JOURNAL OF MATERIALS SCIENCE 21 (1986) 2941–2958

Hot-working and strengthening in metal carbide–graphite composites

D. JOHN*, G. M. JENKINS
Department of Metallurgy and Materials Technology, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK

A study of the hot-pressing of graphite–metal powder mixes up to 2700° C has been effected, concentrating on metals such as titanium, vanadium, niobium, tantalum and zirconium which form stable refractory carbides. In particular, it is shown that titanium/vanadium and graphite/electrographite powder compacts can be deformed plastically and even die-moulded rapidly above 2000° C in a one-stage process to form strong, shock-resistant composite artefacts consisting of a graphite matrix hardened by finely divided metal carbide. The compressive strength is increased by a factor of 10 over a typical electrographite. Densification and strengthening are induced at much lower temperatures than those required for pure carbons and graphite.

1. Introduction: previous work on similar systems

Metal carbides have only limited applications as high temperature refractory materials because of poor thermal shock resistance and difficulties in fabrication. The use of graphite in these applications is limited by low strength and reactivity with oxygen. To take advantage of the desirable properties of carbides and graphite and at the same time minimize their undesirable behaviour, graphite–metal (carbide) composites have been developed.

In the past such composites have been made from compacts of petroleum coke, pitch binder and, typically, ZrC powder, carbonized and graphitized slowly to temperatures in excess of 2300° C [1, 2]. To remove unavoidable porosity these materials were hot-worked at these high temperatures and were found in many cases to have a high degree of plasticity. White and co-workers [3–5] extended the hot-working process above the carbide–graphite eutectic temperature, finding he could express excess carbide in the form of droplets. Hot-working improved density, strength and electrical/thermal conductivities leading to the conclusion that the dispersed carbide was chemically bonded to graphite crystallites.

A technique for hot-pressing graphite–metal composites using a simple one-step operation, employing no binders, was investigated by Harada [6]. He mixed calcined petroleum coke and a series of metal or carbide powders and hot-worked them in a graphite mould above 2800° C. The strength of the composites increased with increasing carbide content. Highest strengths were obtained with additions of niobium, hafnium and molybdenum carbides. Intermediate strengths resulted from additions of zirconium, titanium, boron, beryllium and uranium carbides. Tantalum and thorium carbides yielded low strength composites. Higher processing temperatures and the use of finer powders improved densification and hence the final strength of such composites. Harada [6] attributed the strengthening effects to the formation of a liquid phase at the carbide–carbon eutectic; this allowed carbide diffusion into the graphite.

In Swansea, Matthews *et al.* [7] mixed molybdenum and natural graphite (NG) powders and cold-compacted them to produce cylindrical pre-forms. Hot-working these composites under compressive loads between 2200 and 2700° C considerably increased the compressive strength of the composites.

Matthews [8] extended these studies to investigate the optimum conditions for the production of high strength NG-Mo composites and in so doing identified the fundamental mechanisms and deformation processes occurring. Constant load compressive creep tests indicated that deformation took place in two distinct stages. The primary creep was attributed to pore closure and densification, diffusion of carbon atoms in molybdenum, transformation of cubic molybdenum to hcp Mo_2C (which must result in lattice shrinkage), and deformation of carbide particles. Secondary creep deformation in the densified composite could be attributed to bulk creep of the carbide particles together with some activated creep in the graphite. Microscopic examination of the hot-worked composites showed that the average carbide particle size decreased with increasing time and temperature. The carbide particles were broken up by a process which involved the solution and diffusion of carbon atoms through the carbide and reprecipitation. The carbide particles were then split by the growing graphite crystals. Matthews argued that this process would be enhanced by reducing the particle size of the initial molybdenum powder, resulting in greater strengthening. This was substantiated experimentally.

Diffusion experiments using the layer growth technique proved that the interaction of molybdenum

---

*Present address: Morganite Electrical Carbon Ltd, Morriston, Swansea, UK.

with edge atoms proceeded more rapidly than with basal plane atoms because the edge atoms have unsatisfied primary bonds [9]. Further wetting experiments indicated that molybdenum carbides wet and bond to natural graphite whereas the carbides of titanium, zirconium and niobium were shown to wet, but not bond, at temperatures below 2500° C. Scanning electron micrographs taken of the graphite–carbide interface revealed clearly that a bond was formed between the molybdenum carbide and graphite.

In all this past work natural flake graphite was used as the continuous material. However, synthetic graphite or powdered electrographite can also be used. This is produced by graphitizing good quality cokes above 2500° C, and retains much of the morphology of the original coke and differs markedly from that of natural flake.

May [10] found that freshly ground artificial graphite readily compacted without binders to give high density compacts. De Vere *et al.* [11] showed that multi-compaction and shear under pressure produced stronger compacts and these techniques were adopted in this programme to produce dense pre-forms at room temperature.

2. Aims of this programme

As indicated in the literature survey, much work has been carried out on the addition of various metal or metal carbide powders to conventional binder–filler carbons and such additions have been shown to increase strength and lower the temperature required for densification and hot-working. It has also been shown in Swansea that graphite powder–molybdenum powder mixes can be compacted at room temperatures to produce usefully strong compacts which are subsequently strengthened by hot-working at temperatures above 2000° C, thus producing artefacts by a one stage process [7]. We extend the work here to examine mixes of other metal and refractory metal carbide powders with powdered natural graphite and powdered electrographite to determine what other metal carbide–graphite systems can be usefully formed by straightforward hot-pressing processes above 2000° C [12].

Some of this work was presented at the International Carbon and Graphite Conference in London [13]. We present here a full account of some of the high temperature interactions which were studied, and which can now be released.

3. Experimental details

Mixes, powders and compacts were prepared from natural graphite powders (Ceylon block < 200 mesh) and a number of metal or metal carbide powders (< 200 mesh). Compacts were prepared using standard powder metallurgy techniques. Each compact was designated according to its composition, e.g. NG–25Ti represented a mixture of 25 vol % titanium plus 75 vol % natural graphite.

The dried and sieved metal or carbide powders were mixed with the natural graphite powder by tumbling. The mixed powders were compacted in a 14 mm bore diameter cylindrical cold-pressing die. Multiple compaction between 10 and 300 MPa served to increase the density to a maximum.

3.1. The high temperature furnace and ancillary apparatus

Heat treatment and hot-working was carried out in a 10 kVA graphite-resistance furnace. The furnace interior was redesigned in order to hot-work samples in compression.

The exterior of the cylindrical furnace hood consisted of a double-walled mild steel water-cooled casing. The casing was insulated from the interior heating chamber by a lamp black packing. The base-plate compression rams and electrical contact blocks were all water-cooled. The heating element and compression anvils were machined from fine-grained electro-graphite block. The furnace temperature was maintained by means of an optical pyrometer which sensed the temperature through a fused silica glass sight port and fed a signal back to an automatic control unit. The temperature of a sample was measured by a disappearing filament micropyrometer. This was focused on the sample through a sight port diametrically opposite the control sight port. Correction to the optical pyrometer due to absorption by the fused silica glass windows was made.

Electrographite anvils were positioned in the centre of the heating element such that a specimen placed between them remained aligned in the hot zone of the furnace, as shown in Fig. 1.

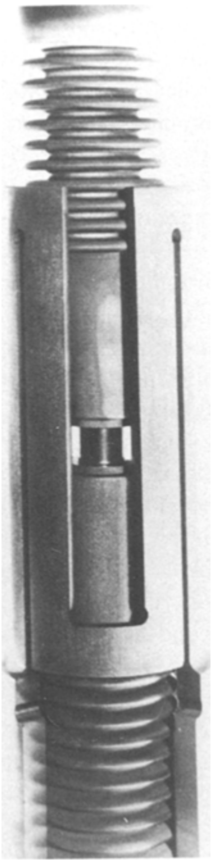


Figure 1 Arrangement of electrographite anvils for hot-working within a graphite resistance furnace above 2000° C.

TABLE I Properties of the as-pressed compacts

Compact	Density (Mg m^{-3})		% deviation from theoretical density	Compressive strength (MPa)
	Apparent	Theoretical		
NG	2.13	2.26	6.1	14.6
NG–20 N	3.08	3.53	14.6	19.1
NG–20 NbC	3.13	3.33	6.4	17.5
NG–20 Ta	4.38	4.69	7.1	17.5
NG–20 TaC	4.41	4.59	4.1	16.2
NG–20 W	4.62	5.68	22.9	21.3
NG–20 V	2.95	3.03	2.7	20.1
NG–30 V	3.06	3.41	11.5	21.4
NG–5 Ti	2.23	2.37	6.3	15.6
NG–15 Ti	2.41	2.60	7.9	21.2
NG–25 Ti	2.59	2.82	8.5	22.1
NG–30 Ti	2.68	2.94	8.8	25.2
NG–40 Ti	2.83	3.16	11.7	28.1

A hydraulic jack supplied compressive force via a steel water-cooled ram, through sliding vacuum seals to the lower anvil. A compressive load applied to a sample held between the anvils was transmitted via an upper steel ram, through a sliding vacuum seal to a load cell. The load cell was connected to the ram and clamped to a cross bar, held on vertical supports, above the load train. A linear transducer was connected to the lower ram and measured displacement of the load train.

3.2. Heat treatment and hot-pressing of compacts

All high temperature work was carried out in an inert atmosphere. Heat treatment of specimens was carried out in a graphite crucible which could be centred in the hot zone of the furnace. The highest treatment temperature used was 2700° C and this was reached in about 30 min.

Specimens were placed in the hot zone between the compression anvils with disposable pyrographite discs separating the specimen from the anvils.

The heating and hot-pressing process involved the two procedures referred to in future as "Method 1" or "Method 2".

Method 1: the sample was heated free of load to the hot working temperature at which it was soaked for 30 min. A compressive load was then gradually applied to the quoted hot-working load and this was maintained for a specified time.

Method 2: the hydraulic jack was clamped during the heating up process. A steadily increasing load due to thermal expansion was applied to the sample until a load of 100 kg was attained. As the temperature continued to rise, the pressure was released to maintain this load at 20 kg. When the hot-working temperaturte was reached, the hot-working load was gradually applied and maintained for the required time, usually 40 min. With Method 1, deformation occurred in the first 5 min after the application of the load. In the case of Method 2, much of the deformation took place during the heating up process.

3.3. Properties of the as-pressed compacts

Table I lists some of the properties of the as-pressed compacts. The theoretical compact densities were calculated from published data [14] on physical constants assuming 2.26 Mg m^{-3} for the graphite density.

The natural graphite powder compacted easily into high-density low-strength compacts. The self-lubricating properties of the graphite allow easy basal shear and bending/twinning of the flakes leading to intimate packing. The low strengths indicate little or no bonding between the flakes.

The strength of the G–Ti compacts increased with titanium content, accompanied by increasing deviation of compact density from the theoretical value. This suggests a transition from graphite powder-type packing to metal powder-type packing. When metal powders are compacted, localized deformation at contact points permits welding between particles, but prohibits tight packing. However, microscopic examination of an as-pressed G–25Ti compact (Fig. 2) reveals an even distribution of titanium particles in a continuous graphite matrix. There is no evidence of bonding of titanium particles due to pressure welding under compaction.

