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Carbothermic reduction as a potential means for the direct production of Fe–WC and Fe–TaC, NbC metal–matrix composites

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The carbothermic reduction of wolframite and columbite ores has been studied as a means of direct production of Fe–WC and Fe–TaC/NbC composite materials. In both cases reduction with graphite at 1600 °C produces a good dispersion of carbides in an austenitic iron matrix. Gangue oxide materials appear to separate, largely as a slag phase. Some residual porosity has however been found in the product materials.

1. Introduction

Cemented carbides are a class of metal-matrix composites comprising tungsten carbide with niobium, tantalum and titanium carbides bonded together with a cobalt matrix. They are widely used for cutting and wear-resistant applications. These materials are produced by the separate production of WC and its subsequent combination with cobalt by a combination of powder metallurgy and liquid-phase sintering [1].

The replacement of the Co binder by a less expensive matrix is clearly desirable; to this end Agte [2] and Moskowitz [3] have, for example, attempted to replace Co with Fe or Fe–Ni alloys. If cheaper process routes to the final cemented carbide can also be developed, it is to be anticipated that a significant increase in the range of applications will result.

In a previous study [4] the present authors demonstrated that the addition of NiO to $FeWO_4$ prior to its carbothermic reduction results in the production of an Fe–Ni–WC mixture. The material produced, however, was very porous. In the present investigation reduction of $FeWO_4$ has been carried out at a higher temperature, 1600 °C, in an attempt to produce a denser material. The main aim has been to investigate whether dispersion of WC, produced *in situ* in liquid Fe–Ni matrices, is possible. Such conditions could lead ultimately to a production route whereby a wear-resistant composite material could be produced in one step direct from raw materials. The use of liquid-state processing will assist in the production of near-net-shaped final components. In addition it has been found that for TiC the production of the carbides *in situ* in the liquid iron aids dispersion [5]. It is likely that similar considerations will apply to WC dispersion.

The reduction of a columbite concentrate with nickel oxide additions has also been investigated in an attempt to identify conditions whereby an Fe–TaC–NbC–TiC composite material can be produced by *in situ* reactions direct from columbite raw material.

2. Experimental Procedure

Reduction/carburization experiments were performed in the apparatus shown in Fig. 1. An impervious alumina reaction tube, closed at both ends and with water-cooled brass heads, was located in the centre of the furnace. A further tube of mullite was placed outside the reaction tube in order to obtain a more uniform temperature distribution. A crucible could be

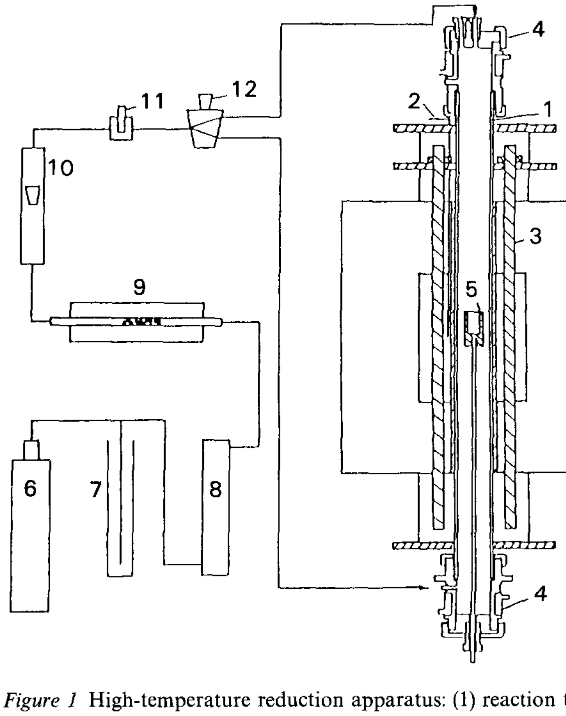

Figure 1 High-temperature reduction apparatus: (1) reaction tube, (2) thermocouple, (3) heating element, (4) brass head, (5) crucible, (6) argon cylinder, (7) blow tube, (8) Magnesium perchlorate tower, (9) titanium furnace, (10) rotameter, (11) needle valve, (12) two-way tap valve.

