a temperature above 3000°C was reached.

V. THERMAL CONDUCTIVITY

Thermal conductivity is an important design parameter in thermal-stress analysis. Therefore, we also determined the room-temperature thermal conductivity, based on comparitive steady-state measurements with standard materials. Table II is a comparison of the experimental and predicted thermal-

TABLE II

PREDICTED AND EXPERIMENTAL THERMAL CONDUCTIVITY OF TaC-Ta (WIRE) HOT-PRESSED COMPOSITE BODIES

			K = W/m-K at 33°C	
P_{TaC}	P_{Ta}	ρ/ρ_o	Predicted	Experimental
0	1.0	1.0		
1.0	0	1.0		
AG (parallel to the pressing direction)				
0.90	0.10	0.8042	0.0838	0.0850
0.70	0.30	0.8300	0.1095	0.1135
0.50	0.50	0.8392	0.1335	0.1470
0.40	0.60	0.8375	0.1421	0.1768
0.30	0.70	0.8069	0.1332	0.200
WG (perpendicular to the pressing direction)				
0.90	0.10	0.8531	0.1075	0.0795
0.70	0.30	0.8480	0.1234	0.0035
0.50	0.50	0.8232	0.1283	0.1140
0.40	0.60	0.8434	0.1515	0.1628
0.30	0.70	0.8125	0.1403	0.1845

conductivity values. The model assumed a dispersion of tantalum wires in a continuous TaC matrix. The axes of the wires were assumed to be parallel to the radial plane of the pressing, but randomly oriented in that plane. Metallographic results confirmed this relationship. Although the fiber orientation would suggest a high degree of anisotropy, the thermal-conductivity results were reasonably isotropic, as were the thermal-stress results.

VI. X-RAY-DIFFRACTION DATA FOR TaC-CHOPPED Ta WIRE COMPOSITES

Because the billets were hot pressed at 1800°C and the intended service temperature was arbitrarily chosen to be above 2300°C, we decided to identify the phases present after hot pressing followed by a heat treatment.

Table III shows x-ray-diffraction data for various TaC-chopped Ta wire composites. The numbers indicate the volume percentage of TaC or Ta wires used. "As pressed" means that the composite was prepared by hot pressing at 1800°C. "Heat treated" means that the hot-pressed samples were exposed to 2300°C for 10 h in a hydrogen environment. The hot-pressed composites show some reaction of the tantalum fiber with the surrounding TaC matrix to produce the lesser carbide, Ta_2C. The heat-treated specimens that had higher tantalum-fiber content show a much more pronounced reaction between the fibers and the surrounding TaC matrix to produce Ta_2C. The strong presence of the hydride phase indicates that even after 10 h at 2300°C, a substantial amount of tantalum remains noncarbided. One might speculate that the lesser metal carbide, Ta_2C, has physical and mechanical properties that differ enough from those of the noncarbide matrix so that crack propagation is stopped or greatly impeded on reaching them. They thus serve to prevent or greatly inhibit fracturing in substantially the same manner that metal fibers do in refractory metals. Metallographic evidence, reflecting the changes in structure as determined by x-ray diffraction, is presented in Figs. 2 and 3.