4. Hot-working of graphite refractory metal (carbide) composites: a preliminary investigation

4.1. Pure natural graphite (NG) compacts and electrographite (EG) blocks

Pure NG compacts were hot-worked for 30 min between 2000 and 2700° C under a compressive load

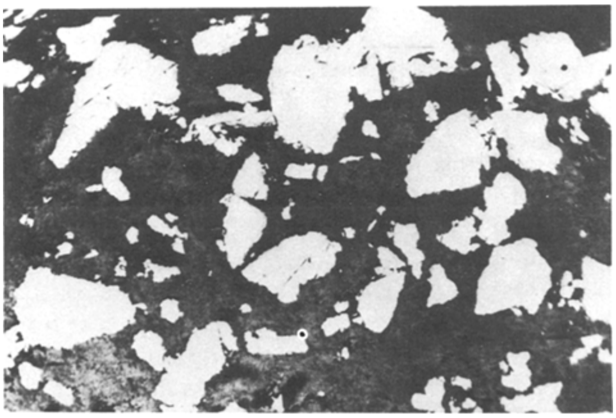


Figure 2 Microstructure in as-pressed graphite–titanium composite (NG–25 Ti); × 280.

TABLE II Compressive strengths and densities of hot-pressed NG compacts and electrographite

Material	Hot-working temperature (° C)	Density (Mg m^{-3})		Compressive strength (MPa)
		Before hot-working	After hot-working	
As-pressed		2.13	–	14
	2000	2.13	2.01	10.5
Natural	2250	2.13	2.02	9.5
Graphite	2500	2.13	2.04	13
	2700	2.13	2.04	15.5
Untreated		1.66	–	37
Electrographite	2000	1.66	1.66	39
	2250	1.66	1.66	53
	2500	1.66	1.67	58
	2700	1.66	1.67	59

of 200 kg using Method 1. The density change and the room temperature compressive strengths were measured after hot-working. The hot-working strain was calculated from the change in height, measured at room temperature, before and after hot-working. Similar tests were performed on samples of EY9 electrographite. The samples were cut from 10 mm diameter rod and measured 10 mm in height. The samples were hot-worked under a compressive stress of 11 MPa. The results are presented in Table II.

It was found that the density of NG compacts was lowered by hot-working. Only those samples hot-worked above 2500° C show any significant plasticity. The room temperature compressive strength is generally decreased as a result of hot-working below 2500° C. The electrographite was not densified significantly under these conditions but there was a steady increase in room temperature compressive strength with hot-working temperature.

Thus any large improvements in strength and density found after addition of a second phase must be attributed to the effect of that phase alone. Of course, higher temperatures and loads will achieve densification and stengthening in the pure graphite alone but this will be the subject of a further paper.

4.2. Heat treatment of NG–titanium systems, free of stress

The G–Ti system was studied to establish a satisfactory hot-working technique and an appropriate composite composition suitable for a preliminary survey.

Sets of compacts were prepared containing 5 and 15 vol % Ti. The compacts were heat treated at 2000, 2250, 2500 and 2700° C, and the height, diameter and weight of each specimen was measured before and after heat treatment. The density change after heat treatment was calculated for each specimen and is shown in Table III. Compact density decreased with increasing heat treatment temperature.

Specimens were cut from the heat treated compacts and compression tested at room temperature. The compressive load was applied parallel to the original compact pressing direction. It can be seen from Table III that the decrease in density with heat treatment was accompanied by a drastic reduction in the compressive strength. Thus, if hot-working is preceded by a heat treatment period, then the advantage of having a very high as-compacted density is lost. The volume change contributing to the decrease in density was due, almost entirely, to an increase in height corresponding to the recovery of strains implanted in the material during the original compaction.

The photomicrograph in Fig. 3 shows the morphological changes which occur in NG–15 Ti compacts from the as-pressed condition to the heat treated state. The as-pressed material shows evenly distributed titanium metal particles in the surrounding flake-like graphite. The largest titanium particles are $\sim 75\,\mu$m diameter. There is no evidence of metal–metal welding. The increased strength over as-compacted natural graphite recorded in Table I cannot, therefore, be accounted for by the formation of a network structure capable of supporting higher loads. At this low metal concentration such a formation would be highly unlikely anyway. The angular titanium particles are fairly uniform in shape, with rough surfaces. There appears to be good metal–graphite contact.

X-ray data showed that the formation of TiC was complete after heat treatment for 30 min at 2000° C. Fig. 3a shows that the appearance of the TiC particles is significantly different from the titanium particles in the as-pressed structure; the carbide particles have become hollow spheres. The interiors of the sectioned spheres are filled with mounting agent (darker areas). A possible explanation for this rather unusual structure will be given later.

At 2000° C the carbides have a porous spongy appearance whereas at 2250° C (Fig. 3b) they have sintered into much denser particles although some porosity still persists. At 2500° C (Fig. 3c) the carbides are dense and the spheres show a tendency to break

TABLE III Properties of heat treated NG–Ti compacts

Compact	Heat treatment temperature (° C)	Final apparent density (Mg m^{-3})	Density change (Mg m^{-3})	RT compressive strength (MPa)
G–5 Ti	As-pressed	2.23	–	15.4
	2000	2.03	–0.20	13.0
	2250	1.99	–0.24	11.1
	2500	1.96	–0.27	10.0
	2700	1.95	–0.28	8.9
G–15 Ti	As-pressed	2.41	–	22.0
	2000	2.32	–0.12	16.1
	2250	2.12	–0.29	15.2
	2500	2.08	–0.33	14.6
	2700	2.08	–0.40	13.1

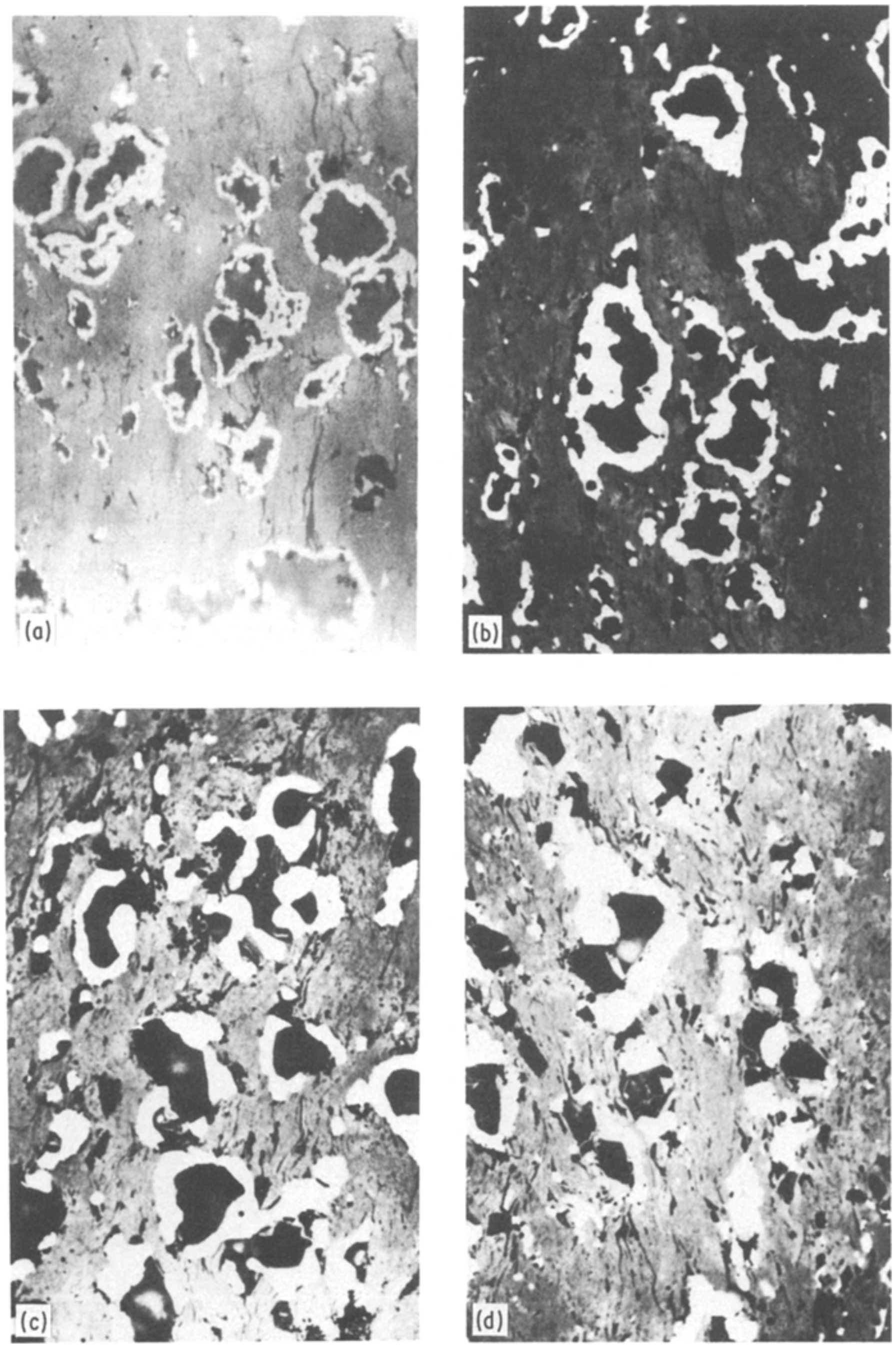


Figure 3 Microstructures of graphite–titanium composites (NG–15Ti) heated at 2000, 2250, 2500, 2700, free of stress; × 240.

up. The sphere wall thickness has generally increased. Break-up has progressed further at 2700° C (Fig. 3d). The carbides appear as dense angular particles which are fragments of the original spheres. The holes have been retained but have been filled with mounting agent.

Comparing Figs 3a, b, c and d, it can be seen that the graphite matrix becomes increasingly less dense and well compacted as the heat treatment temperature is increased. Microcracks have opened up perpendicular to the compacting direction after heat treatment at 2000° C. The cracks open up further with increasing temperature and appear as wide fissures at 2700° C. The density of the graphite matrix is, therefore, considerably decreased as indicated by the decrease in composite density recorded in Table III. This decrease in density is accompanied by a decrease in strength.