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TABLE I Chemical analysis of wolframite and columbite ores (wt %)

Wolframite		Columbite	
WO_3	42.2	Nb_2O_5	56.5
Fe_2O_3	22.16	Ta_2O_5	6.5
FeO	9.93	FeO	14.37
MnO	3.0	Fe_2O_3	6.12
SiO_2	3.9	MnO	1.93
SnO_2	11.49	CaO	0.08
PbO	0.05	SiO_2	0.8
CaO	0.56	SnO_2	0.99
CuO	0.08	TiO_2	4.98
		Al_2O_3	0.38

TABLE II Phases produced by the reduction of natural wolframite and nickel oxide with graphite at 1600 °C for 1 h

Run	NiO addition (wt %)	Fe:Ni ratio in binder	Phases present
R1	0	–	M_6C, β-Sn, Fe, α-W_2C
R2	7.5	4:1	Fe, WC, γ-(Fe, Ni), β-Sn, M_6C (trace)
R3	10	3:1	β-Sn, WC, α-W_2C, γ-(Fe, Ni)
R4	30	1:1	β-Sn, WC, α-W_2C, γ-(Fe, Ni)
R5	90	1:3	β-Sn, WC, α-W_2C, γ-(Fe, Ni)

raised rapidly into or withdrawn from the hot zone of the furnace by means of a mullite rod. The temperature profile of the furnace gave a hot zone 4 cm in height in which the temperature variation was ± 1 °C.

All reduction experiments were performed in an atmosphere of argon flowing at $1\ l\,min^{-1}$, measured at ambient temperature. The reductant–oxide mixtures were such that the mixture contained the stoichiometric quantity of carbon required for all the oxygen to form CO. Samples were thoroughly mixed by keeping them on rolls overnight before pelletizing. The samples used were in the form of pellets approximately 6 mm in height, made by pressing in a closed die of 6.25 mm diameter under a pressure of $2\ tonne\,cm^{-2}$.

The sample was contained in a recrystallized alumina crucible placed in a larger graphite crucible. The sample was initially kept at the water-cooled end of the furnace and was then raised up to the hot zone with the support rod to commence the experiment. After reduction the crucible was lowered to the water-cooled end and kept there for 30 min before removal.

The chemical composition of the columbite and wolframite ores used in the investigation is given in Table I. Specpure graphite of pelletable grade with a total maximum impurity content of 5 p.p.m. was employed as a reductant. Nickel oxide used as an additive in reduction experiments was employed in the form of a reagent grade salt. The product phases obtained in the experiments were examined by X-ray diffraction and optical and scanning electron microscopy.

3. Results and discussion

3.1. Carbothermic reduction of wolframite

Wolframite with varying amounts of nickel oxide addition was reduced with stoichiometric carbon in the form of graphite at 1600 °C for 1 h. The results of X-ray diffraction of the products are shown in Table II. The product materials were examined by optical and electron microscopy. Electron micrographs and electron probe microanalysis (EPMA) elemental displays for experiments R3 and R2 are shown in Figs 2 and 3, respectively.

Small amounts of iron and manganese oxides with alumina, silica and lime impurities of the ore were seen to react to form a slag which separated from the rest of the product material. The reduction of wolframite without nickel oxide additions resulted in a material which showed the presence of large amounts of the M_6C_X η-carbide phase.

The addition of 7.5 wt % NiO to the wolframite before reduction led to the disappearance of the η-phase. In this case the binder iron phase produced was found to be slightly martensitic, due to the transformation of austenite formed at higher temperatures during subsequent furnace cooling. This observation is in substantial agreement with the observations of