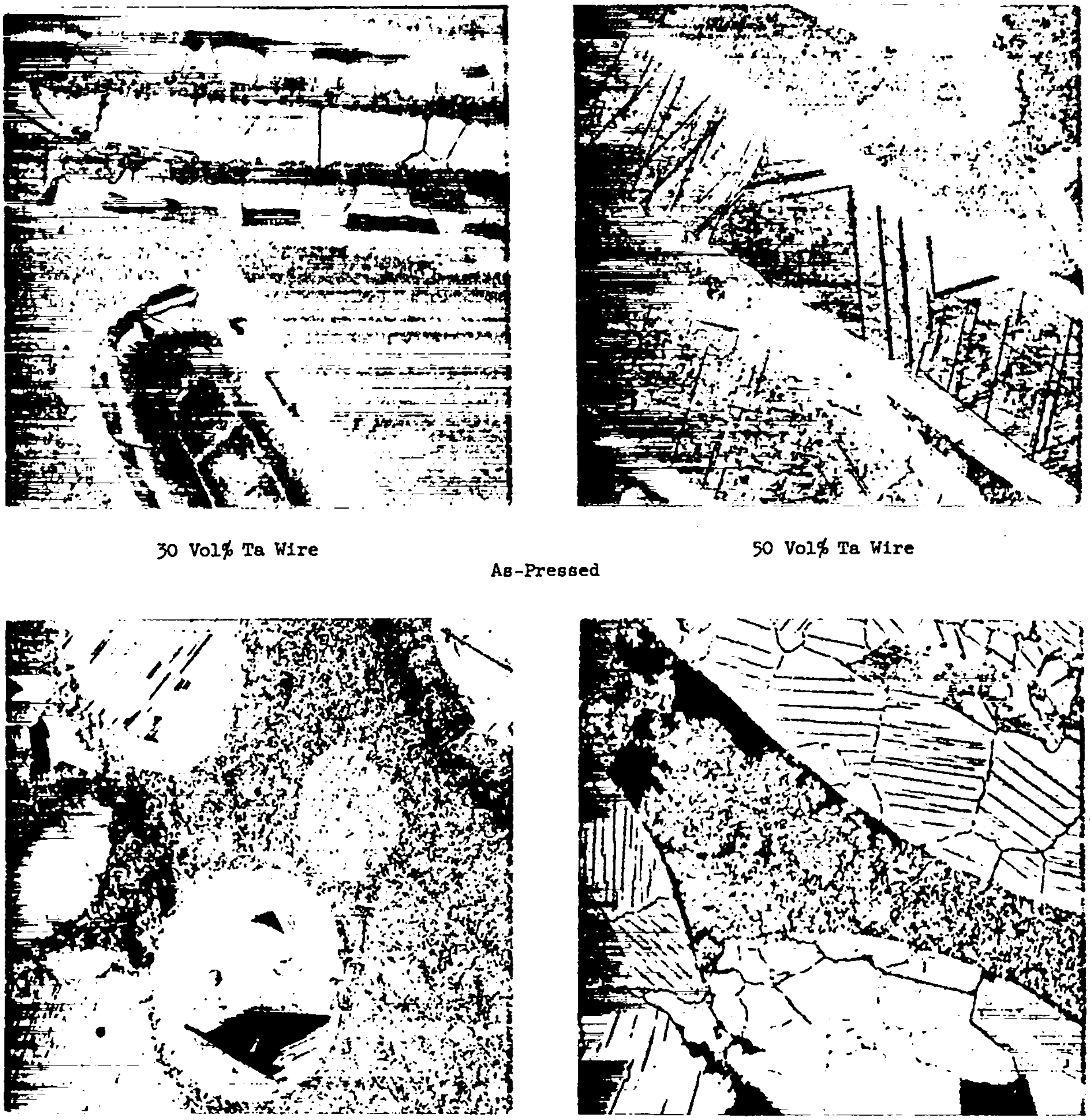
TABLE III

X-RAY-DIFFRACTION DATA FOR TaC-CHOPPED Ta WIRE COMPOSITES

	Phases Present		
Sample	Strong	Medium	Weak
90 TaC-10 Ta as-pressed	TaC		Ta_2C
70 TaC-30 Ta as-pressed	TaC		Ta_2C
50 TaC-50 Ta as-pressed	TaC	Ta_2C	
40 TaC-60 Ta as-pressed	TaC	Ta_2C	
30 TaC-70 Ta as-pressed	TaC		Ta_2C
90 TaC-10 Ta heat-treated	TaC		
70 TaC-30 Ta heat-treated	TaC		Ta_2C
50 TaC-50 Ta heat-treated	Ta_2C $TaH_{0.8}$		TaC
40 TaC-60 Ta heat-treated	Ta_2C TaC $TaH_{0.8}$		
30 TaC-70 Ta heat-treated	Ta_2C TaC $TaH_{0.8}$		

VII. SUMMARY AND CONCLUSIONS

Refractory metal carbide-refractory metal fiber composites can be formed readily by hot pressing. Although various refractory-metal carbides can be used as the matrix material, it is desirable that the carbide be a mono rather than a lesser carbide. We feel that various chopped refractory-metal fibers such as tantalum, molybdenum, 75 wt% W-25 wt% Re, and rhenium can be used. The limiting factor in the use of any particular metal fiber is the formation of the metal carbide-carbon eutectic. The temperatures at which the various refractory-metal carbides form eutectics with carbon are well known, and it