4.3. Hot-pressing of G–Ti compacts

NG–5Ti and NG–15Ti compacts were studied in order to develop a satisfactory hot-working technique. Method 1 was tried first: a small load of approximately 5 kg was applied. As the temperature increased, the pressure on the sample (caused by thermal expansion) was released to maintain a load of approximately 2 kg. After accounting for the thermal expansion of the apparatus, the final height of the sample at temperature was calculated. Each specimen was soaked for 30 min at the hot-working temperature. A compressive load was then slowly applied to the sample increasing from 0 to 200 kg in about 5 min and maintained for 30 min. After 30 min under load, the rate of deformation became very slow. The power was switched off, and the load was maintained on the sample until the temperature was below 2000° C. The weight and dimensions of each sample were measured

TABLE IV Properties of hot-worked G–Ti composites

Compact	Hot-working temperature	% strain at hot-working temperature	% strain at RT	RT compressive strength (MPa)	Final density (Mg m^{-3})	Density change (Mg m^{-3})
G–5 Ti	2000	5.2	−0.2	16.3	2.11	−0.12
	2250	7.0	1.5	15.5	2.15	−0.08
	2500	13.2	7.2	16.9	2.16	−0.07
	2700	15.9	8.2	30.5	2.19	−0.04
G–15 Ti	2500	20.9	14.6	39.7	2.42	0.01
	2700	29.7	20.3	48.4	2.44	0.02
	2700*	24.0*	22.3*	82.3*	2.53*	0.12*
G–25 Ti	2500*	27*	24.2*	92.8*	2.87*	0.28*
	2700	40	35.6	136.6*	2.89	0.30

*Hot-worked by Method 2.

after removal from the furnace. The per cent strain at temperature was calculated and recorded in Table IV. A large proportion of the compressive strain at temperature can be accounted for by suppression of the thermal expansion. Table IV shows that for G–5 Ti composites, hot-worked below 2250° C, the hot-working strain was completely recovered on cooling. The room temperature compressive strength of these samples was similar to that of the as-pressed material (Table III). At 2500 and 2700° C plastic deformation took place and this was reflected in an increase in room temperature compressive strength, small at 2500° C, but significant at 2700° C.

Barrelling occurred at 2500 and 2700° C. Fig. 4 shows that the surface at 2500° C appears smooth and shiny, whereas the 2700° C sample was duller and mottled in appearance. It was subsequently found throughout this work that a dull mottled surface was generally indicative of a high strength composite.

The work on these composites indicates that considerable deterioration occurs during the heating-up period due to thermal expansion. The advantage of the high compactibility of natural graphite compacts is virtually lost.

A second method of hot-working (Method 2) was tried whereby the thermal expansion in the compacting direction was constrained. In this case, the hydraulic ram was clamped during the first part of the heating-up process. The sample was thus subjected to a continuously increasing compressive load, caused by thermal expansion of the sample against the anvils. When the load had reached 100 kg, the pressure was released slightly and thereafter maintained at 20 kg. Much smaller expansions were recorded compared to samples heated by Method 1. The result was a much stronger composite.

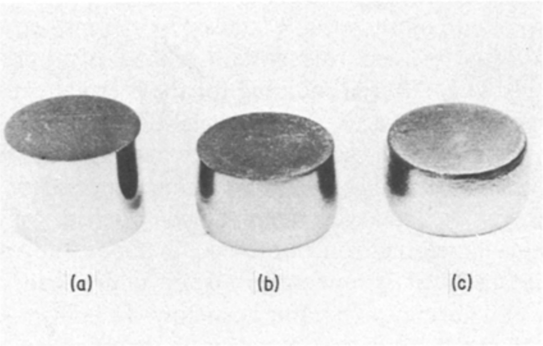


Figure 4 As-pressed titanium–graphite composites (NG–25 Ti) and hot-worked at 2500 and 2700° C.

A further indication of the advantage of Method 2 over Method 1 can be seen from the densities of the hot-worked composites shown in Table IV. The final apparent densities of G–5 Ti composites hot-worked using Method 1 were all less than the as-pressed density. Only small increases in density were achieved for G–15 Ti composites with Method 1 at 2500 and 2700° C. However, a G–25 Ti composite hot-worked at 2700° C using Method 2 had a final density 2.89 Mg m^{-3}, representing an increase of 5%.

The microstructure and morphology of the carbides in G–15 Ti samples hot-worked at 2700° C using Methods 1 and 2 were compared by microscopic examination (Fig. 5). In both cases, the particles sintered into dense, distinct solid shapes preferentially aligned normal to the hot-working direction. There is one noticeable difference between Fig. 5a and b. There is a much greater proportion of fine carbide particles in the sample hot-worked using Method 2 than in that using Method 1. The significance of this observation and its contribution to the strength increase will be discussed later.

A further set of composites were prepared containing 25 vol % Ti, G–25 Ti. These were hot worked at 2500 and 2700° C. Table IV shows that large deformations occurred with this composition. The room temperature compressive strength after hot-working at 2700° C is six times greater than the as-pressed compact and represents a ten-fold increase over the strength of hot-worked natural graphite compacts. Significant strengthening also occurred at 2500° C. These composites were hot-worked using Method 2.

The microstructure of the hot-worked G–25 Ti sample is shown in Fig. 6. It can be seen that there is a continuous graphite–carbide interface suggesting a strong bond. The carbides are dense and strung out in a plane normal to the hot-working direction. The graphite matrix is dense with little evidence of cracks or fissures.

4.4. Summary of hot-pressing results for NG–Ti composites

We have shown that:

1. the high temperature plasticity in G–Ti compacts is greater than that in pure NG compacts and increases with proportion of titanium;

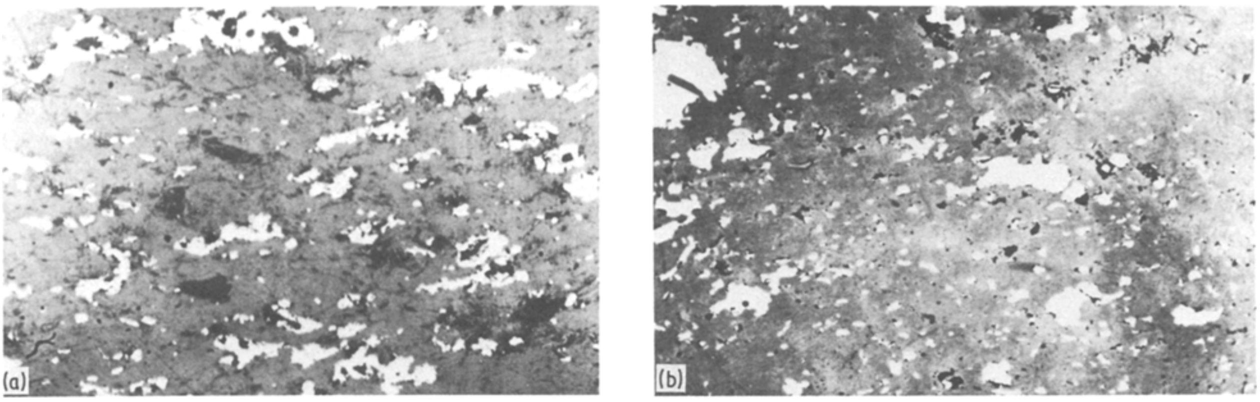


Figure 5 Microstructures of graphite–titanium composites (NG–15 Ti) hot-worked by Methods 1 and 2; × 137.5.

2. hot-working of the composite materials above 2500° C produces signficant increases in room temperature strength;
3. the strength increase is enhanced by increasing proportions of titanium, higher hot-working temperatures (up to 2700° C), and the application of a load during the heating up period.

It was decided that for a preliminary survey of other composite materials:

1. composites would be prepared containing 20 vol % metal;
2. composites would be hot-worked between 2000 and 2700° C;
3. composites would be hot-worked using "Method 2".

4.5. NG–niobium and NG–tantalum

Compacts of NG–20 Nb and NG–20 Ta were hot-worked at 2000, 2250, 2500 and 2700° C using Method 2. Cubic samples were cut from each hot-worked composite and compression tested at room temperature parallel to the hot-working direction.

Table V shows that for the same load of 200 kg the hot-working strain, measured at room temperature, increases with temperature for both sets of composites. The relatively high strains, however, were not accompanied by the expected strengthening. The results for the NG–20Ta and NG–20 Nb composites were not encouraging in comparison with those for titanium and vanadium.

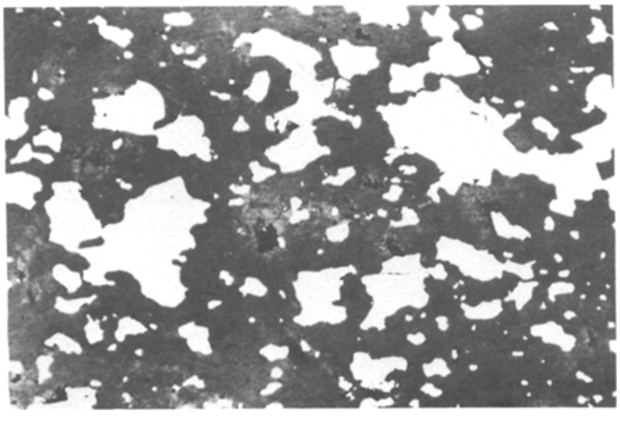


Figure 6 Microstructure of graphite–titanium composite (NG–25 Ti) hot-worked by Method 2; × 280.

In photomicrographs of the hot-worked G–20 Nb composites (Figs 7a, b, c) revealed that at 2250° C (and below) the carbides appear as large porous particles and are apparently agglomerates of smaller particles, elongated normal to the hot-working direction. At 2500° C the carbides were still porous, but showed a tendency towards densification. At 2700° C the carbides sintered into dense particles with little sign of porosity.

The occurrence of microcracks in the graphite matrix decreases as the hot-working temperature increases. This together with the decrease in porosity of the carbides explains the positive increase in density with temperature recorded in Table V.

Tantalum proved to be a less effective strengthening agent than niobium. At 2000° C the carbides exist as porous agglomerates spread out in a plane perpendicular to the hot-working direction. Unlike G–20 Nb, however, the porosity of the carbides does not decrease much with hot-working temperature.

X-ray analysis revealed that complete conversion to NbC and TaC had taken place at 2700° C. It was, therefore, decided to investigate the effect of hot-working composites produced initially by mixing the carbides NbC and TaC rather than the metals with NG.

Composites of NG–20 NbC and NG–20 TaC were hot-worked as above. The compressive strain, density change and room temperature compressive strength were measured. Significant additional strengthening occurred. At 2700° C, the carbide particles in both cases were dense and discrete with no evidence of agglomeration. The average particle size was therefore less than in the NG–20 Nb and NG–20 Ta composites. This accounts for significant additional strengthening despite the lower volume of carbide in these composites. The density changes at 2700° C were less than for the NG–metal composites.

4.6. NG–tungsten; NG–zirconium carbide

Because fine zirconium metal powder is pyrophoric, composites were prepared from the carbide, ZrC. The results of the G–NbC and G–TaC composites showed that there was little difference in the strengthening effect of the carbide compared to that of the metal. NG–20 ZrC, and NG–20 W compacts were hot-worked at 2000, 2250, 2500 and 2700° C using Method 2.