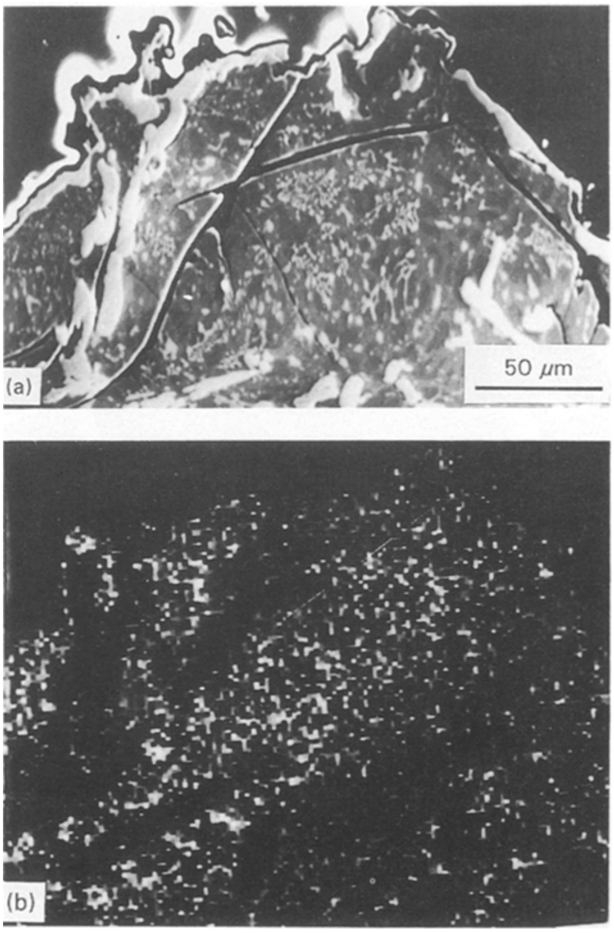
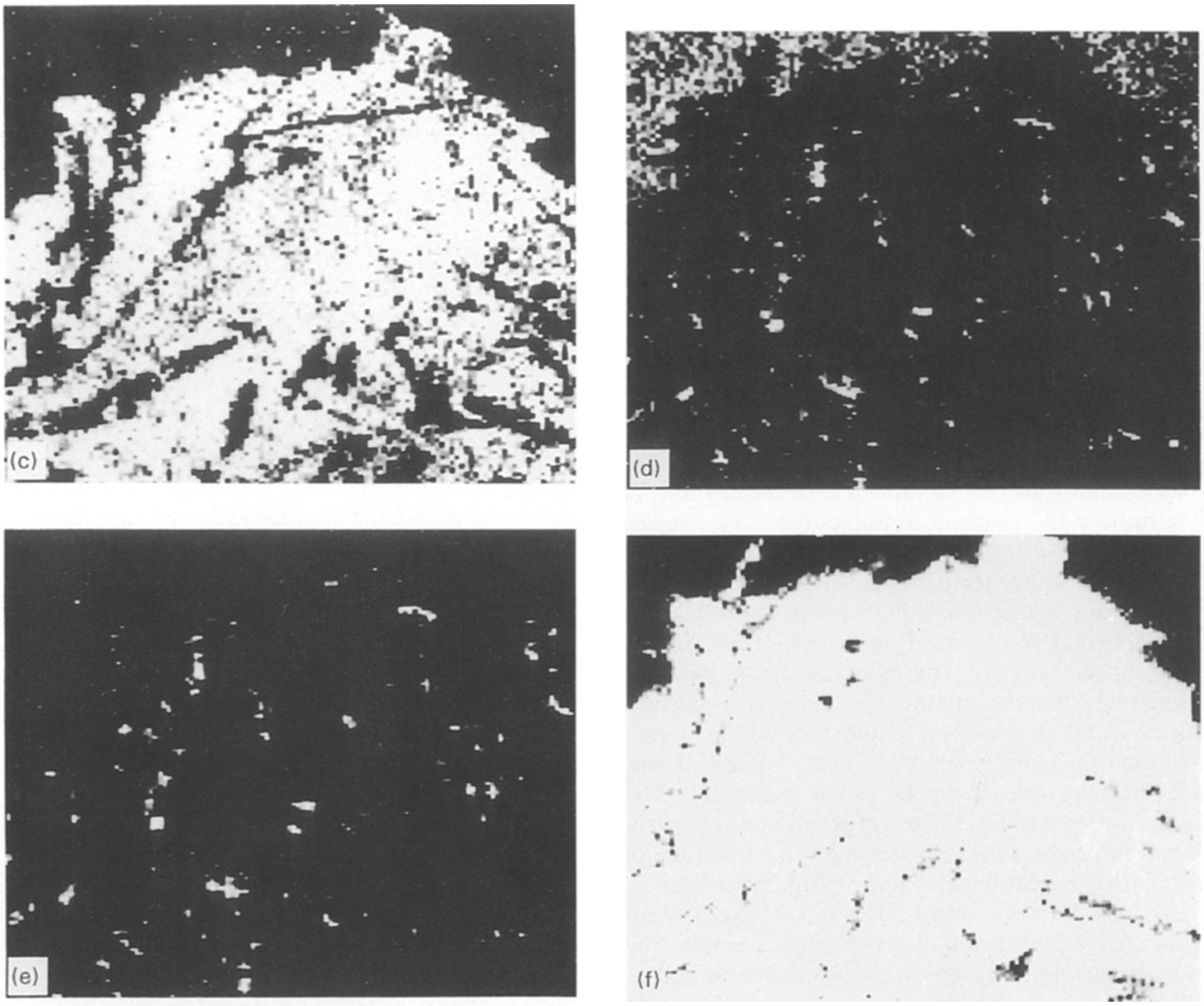


Figure 2 Natural wolframite with NiO additions such that Ni:Fe = 1:3 reduced with graphite at 1600 °C. (a) Electron micrograph and EPMA displays for (b) nickel, (c) manganese, (d) calcium, (e) tin, (f) iron and (g) tungsten.