30 Vol% Ta Wire

50 Vol% Ta Wire

As-Pressed

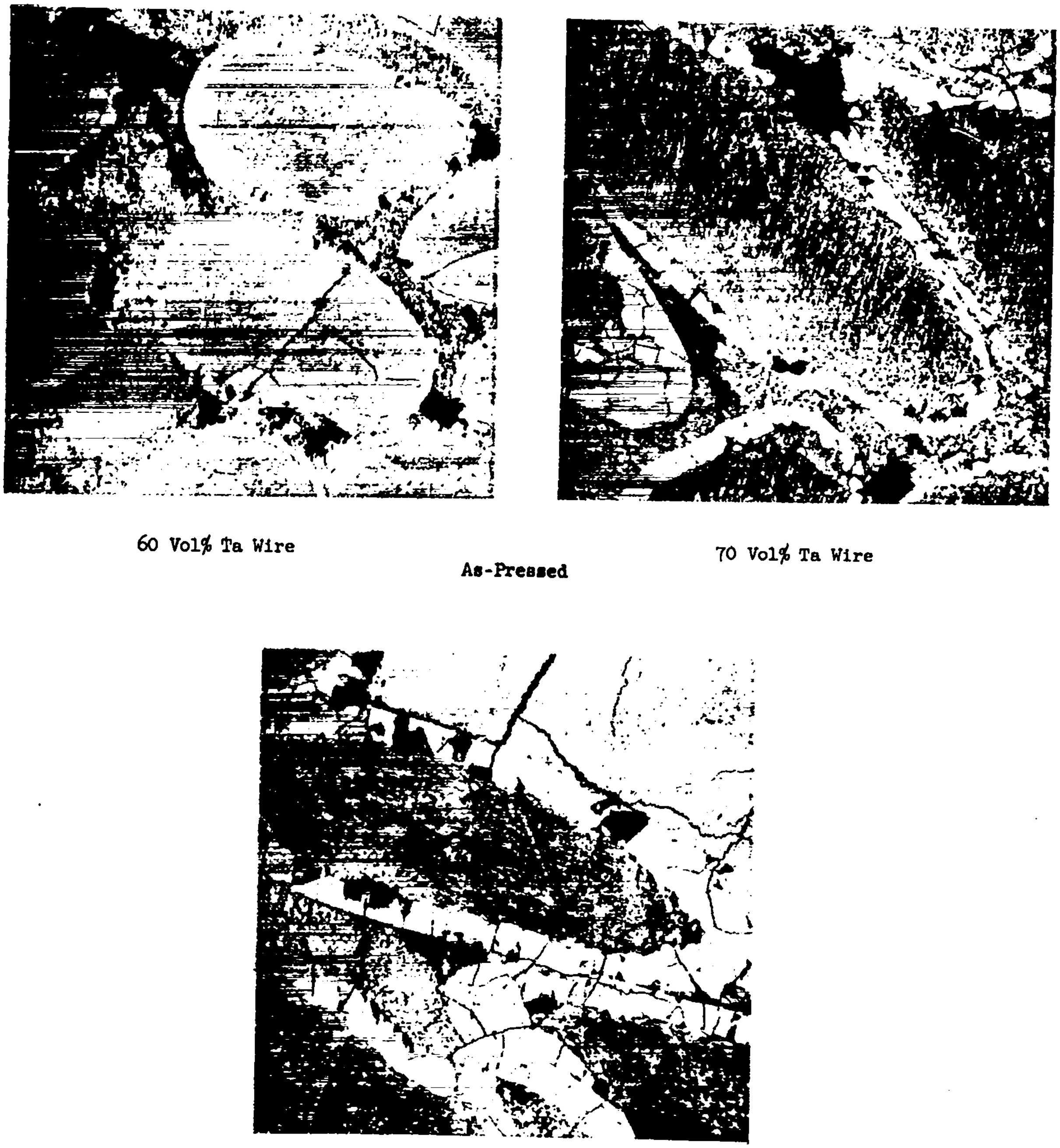
30 Vol% Ta Wire

50 Vol% Ta Wire

Heat-Treated at 2300°C - 2 h - H_2

Fig. 2. Microstructures of TaC-chopped Ta wire specimens (100X).

immediately becomes evident why we chose tantalum for this investigation. We therefore conclude that the thermal-stress resistance of refractory-metal carbides is substantially improved by the addition of chopped metal fibers. We have found that a composite consisting of 50 vol% TaC-50 vol% chopped Ta wire has approximately 40% more thermal-stress resistance than does pure TaC. Near-isotropic properties were obtained for most of the compositions tested. Although not verified, this may indicate that wire diameter and length are not critical. Indeed, it suggests that the metal need not be present as fibers at all, but may serve as well in an irregular particulate form wherein particle size, in all probability, will be an important factor. We plan to do more work on the various combinations we believe to be workable.



60 Vol% Ta Wire

As-Pressed

70 Vol% Ta Wire

60 Vol% Ta Wire

Heat-Treated at 2300°C - 2 h - H_2

Fig. 3. Microstructures of TaC-chopped Ta wire specimens (100X).

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