TABLE V Properties of hot-pressed NG–20 Nb and NG–20 Ta composites

Compact	Hot-working temperature (° C)	Final density ($Mg\,m^{-3}$)	% density change	% hot-working strain	RT compressive strength (MPa)	RT compressive strain (%)
NG–20 Nb	2000	–	–	–	–	–
	2250	3.23	4.9	21.0	36.3	2.11
	2500	3.23	4.9	23.0	35.7	2.08
	2700	3.25	8.8	29.5	62.0	2.53
NG–20 NbC	2000	3.27	4.5	4.4	47.9	1.81
	2250	3.28	4.8	14.0	51.2	1.84
	2500	3.29	5.1	17.7	69.0	2.13
	2700	3.33	6.4	26.8	89.2	2.47
NG–20 Ta	2000	–	–	–	–	–
	2250	4.40	0.46	13.0	25.6	1.42
	2500	4.45	1.6	20.2	27.4	1.39
	2700	4.52	3.4	25.3	40.0	2.31
NG–20 TaC	2000	4.48	1.6	3.2	27.7	1.40
	2250	4.49	1.8	9.0	33.6	1.51
	2500	4.50	2.0	15.8	48.2	2.27
	2700	4.54	3.0	22.6	72.8	2.30

The room temperature compressive strengths of the G–20 ZrC composites increased with hot-working temperature (Table VI). The surfaces of composites after hot-working at 2700° C were smooth and free of cracks. The composites were firm and in no way friable. The room temperature compressive strengths were disappointing, reaching only 57 MPa at 2700° C. The microstructures were very similar to the hot-worked NG–20 NbC and NG–20 TaC composites. The carbides were fine, dense and uniformly dispersed. They were apparently undeformed at all temperatures.

It can be inferred that there was a lack of strong bonding between natural graphite and the carbides of zirconium, niobium and tantalum even after hot-working at 2700° C. There is an obvious similarity between the properties of hot-worked NG–20 Nb (NbC), NG–20 Ta (TaC) and G–20 ZrC composites.

The last composite material studied in this group was NG–20 W. There was an increasing tendency to barrel with increasing temperature. At 2700° C, barrelling became so severe that small fissures appeared on the outer surface parallel to the hot-working direction.

Samples for compression tests were cut from the centre of the composite, beyond the extent of the surface cracks. The room temperature compressive strengths in Table VI show a significant strengthening effect even at 2000° C. At 2700° C substantial strengthening had taken place, the composite having a room temperature compressive strength of 125 MPa.

Micrograpy (Figs 8a, b and c) revealed that at 2550° C, the morphology of the carbides was similar to that of the NG–20 Ta composite hot-worked at 2700° C. The porous agglomerates were spread out normal to the hot-working direction. There was, however, definite evidence of sintering and densification. At 2500° C the carbides were much less porous and

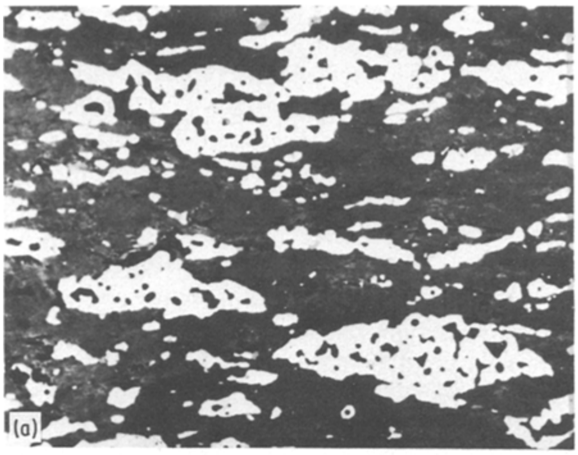
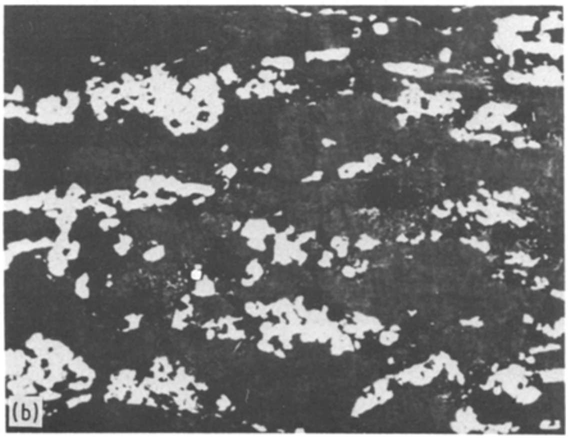


Figure 7 Microstructure of graphite–niobium composites (NG–20 Nb) hot-worked at 2250, 2500, 26700° C; × 225.



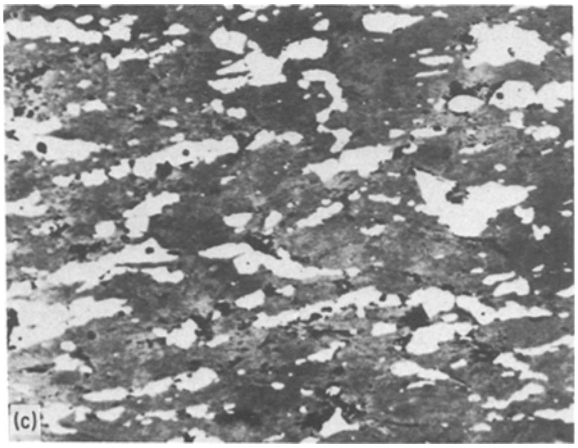


TABLE VI Densities of hot-pressed G–20 ZrC and NG–20 W composites

Compact	Hot-working temperature (°C)	Final apparent density (Mg m^{-3})	Density change (Mg m^{-3})	% hot-working strain at RT	RT compressive strength (MPa)	RT compressive strain (%)
NG-20 ZrC	2000	3.26	3.5	6.5	26.8	1.43
	2250	3.35	6.4	11.3	25.4	1.37
	2500	3.47	10.1	15.1	33.2	1.79
	2700	3.55	12.7	23.3	57.9	2.13
NG–20 W	2000	5.24	13.9	23.8	49.8	1.96
	2250	5.34	16.1	25.9	58.1	2.47
	2500	5.62	22.2	28.1	100.4	2.96
	2700	5.69	23.7	30.3	124.8	3.27

appeared to be more elongated in section. At 2700° C the porosity disappeared and the carbides were so spread out that in sections they appeared like strands. The graphite matrix was densified during hot-working, although some fissures were present after hot-working at 2700° C.

The density change after hot-working is recorded in Table VI. The density changes between 2000 and 2700° C were a result mainly of the densification of the carbides. Densification was substantial over the whole temperature range.

4.7. NG–vanadium

The final system studied in the preliminary investigations was NG–V. It had been shown that titanium was an effective strengthening agent. It was considered, therefore, that vanadium, which, in common with titanium, has a low melting point of the metal and a high melting point of the carbide, might also yield satisfactory results.

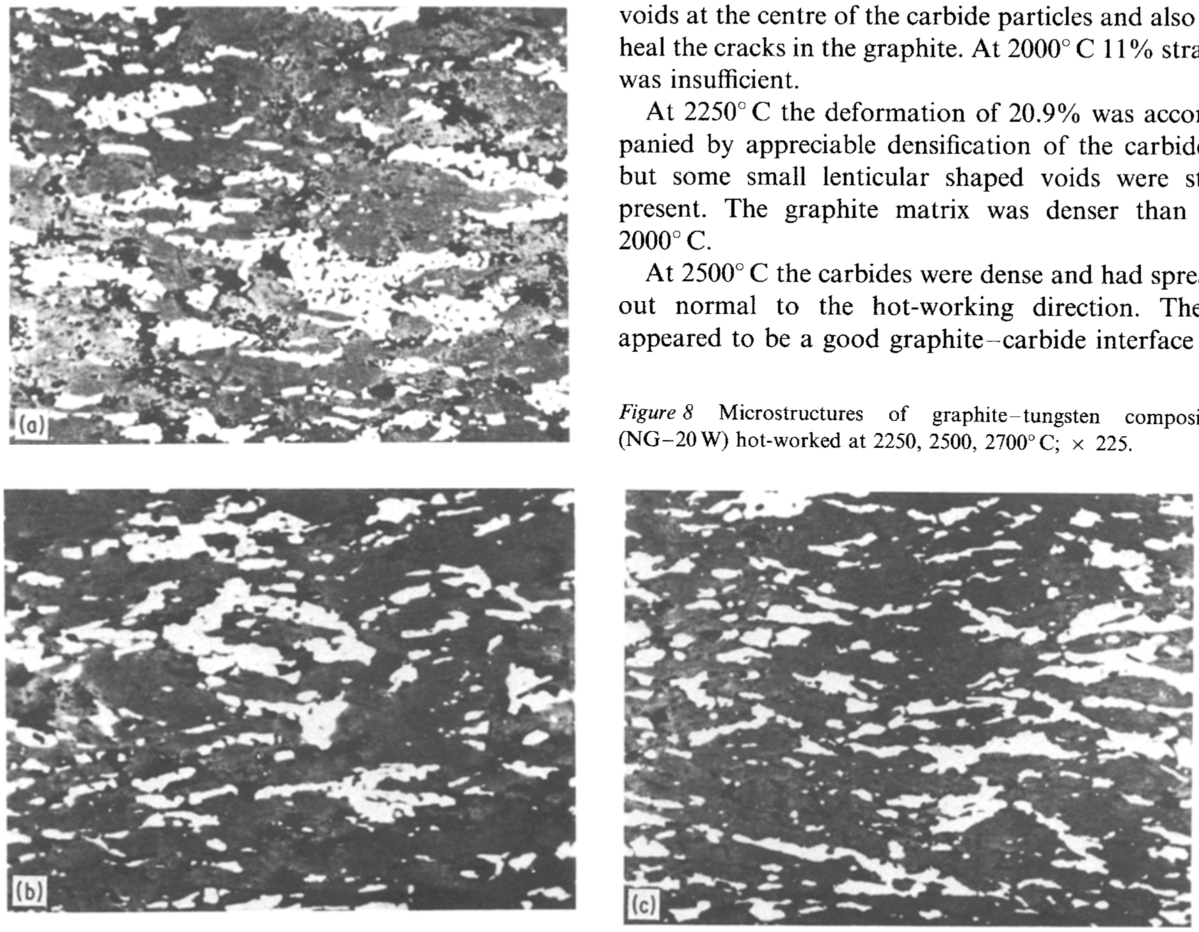


Figure 8 Microstructures of graphite–tungsten composites (NG–20 W) hot-worked at 2250, 2500, 2700° C; × 225.

Compacts of NG–20 V were hot-worked at 2000, 2250, 2500 and 2700° C using Method 2. The composites were not severely barrelled even after hot-working at 2700° C. At 2550° C and above the surfaces lost their smooth shiny appearance and became distinctly rippled, promising a high strength. At 2700° C large drops of liquid vanadium carbide, VC, were extruded from the free surface.

Composites hot-worked at 2250 and 2500° C underwent up to 25% room temperature deformation (Table VII). The room temperature compressive strength of the composite hot-worked at 2500° C was 145 MPa. This was the strongest material produced in the preliminary survey. The explanation for this apparently anomalous behaviour is found in photomicrographs (Figs 9a, b and c). At 2000° C the carbides appeared in the plane of polishing, as sections through hollow spheres, similar to the structure observed in heat treated G–Ti composites. Numerous cracks and fissures were present in the graphite matrix. Clearly, large plastic deformations were necessary to close the voids at the centre of the carbide particles and also to heal the cracks in the graphite. At 2000° C 11% strain was insufficient.