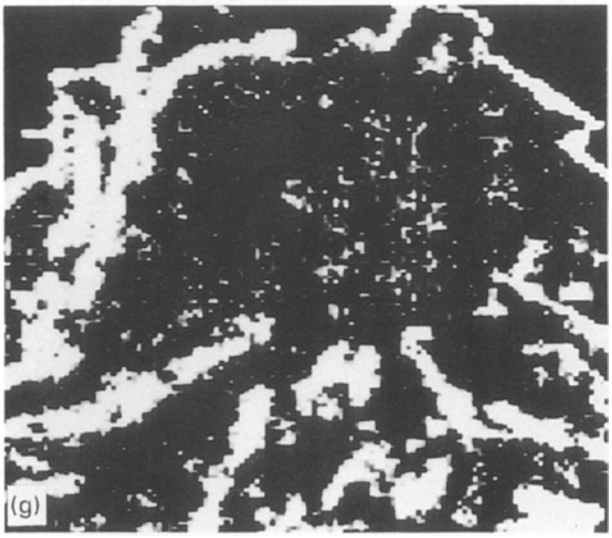


Figure 2 (continued).

Moskowitz [3]. In all cases the tin content of the original wolframite concentrate was reduced to metallic tin; W_2C was obtained as an intermediate product. This observation is in agreement with our previous low-temperature studies of wolframite reduction [4]. The results of the present study indicate that reaction times in excess of 1 h are required for complete conversion to WC using graphite as a reductant.

The product materials obtained were found to contain some porosity and voids, presumably as a result of CO evolution during the reduction reaction.

3.2. Reduction of columbite concentrate

Similar reduction experiments were performed on columbite at 1600 °C with nickel oxide additions, to produce an austenitic iron and NbC–TaC composite. Fig. 4 shows a typical result, in this case the microstructure obtained from the reduction of columbite ore with additions of NiO to produce an Fe:Ni ratio of 3:1. Ilmenite grains in the original columbite were seen to reduce to iron and titanium carbide. The niobium and tantalum components reduced to NbC and TaC. The latter carbide phases formed as plates embedded in a γ (Fe, Ni) matrix.

3.3. Prospects for *in situ* production of composites

The results of the present study offer some promise for the prospects of *in situ* production of carbide composites by reduction of oxides. It has proved possible to produce carbides, apparently well dispersed, in