At 2250° C the deformation of 20.9% was accompanied by appreciable densification of the carbides, but some small lenticular shaped voids were still present. The graphite matrix was denser than at 2000° C.

At 2500° C the carbides were dense and had spread out normal to the hot-working direction. There appeared to be a good graphite–carbide interface at

TABLE VII Properties of hot-pressed NG–20 V composites

% hot-working strain at RT	RT compressive strength (MPa)	RT compressive strain (%)	Final apparent density ($Mg\,m^{-3}$)	Density change ($Mg\,m^{-3}$)
11.0	34.3	1.86	2.75	−0.20
20.9	81.9	2.03	2.95	0
26.3	145	2.65	3.18	0.23
40.0	100	2.37	3.01	0.06

2250 and 2500° C suggesting that a strong bond was formed after hot-working at these temperatures.

5. Optimization of the properties of graphite–titanium and graphite–vanadium composites

As a result of the preliminary survey, the G–Ti and G–V systems were selected for further investigation. In the first place the aim was to optimize both systems in terms of composition, hot-working temperature and load. Thereafter some studies of the mouldability of the composites were made to determine ease of fabrication. Composites were prepared with electrographite powder as well as natural graphite powder to determine whether any improvement in properties could be achieved thereby.

5.1. Effect of metal content

NG–30 Ti, NG–40 Ti and NG–30 V composites were prepared and hot-worked under a compressive load of 200 kg using Method 2. The NG–Ti composites were worked at 2700° C and the G–V at 2500° C. The samples were sectioned for mechanical testing and metallography. The properties of these composites, together with those obtained in the preliminary investigations are summarized in Table VIII.

The data in Table VIII indicate that the hot-working strain increased with metal content. Since natural graphite was strained to only 5.1% after hot-working at 2700° C, the extra strain must be due mainly to bulk deformation of the carbides. The results plotted in Fig. 10 show that the relationship is linear.

The room temperature compressive strength also increased linearly with metal concentration (Fig. 11). The slopes of the two lines demonstrate that vanadium was a more efficient strengthening additive.

Composites, compression tested at room temperature, were strained by deformation of the matrix graphite. Table VIII shows that this strain decreased with increasing metal concentration. These results suggest that the graphite was continuous. This is supported by the optical micrographs in Figs 12 and 13.

The microstructure of the hot-worked G–30 V sample shows there is a good graphite–carbide interface with very few gaps (from which particles have been torn during polishing). The graphite matrix is dense and free of cracks and fissures. Average carbide particles size is greater in the G–30 V composite than in the G–20 V composite.

The microstructures of the hot-worked G–30 Ti and G–40 Ti composites when compared to the G–15 Ti and G–25 Ti composites show clearly that the average carbide particle size tends to increase with titanium concentration. This observation will be discussed later. The ease of polishing these surfaces again indicates a good graphite carbide interface suggesting a strongly bonded structure.

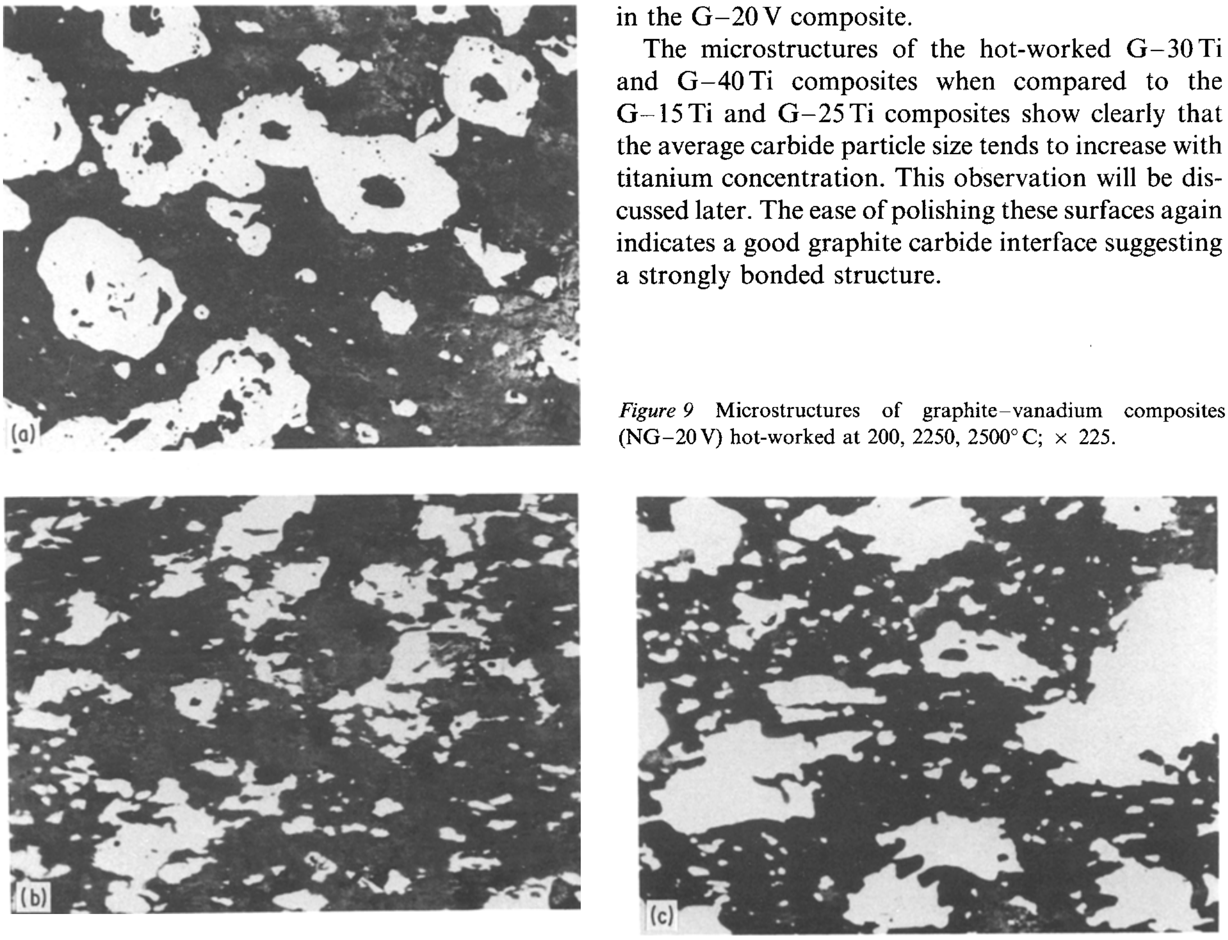


Figure 9 Microstructures of graphite–vanadium composites (NG–20 V) hot-worked at 200, 2250, 2500° C; × 225.

TABLE VIII Effect of metal content on the properties of hot-pressed NG–Ti and NG–V composites

Compact	% hot-working strain	RT compressive strength (MPa)	RT compressive strain (%)	Final density ($Mg\,m^{-3}$)	% density change
G–5Ti	8.2	30	2.65	2.19	−1.8
G–15Ti	22.3	82	2.43	2.53	5.0
G–25Ti	35.6	140	2.27	2.89	11.6
G–30Ti	47.0	170	1.89	3.15	17.9
G–40Ti	62.1	214	0.82	3.55	25.5
G–20V	25.0	145	2.65	3.18	7.2
G–30V	38.2	245	1.46	3.55	16.0

5.2. Effect of hot-working load

Clearly, the amount of hot-working strain is the most important single parameter controlling the strengthening of graphite–metal composites. The only way to increase the strain at a particular temperature is to increase the compressive load.

NG–30Ti was chosen to study the effect of hot-working load on room temperature compressive stress. Samples were hot-worked at 2700° C under compressive loads of 200, 300 and 400 kg. It was found that under 300 and 400 kg the hot-worked samples were severely barrelled and cracked on the outer surface. The cracks were aligned parallel to the hot-working direction. The properties of these composites are recorded in Table IX.

At 2700° C the hot-working strain increased with applied load. The room temperature compressive strength, however, decreased. The decrease is attributed to cracks, formed as a result of barrelling. The final apparent densities also decreased with load.

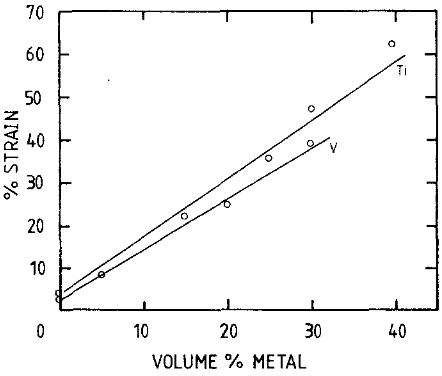


Figure 10 Possible hot-working strain against volume fraction titanium and vanadium in composites with graphite.

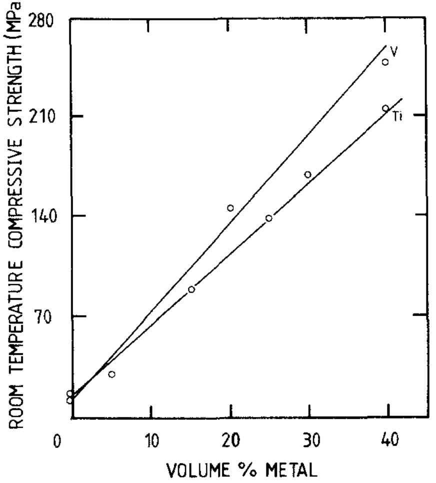


Figure 11 Compressive strength of hot-worked vanadium/titanium–graphite composites against volume fraction metal.

5.3. Die-moulding of natural graphite–titanium and vanadium composites

In an effort to increase the hot-working strain and inhibit barrelling, compacts were hot-worked into cylindrical graphite dies of diameter slightly greater than that of the samples. The dies, (Fig. 14) machined from EY9 electrographite, were 25 mm in height with a wall thickness of 5 mm. The lower surface of the die rested on an end-plate (an electrographite disc) which was positioned on the lower compression anvil in the furnace.

The sample slid down the bore of the die to rest on the end-plate. An electrographite plunger rested on the upper surface of the sample. The upper compression anvil was positioned on top of the plunger, ready for hot-working in the usual manner.

NG–25Ti samples hot-worked under 400 kg load using the above die had a room temperature compressive strength less than a sample hot-worked under 200 kg without die (see Table IX). The densities of the two samples were similar, but the strain in the composite hot-worked in the die was less than in the hot-worked free-standing sample. The relatively low strength of the NG–25Ti composite pressed into a 14.5 mm diameter die suggested that in order to achieve maximum strengthening, some radial strain was necessary during hot-working. The experiments were, therefore, extended further, to study the effect of pressing into dies of diameter greater than that of the

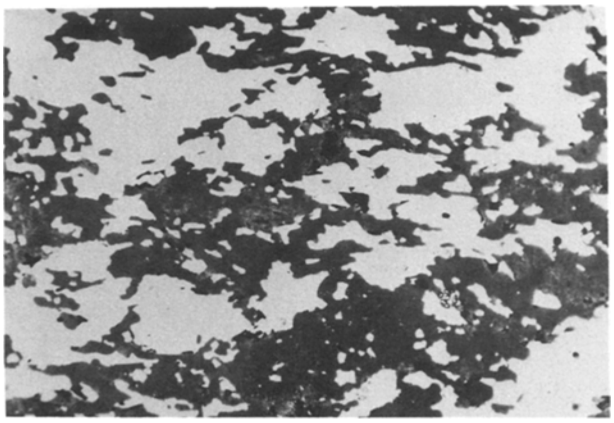


Figure 12 Microstructures of graphite–vanadium composite (NG–30V) hot-worked at 2500° C; × 280.

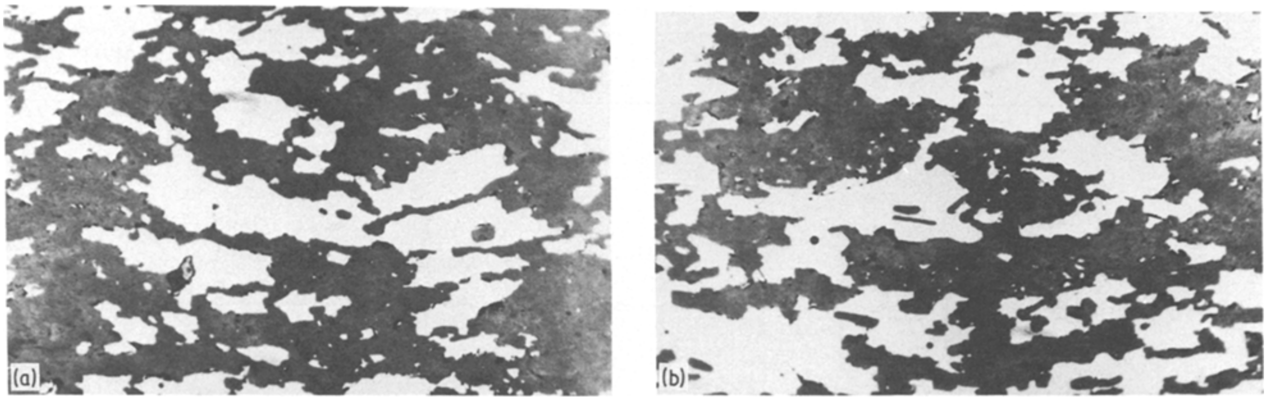


Figure 13 Microstructures of graphite–titanium composites (NG–30 Ti) hot-worked and die-moulded at 2700° C; × 275.

sample. In this way 14 mm diameter compacts were pressed into 16.5 mm diameter and 19.0 mm diameter dies under a compressive load of 300 kg. The properties of some of these hot-worked composites are shown in Table X.

Samples took up the shape of the dies almost exactly. The radial strains were limited by the walls of the dies. The longitudinal strains were similar to those of the equivalent free-standing composites. Barrelling must have occurred during the initial stages of deformation but the later deleterious stage was effectively constrained by the die wall so that there was no evidence of cracking on the surface of samples (see Fig. 15).

For room temperature compression tests small samples were cut from the hot-worked composite, from the edge and from the centre. Specimen were tested normal and parallel to the hot-working direction. Table X shows that the strength normal to the hot-working direction was only slightly less than that parallel. The room temperature compressive strains in both directions were also very similar. The final material was therefore fairly isotropic. The strengths of these die-pressed composites were significantly greater than those of the corresponding free-standing composites.

5.4. Die-moulding of electrographite–titanium and vanadium compacts

A final set of experiments was performed to study the effects of replacing the natural graphite matrix with electrographite using technology developed previously [11] for pure synthetic graphite powder. For this research, micronized electrographite powder was acquired with an average particle size of 8 μm. This powder compacted fairly easily giving green compacts with a room temperature compressive strength of 9.1 MPa. A range of compacts were prepared with titanium and vanadium powders. The properties of the as-pressed compacts are shown in Table XI. The as-pressed electrographite composites were weaker and more friable than the as-pressed natural composites. There were cracks present, aligned normal to the pressing direction, on the cylindrical surface of all the compacts. The cracks resulted from expansion in the pressing direction after ejection from the die. The apparent compact densities were therefore much lower than the theoretical value (see Table XI). The deviation from the theoretical densities was much greater than with the corresponding NG compacts. Increasing volume fractions of titanium resulted in only small increases in the green strength.

TABLE IX Effect of hot-working load on the properties of NG–Ti composites

Compact	Hot-working load (kg)	% hot-working strain	Density change (Mg m^{-3})	RT compressive strength (MPa)
G–30 Ti	200	47.0	0.48	170
	300	60.0	0.46	155
	400	66.0	0.42	120
G–25 Ti	200	35.6	0.30	140
	400*	27.0*	0.28*	120*

*Pressed into a 14.5 mm diameter graphite die.

TABLE X Properties of NG–Ti composites hot-pressed into dies

Compact	% hot-working strain (longitudinal)	% radial strain (lateral)	Final density (Mg m^{-3})	Compressive strength (MPa)
NG–30 Ti pressed into a 16.5 mm diameter die	41	12.5	3.14	239
NG–40Ti pressed into a 19.0 mm diameter die	65	27.8	3.5	252 ± 10*

*Mean of four sectional specimens cut in different directions.

TABLE XI Properties of as-pressed electrographite–titanium and vanadium compacts

Compact	Apparent density ($Mg\,m^{-3}$)	Theoretical density ($Mg\,m^{-3}$)	% deviation from theoretical density	RT compressive strength (MPa)
EG	1.70	2.26	22.1	9.1
EG–25 Ti	2.32	2.82	17.7	9.8
EG–30 Ti	2.39	2.94	18.7	11.2
EG–40 Ti	2.34	3.16	26.8	13.0
EG–30 V	2.89	3.41	15.5	12.0

TABLE XII Properties of hot-pressed and die-moulded electrographite and titanium and vanadium composites

Compact		% hot-working strain	Final density ($Mg\,m^{-3}$)	RT compressive strain (%)	Compressive strength (MPa)
EG–25 Ti	hot-pressed under 200 kg	43.1	2.92	2.33	162
EG–30 Ti	hot-pressed under 200 kg	62.7	3.09	1.34	262
EG–40 Ti	die-moulded into a 19.05 mm diameter die under 300 kg	54.6	3.55	0.29	392
EG–30 V	hot-pressed under 200 kg	62.3	3.54	1.24	291
EG–30 V	die-moulded into a 19.05 mm diameter die under 300 kg	58.9	3.54	0.41	406

EG–Ti and EG–V compacts were hot-pressed and die-moulded at 2700 and 2500° C, respectively. The results are given in Table XII. A large proportion of the hot-working strain was taken up in recovering the expansion of the compact after ejection from the die. A true value of the strain is difficult to estimate.

In spite of the low density of the as-pressed materials, the final apparent densities of the hot-worked EG composites were very similar to those of the corresponding hot-worked NG composites.

The EG–40 Ti and EG–30 V composites hot-pressed into dies took up the shape of the dies exactly. The room temperature compressive strengths are recorded in Table XII.

The room temperature compressive strengths of the hot-worked, free-standing EG–25 Ti and EG–30 Ti composites were significantly greater than the corresponding natural graphite composites. The result of hot-pressing the EG–40 Ti compact into a die was to produce an extremely strong composite material. The room temperature compressive strength of 392 MPa is by far the highest strength achieved with composites containing titanium.

An even greater strengthening effect was obtained with EG–V composites with a lower volume fraction of metal. Table XII shows the effect of hot-working EG–30 V compacts with and without die. The composite pressed into the die is almost 50% stronger than the hot-pressed free-standing composite. The room temperature compressive strength of 406 MPa represents the highest value obtained during this research programme.

The results demonstrate clearly that an electrographite matrix is strengthened to a much greater degree than natural graphite. The micrographs in Figs 16 to 19 help to explain this. The carbide particles in the EG composites are much finer, more uniform in size and more evenly distributed than in the NG composites. The carbide particle size is much finer in the hot-worked EG–V composites than in the EG–Ti composites and reflects the higher strength of the EG–V composites. The coherent EG–carbide interface

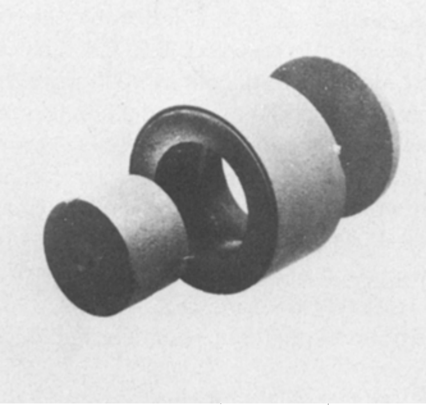


Figure 14 Electrographite mould pieces for hot die-moulding above 2000° C.

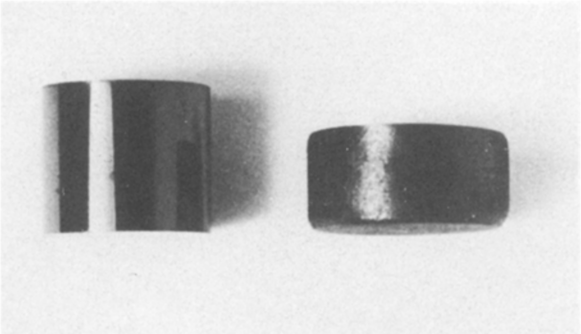


Figure 15 Natural graphite–titanium composites (NG–30 Ti) before and after die-moulding at 2700° C.

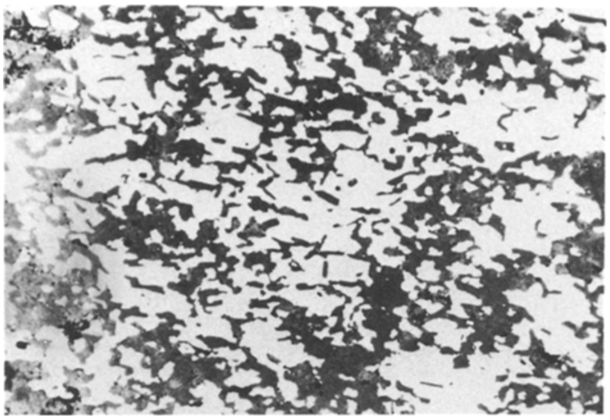


Figure 16 Microstructure of electrographite–titanium composite (EG–40 Ti) die-moulded at 2700° C; × 280.

also indicates strong bonding. The effect of larger plastic strains in die-moulding over those induced in straight pressing is also apparent in Figs 18 and 19. There is a finer distribution of carbide particle because of diffusion of metal and metal oxide into all available porosity.

The electrographite is free of cracks and fissures and is still the continuous phase in the EG–30 Ti, EG–30 V and EG–40 Ti composites. The holes in the graphite in some of these composite sections are polishing artefacts; the hard carbide particles prevent contact between the graphite and the polishing surface.