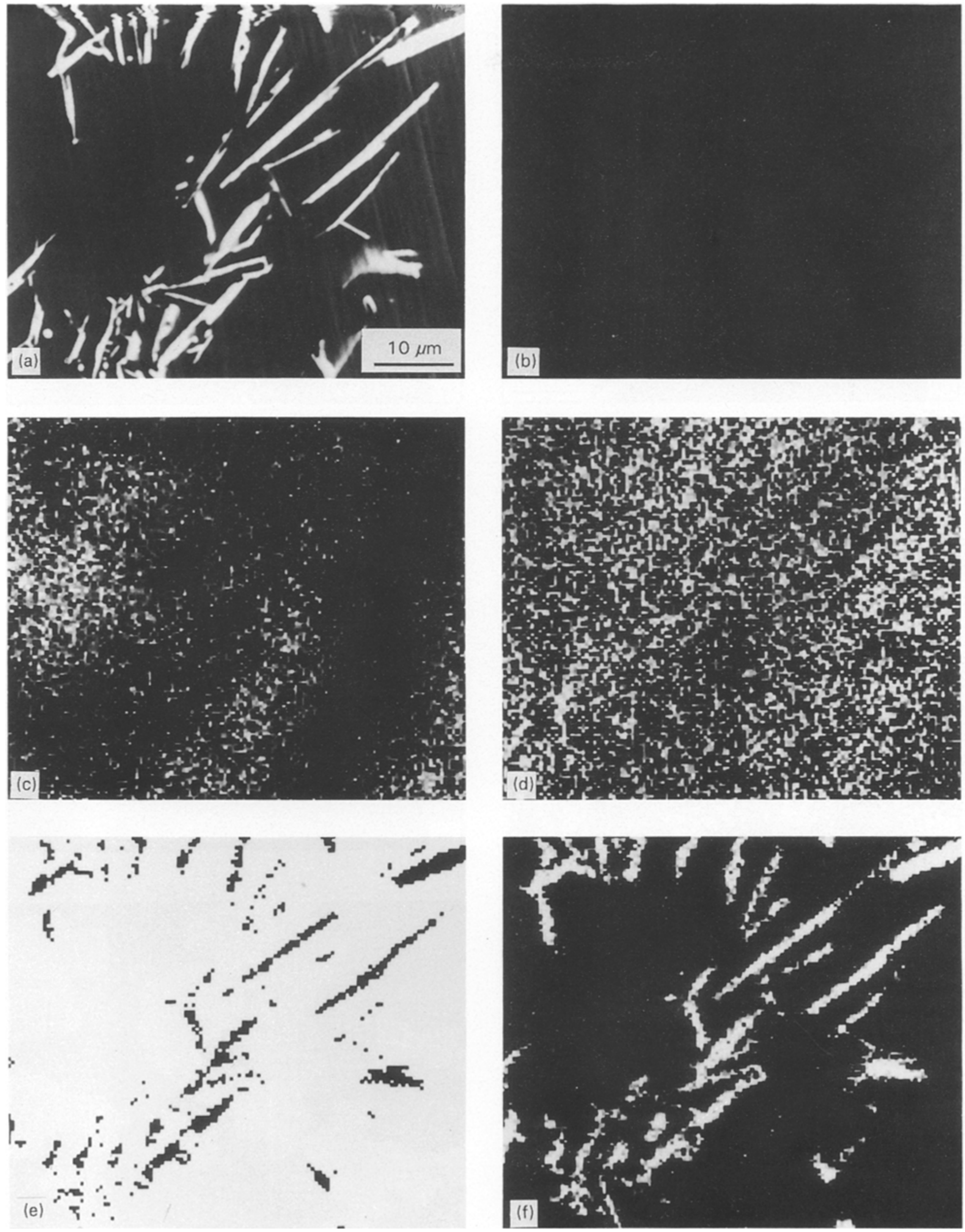


Figure 3 Wolframite with NiO additions reduced at 1600 °C with graphite (Ni:Fe = 1:4, total carbide content = 10%). (a) Electron micrograph and EPMA digital maps for (b) manganese, (c) nickel, (d) tin, (e) iron and (f) tungsten.

austenitic iron by adding appropriate quantities of NiO prior to reduction.

In the case of Fe–Ni–WC production by reduction of wolframite, it is encouraging that gangue oxide materials appear to form a slag phase which separates easily. The tin content of the ore studied is reduced, largely to metallic tin, and the effects of this tin on the mechanical properties of the product need to be studied. It may be that a low-tin wolframite raw material would be a better starting material.

Reduction kinetics could almost certainly be improved by using a more reactive form of carbon such as coal rather than the relatively unreactive graphite used in this study.