6. Discussion

6.1. Hot-working behaviour

The fundamental operations used to produce NG–metal (carbide) composites are analogous to the standard powder metallurgy technique of cold compaction of powder mixtures followed by sintering under pressure. The hot-working step can be called "activated sintering", either liquid-phase sintering as described by Kingery [15] or sintering in the presence of "metallic activators". In simple terms, a second phase acts as a path for mass transport of material to preferred sites, thereby increasing the density and activating sintering. The simple kinetics of the thermally activated processes occurring during compressive hot-working, i.e. creep and diffusion, have already been studied by Matthews [8].

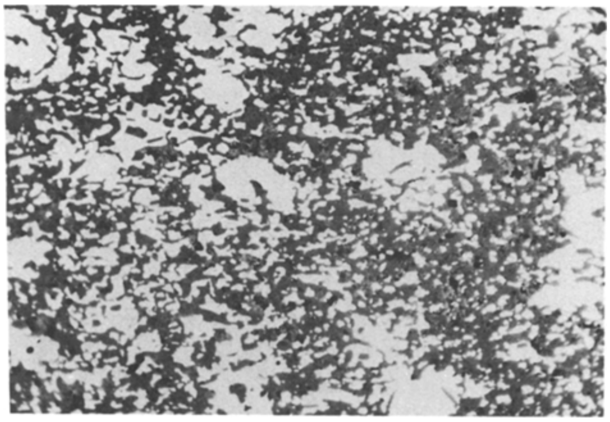


Figure 17 Microstructure of electrographite–vanadium composite (EG–30 V) die-moulded at 2500° C; × 280.

In multiphase systems such as have been studied in this work, it is apparent that more than one mechanism is operating simultaneously during hot working. Some of the systems were characterized by the formation of a liquid phase at some stage in the hot-working process. In others no liquid phase at all was formed up to or at the hot-working temperature.

6.2. NG–titanium and vanadium/graphite systems

The first system studied, NG–Ti, was one in which a transitory liquid phase formed during the heating-up period. According to the phase diagram [16] an individual titanium particle is not completely solid until the carbon/titanium atom ratio has reached 0.5 to 0.7.

Heat treatment of NG–Ti compacts produced hollow spherical particles which X-ray analysis showed to be TiC. It is possible that liquid, which first forms at 1668° C, agglomerates by capillary action with closely adjacent droplets. There is a driving force to lower the overall surface energy. The periphery of the droplets in close contact with the graphite reacts to form TiC.

TiC is a solid at approximately 1700° C and occupies a smaller volume than titanium. As the solid peripheral shell of TiC grows by diffusion of carbon atoms inwards, the titanium shrinks outwards from the centre, leaving a void. There is considerable porosity in the carbides and the graphite. This accounts for the large hot-working strains encountered in G–Ti composites hot-worked using Method 1. Further heating, after complete conversion of TiC, sinters out the porosity in the particle walls.

A load applied to a G–Ti compact during the heating-up process forces liquid through fissures and into pores in the graphite aiding its re-distribution to ideal sites. The droplets are spread out more and react more quickly under pressure. After hot-working by Method 2, the particles are finer and more elongated than normal to the hot-working direction. Thus Method 2, apart from eliminating much of gross thermal expansion on heating, also has an important effect on the morphology of the carbides. The result, as Table IV indicates, is the production of significantly stronger composites.

V–G composites also undergo solid–liquid–solid phase transformations. The melting point of vanadium is 1880° C. According to the phase diagram [16], above 1630° C a particle is not solid until the carbon/vanadium atom ratio reaches 0.3 to 0.4. The carbides are present as hollow spheres at 2000° C, even after hot-working. The explanation for their formation is similar to that for the heat treated G–Ti composites. In this case, however, there is a shorter composition range over which liquid is present. Transformation to the carbide V_2C occurs more rapidly allowing less time for dispersion of liquid. The carbide particles are probably relatively deformation resistant at 2000° C so that the hollow spheres are not densified during hot working.

Up to 2250° C, any V_2C formed during the heating process transforms via a peritectic reaction:

$$V_2C \rightleftharpoons \text{liquid} + VC$$

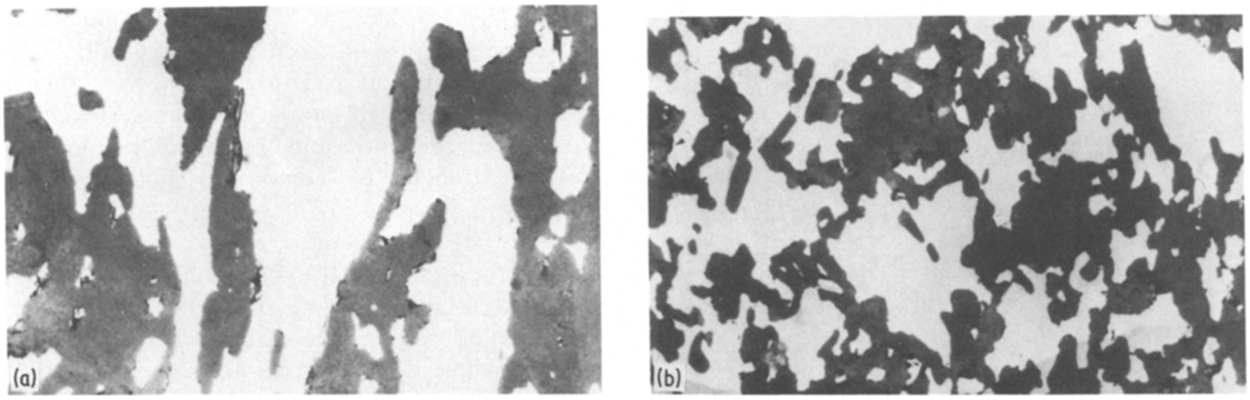


Figure 18 Microstructures of electrographite–titanium composite (EG–30 Ti): (a) hot-pressed; (b) die-moulded at 2700° C; × 60.5.

All the remaining liquid then transforms by diffusion directly to VC. 2250° C is closer to the melting point of VC (2700 ± 50° C). The carbides deform more easily which enhances the formation of any bond with the graphite.

Deformation and bonding is further enhanced at 2500° C by the wide composition range at which liquid is present. Also, the VC is close to its melting point and is easily deformed. Thus the strength of hot-worked G–V composites is greatly increased with rise in temperature between 2000 and 2500° C.

The enormous increase in strength of hot-worked NG–Ti and NG–V composites over hot-worked NG must result from the formation of strong carbide–graphite bonds. Scanning electron micrographs (Fig. 20) of the fracture surfaces of a G–40 Ti composite hot-worked at 2700° C indicate that TiC forms bonds at the edges of the graphite flakes. The strong preferred orientation in these NG composites is clearly visible with much parallel alignment of flakes.

The folded and convoluted structure in electrographite particles is well illustrated in Fig. 21 which shows the fracture surface of a titanium–electrographite composite (EG–40 Ti) hot-worked at 2700° C. Again the carbide particles appear to forge edge-to-edge bonding of graphite sheets. The preferred orientation is much less pronounced than in the equivalent NG composite. The carbide therefore cements the graphite sheets to form a three-dimensional framework of greater rigidity in EG than in NG.

A dispersion of such carbide particles throughout the composite will "cement" graphite flakes together and impede shear of basal surfaces. Hot-working has forced the carbides into crevices between the flakes improving contact and enhancing the formation of a bond. It is logical to conclude that any method which serves to distribute the carbides in a finer dispersion will enhance the cementing effect and increase the strength of the composite.

Matthews has shown [8] that during cold compressive deformation a fracture path propagates through the graphite matrix, and that the crack length depends on the number of interactions with carbide particles. Consequently, the mere presence of bonded particles should serve to strengthen the graphite by simply increasing the energy of crack propagation.

6.3. Other graphite–metal systems

The phase diagrams [16] for C–Nb and C–Ta are very similar to those of C–V, but on a higher temperature scale. Some liquid forms above about 2335° C during the hot-working of G–Nb composites. No liquid forms up to 2700° C with G–Ta composites. G–20 Ta and G–20 Nb composites strengthen very little between 2000 and 2700° C. The reason for the lack of strengthening is that NbC and TaC do not form sufficiently strong bonds with graphite. Stereoscan studies of the fracture surfaces revealed no well bonded carbide particles such as those found in G–Ti and G–V composites. The addition of the carbides to the original mix does not significantly increase the final strength. Although dense undeformed particles are observed on the fracture surface of G–20 NbC hot-worked at 2700° C, again there was no evidence of bonding.

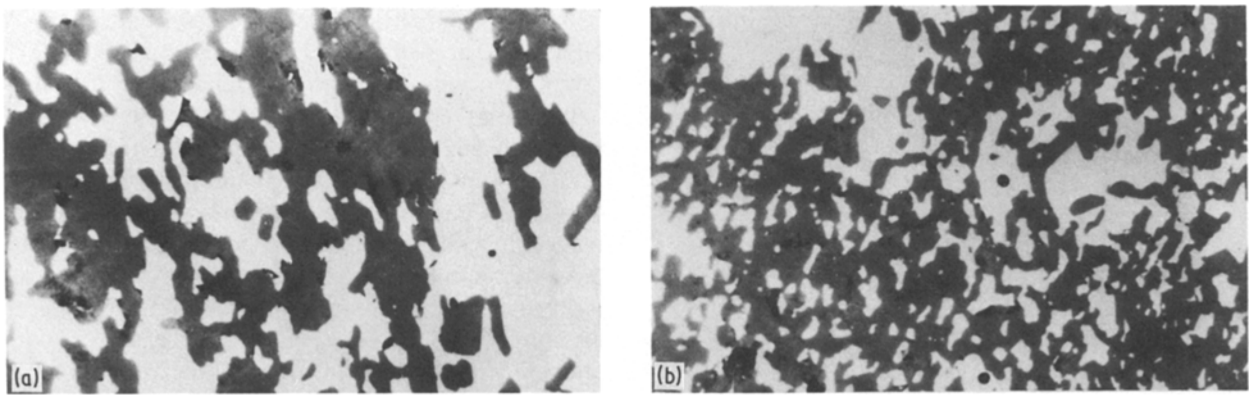


Figure 19 Microstructures of electrographite–vanadium composite (EG–30 V): (a) hot-pressed; (b) die-moulded at 2500° C; × 60.5.

Figure 20 Scanning electron micrograph of a fracture surface of a natural graphite–titanium composite (NG–40Ti) hot-worked at 2700; × 2000.

Tungsten is a good strengthening agent. The results compare favourably with those of the G–Mo composites studied by Matthews and co-workers [7, 8]. The C–Mo and C–W phase diagrams are similar in construction [16]. Matthews pointed out that the solubility of carbon in MoC_{1-x} decreased between 2580 and 1960° C. On cooling between these temperatures, graphite precipitates from the carbide. The graphite crystals grow and split the carbides into smaller particles, decreasing the average particle size.

The W–C phase diagram also exhibits a decreasing solid solubility line, of carbon in WC_{1-x}. The range is narrower than for MoC_{1-x} and occurs between 2530 and 2720° C. X-ray analysis shows that WC_{1-x} is present at 2700° C. Photomicrographs suggest that some fragmentation of the carbides has occurred after hot-working at 2700° C and that the average particle size has decreased. If, as Matthews [8] claimed, the nucleation and precipitation process contributes to the strengthening of NG–Mo composites, then it could well be effective in NG–W composites and is possibly reflected in the good room temperature compressive strength of composites hot-worked at 2700° C.

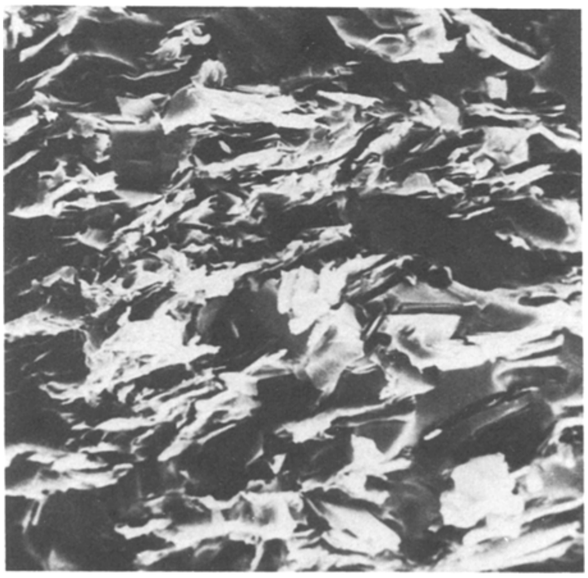


Figure 21 Scanning electron micrograph of a fracture surface of an electrographite–titanium composite (EG–40Ti) hot-worked at 2700; × 2000.

6.4. Comparison of the systems

The method and function of the bonding between graphite and the various carbides has been established. The question now arises as to why the carbides exhibit such a wide range of strengthening efficiences, e.g. NG–Ti compared to NG–Ta.

The thermal expansion data for these materials [14, 16, 17] is incomplete but the available information suggests that the coefficients of thermal or structural deterioration caused by differential thermal contraction on cooling would be common to all the composites and therefore does not explain the wide difference in properties.

The heats of formation [14, 16, 17] indicate that molybdenum carbides are amongst the least stable, yet high strength G–Mo composites can be produced at relatively low hot-working temperatures. The carbides of niobium, tantalum, zirconium, etc., are much more stable, but their hot-worked composites are weak.

Since wetting and bonding probably involve atomic interaction between the carbides and graphite, then all the carbides would be expected to wet and form strong interfacial bonds with graphite. Matthews and Jenkins [9] have shown that the carbides of titanium, zirconium and niobium readily wet graphite but do not bond below 2500° C. Matthews and Jenkins [9] show that for NG–Mo the interfacial strength is aided by the epitaxial fit between Mo_2C and graphite. According to the lattice parameters, this model would not apply to any other carbide. But, titanium, vanadium and tungsten carbides do bond, so some strong interatomic arrangement must exist at a high enough temperature.

The explanation does not lie in the phase relationships between the respective metals and carbon. The existence of a decreasing solid solubility for MoC_{1-x}, resulting in precipitation of graphite and splitting of the carbides, is an insufficient criterion to label the G–Mo system as unique. The G–Ti and G–V systems do not exhibit a decreasing solubility line, yet they strengthen significantly.

A close examination of the melting points in Table XIII together with the phase diagrams [14, 16, 17] reveal an interesting trend in relation to the room temperature compressive strengths. The lower the minimum permanent liquid temperature for the composite, the greater the strengthening effect after hot-working. Clearly the strongest materials are produced from composites which can be hot-worked as close as possible to, but below, this temperature.

Furthermore, a graph of maximum room temperature compressive strength against hot-working temperature (Fig. 22) indicates an upward trend for all the composites (see also Table XIV). The logical conclusion from these results is that all the refractory

TABLE XIII Properties of carbides

Carbide	Approximate melting point (°C)	Heat of formation (kJ mol^{-1})	Coefficient of thermal expansion (10^{-6} °C^{-1})	Density (Mg m^{-3})
Mo_2C	2410	−23	6.15	9.06
MoC_{1-x}	2550	−12.5	5.95	9.46
W_2C	2800	−26.4	4.72	17.2
WC	2755	−35.2	5.82	15.77
Nb_2C	3160	−97.5	−	7.8
NbC	3480	−141	7.46	7.79
Ta_2C	3400	−193	−	15.22
TaC	3880	−159	6.67	14.48
V_2C	2200	−69	−	5.66
VC	2830	−103	−	5.65
TiC	3140	−240	7.9	4.94
ZrC	3420	−206	7.65	6.57

carbide–natural graphite composites studied are capable of being strengthened provided the hot-working temperature is sufficiently high.

7. General conclusions

It is concluded that, in general, the addition of refractory metal carbides increases the plasticity of graphite matrices in such a way as to allow us to densify and strengthen the composites appreciably by hot-working at temperatures less than those required for densification of electrographite. Exceptionally strong composites are made by introducing titanium and vanadium carbides into electrographite matrices and artefacts can be made in a one-stage process by the rapid moulding of metal/graphite powder mixes in electrographite dies a little above 2000° C. Both G–Ti and G–V composites, in particular, are very amenable to die-moulding. The ease with which these composites press into the dies suggests that an extension to more complicated shapes would also prove successful. Ductility increases with initial metal content. Increasingly complicated shapes would require increasingly higher initial metal contents to facilitate moulding.

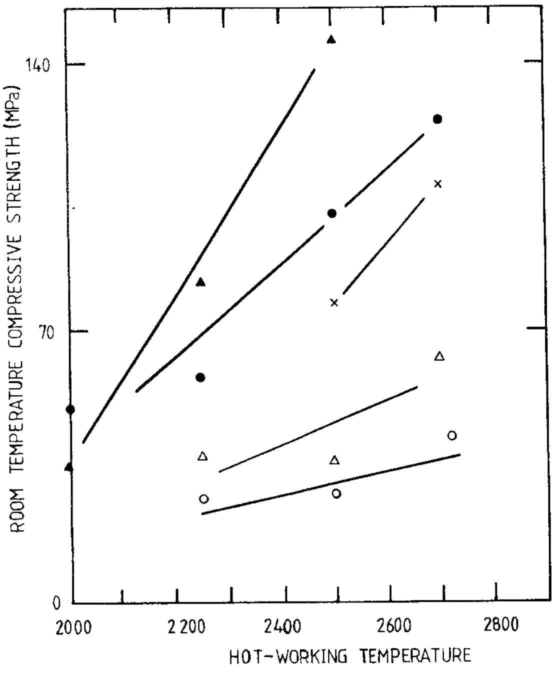


Figure 22 Compressive strengths of NG–20 vol % metal composites against hot-working temperature for ▲ vanadium, ● tungsten, x titanium, △ niobium, and ○ tantalum systems.

TABLE XIV Relationship between composite strength and minum permanent liquid temperature*

Compact	Maximum hot-working temperature (°C)	Maximum RT compressive strength (MPa)	Minimum permanent liquid temperature (°C)
G–20 Mo	2500	140	2580
G–20 V	2500	145	2700
G–20 Ti	2700	105	2776
G–20 W	2700	130	2776
G–20 Nb	2700	65	3300
G–20 Ta	2700	42	3400
G–20 ZrC	2700	60	3420

*From the phase diagrams [14, 16, 17].

The materials themselves are not as strong at room temperature as, say, Al_2O_3/ZrO_2 composites or hot-pressed SiC but they can be more shock resistant, will conduct electricity and heat well and will retain appreciable strength to higher temperatures albeit in an oxygen-free ambience. The densification process removes available porosity and so oxidation burn-off rates in oxygen at high temperatures are lowered. The materials retain the high lubricity of graphitic materials.

Moreover, the V–EG and Ti–EG composites have useful compressive strength in excess of 400 MPa which is a great improvement on mechanical grade electrographites with compressive strengths of between 40 and 50 MPa. Densifying and hot-working such electrographite above 2700° C does improve this to a little above 90 MPa. Even densified three-dimensional orthogonal weave carbon fibre-reinforced carbon composites, which are the strongest "isotropic" carbons on the market [18], exhibit strengths only marginally greater than 160 MPa and so do not approach the strengths of V–EG composites described here.

Applications of these materials would be found in the aerospace industries as light-weight refractory components, for spark-machining electrodes and, because of the proven biocompatibility of both titanium and graphite, in implantable prostheses for joints, etc. [19].

Further work has been carried out on the introduction of various metal and silicon powders to densify and strengthen carbon fibre-reinforced carbon matrices and this will be described and discussed in a following paper.

Acknowledgement

D. John was in receipt of a grant from the UK Science and Engineering Research Council.

References

1. M. HUMENIK, D. W. HALL and R. L. VAN ALSTEN, *Metal Prog.* **18** (1962) 101.
2. J. L. WHITE and R. J. PRICE, *Carbon* **2** (1965) 327.
3. J. L. WHITE and J. M. PONTELANDOLFO, *ibid.* **4** (1966) 305.

4. *Idem, ibid.* **6** (1968) 1.
5. J. L. WHITE and K. KOYAMA, *J. Amer. Ceram. Soc.* **51** (1968) 51.
6. Y. HARADA, "Graphite-Metal Carbide Composites", NASA Contractor Report (Illinois Institute of Technology Research Institute, Chicago, Illinois, 1966).
7. R. B. MATTHEWS, D. B. FISHBACH and G. M. JENKINS, "The Compaction and Hot Working of Graphite-Molybdenum Carbide Composites", presented to The Third Conference on Industrial Carbons and Graphite, London (1970), pp. 515–9; also UK Patent 58501/69 "Graphite/Metal Composites".
8. R. B. MATTHEWS, PhD thesis, University of Wales (1971).
9. R. B. MATTHEWS and G. M. JENKINS, *J. Mater. Sci.* **10** (1973) 1976.
10. J. R. MAY, Proceedings of the Fifth Conference on Carbon, Vol. I (Pergamon Press, 1961) p. 611.
11. R. H. DeVERE, V. FIDLERIS, G. M. JENKINS and J. W. PHILLIPS, *Powder Metall.* **11** (1963) 23.
12. D. JOHN, MSc thesis, University of Wales (1974).
13. G. M. JENKINS and D. JOHN, Proceedings of the Fourth International Carbon and Graphite Conference London (1974) (Society of Chemical Industry, 1976) pp. 304–9.
14. E. K. STORMS, "The Refractory Carbides" (Academic Press, New York, 1967).
15. W. D. KINGERY, *J. Appl. Phys.* **30** (1959) 301.
16. H. J. GOLDSCHIDT, "Interstitial Alloys" (Butterworths, London, 1967).
17. P. T. B. SCHAFFER, "High Temperature Materials" (Plenum Press, New York, 1964).
18. L. E. McALLISTER and W. L. LACHMAN, "Handbook of Composites", Vol. IV "Fabrication of Composites", edited by A. Kelly (North Holland, 1983) pp. 109–75.
19. G. M. JENKINS, *Clin. Phys. Physiol. Meas.* **1** (1980) 171.

Received 23 July
and accepted 23 October 1985