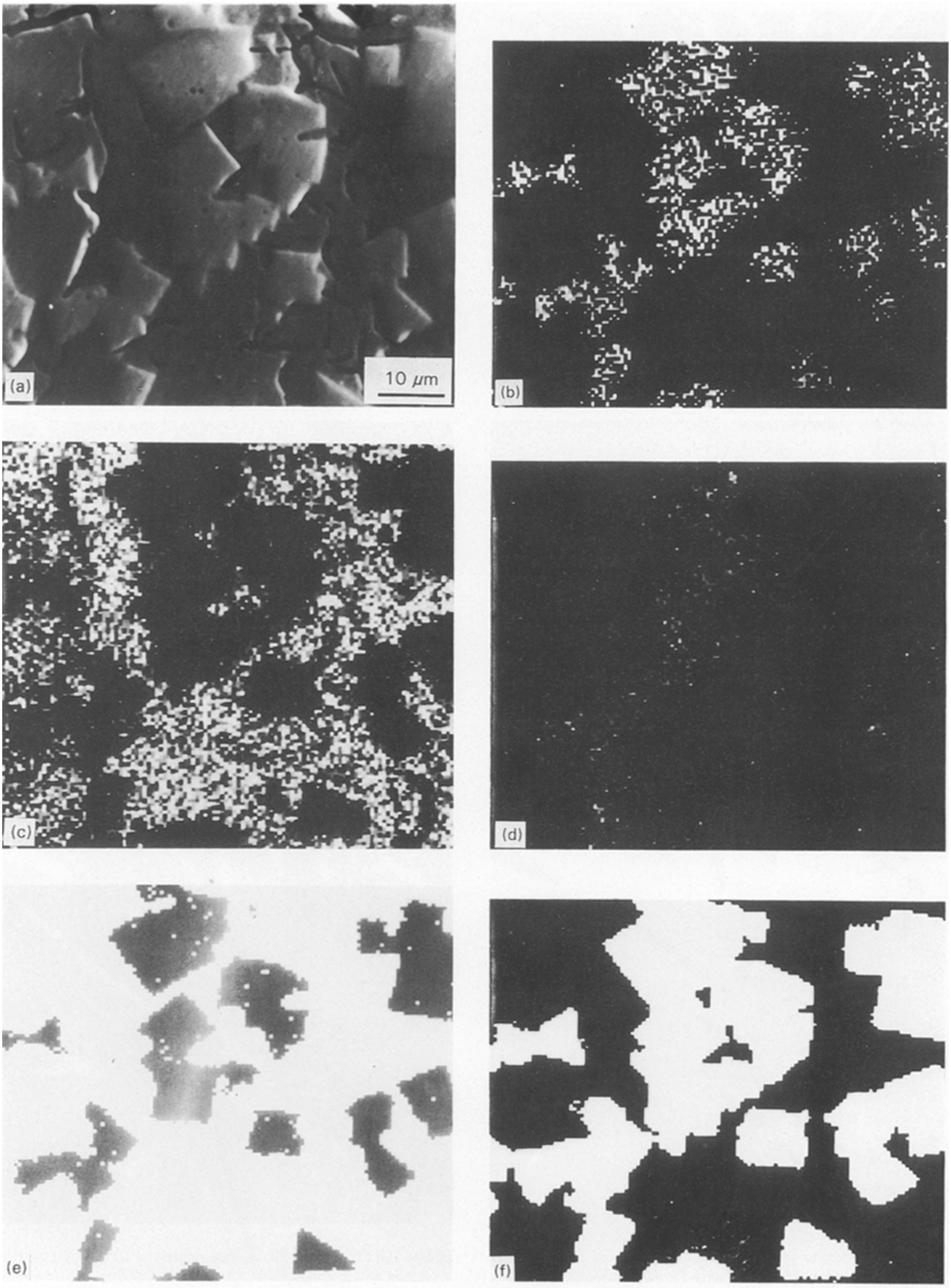


Figure 4 Columbite with NiO addition reduced with graphite at 1600 °C (Fe:Ni = 3:1, total carbide content = 15%). (a) Electron micrograph and EPMA X-ray digital maps for (b) titanium, (c) nickel, (d) tantalum, (e) iron and (f) niobium.

In the case of columbite reduction, a good dispersion of TiC, NbC and TaC in γ-iron was obtained. However, some residual porosity was found in the products of reduction of both wolframite and columbite, presumably because of CO evolution during the reduction process. This porosity requires removal, either by holding the reaction products at the reaction temperature for longer periods or employing a higher temperature to give the liquid iron–nickel matrix an increased chance to fill up pores, or by employing a subsequent pressing step to achieve increased density.

In all cases there is now a need to examine the reduction experiments on a larger scale in order that more material can be gathered for an assessment of mechanical properties. Some larger-scale work has already been reported for the production of Fe–TiC composites by reduction of $FeTiO_3$ [6]. As both wolframite and columbite reduction proceeded in such a way that the pellets employed maintained their integrity throughout the reduction process, there is a possibility that a continuously fed pellet-based process could ultimately be used for large-scale production of material. The further possibility exists that as austenite is produced by the reduction reactions studied, quenching and subsequent heat-treatment procedures could be utilized to modify the properties of the metal matrix. Reduction kinetics would be appreciably improved by the use of a more reactive form of carbon than graphite.

4. Conclusions

Iron–nickel bonded transition metal composites are produced when natural transition metal oxide ores with nickel oxide additions are reduced with stoichiometric carbon at 1600 °C. Alumina and lime impurities in the natural ores form a liquid slag containing some manganese and iron oxides which separates from the metal alloy–metal carbide composite material.

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