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Carbothermic reduction of a columbite concentrate to produce cemented carbides and metal–matrix composites

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Abstract

The study of the carbothermic reduction of a columbite concentrate was carried out to form cemented carbides based on particles of (Nb, Ta)C solid solution bonded together by ferromanganese. The effect of various parameters on the kinetics of reaction were examined. Complete wetting of the carbide phase by the metal was achieved. Metal–matrix composites (MMC) based on (Nb, Ta)C and cast iron were also obtained and the morphology is described. Addition of Ni to the MMC had a profound effect on the microstructure and carbide distribution in the matrix.

1. Introduction

Transition metal carbides are widely used in materials requiring strength and wear-resistance such as cutting tools. The commercial production of these materials is a multi-stage process which is both cost- and energy-consuming. It involves the conversion of ores to pure oxides, the reduction of oxides to the pure metal or carbide followed by more processing to produce a cemented carbide or a metal–matrix composite (MMC). In addition to this, it was predicted that between 1985 and 2000, the demand for such strategic materials would rise by more than 3% per annum [1]. The need for more efficient and cheaper processing of these materials is therefore becoming a priority. The direct reduction of concentrates with carbon to produce cemented carbides or an MMC is a potential alternative. Cemented carbides based on TaC and NbC normally use Ni as the bonding metal [2] which is expensive. Replacement of Ni with Fe is another objective of this study.

The carbothermic reduction of mineral concentrates has been used extensively to produce ferro-alloys [3–5]. The reduction/carburization of $CoWO_4/WO_3$ mixtures with CO/CO_2 and CH_4/H_2 mixtures was reported by Gortsema and Kotual [6]. Using only $CoWO_4$, Halliday *et al.* [7] reported the formation of a Co–WC alloy which occurred by the decomposition of the η-carbide Co_6W_6C. The reduction of Nb_2O_5 and Ta_2O_5 has been extensively studied [8]. Other than the formation of ferroniobium and ferrotantalum [3], the reduction of columbite to produce cemented carbides and MMCs has been largely ignored. The objective of this investigation was therefore to examine the possibilities of using a columbite concentrate for the production of (a) cemented carbides based on (Fe, Mn) and (Nb, Ta)C, and (b) an MMC based on cast iron and (Nb, Ta)C. This MMC may have attractive properties as a wear-resistant cast iron. A dispersoid composition of carbides of 20 wt.% was aimed for.

2. Experimental details and raw materials

Columbite is a complex mineral with the chemical formula $(Fe, Mn)(Nb, Ta)_2O_6$. The raw material used was a Zimbabwean concentrate which was supplied with an average particle size of 150 μm. Part of this was subsequently ground to 30 μm so that the effect of particle size on the reaction rate could be examined. A chemical analysis of the mineral produced the composition shown in Table 1. X-ray diffraction (XRD) analysis confirmed the presence of columbite with traces of the ixiolite phase $(Ta, Fe, Sn, Nb, Mn)_4O_8$. Carbon black was the reducing agent used throughout. For the production of MMCs, the raw materials were diluted with Fe and Ni shot of 99.9% purity.

The reduction experiments were performed in alumina crucibles heated in an electrical resistance furnace in a flowing argon atmosphere. All samples were weighed prior to and after reaction, and the weight loss recorded. MMCs were produced in graphite crucibles heated in a low frequency induction furnace under a flowing inert

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TABLE 1. Chemical analysis of columbite concentrate

Element	Composition (wt.%)
Nb	29.9
Ta	27.3
Fe	9.11
Mn	2.95
W	0.41
Co	0.03
Ti	0.16
Al	0.17
Cr	0.03
Hf	0.01
Mo	0.03
Ni	0.13
V	0.06
Zn	0.13
Zr	0.06

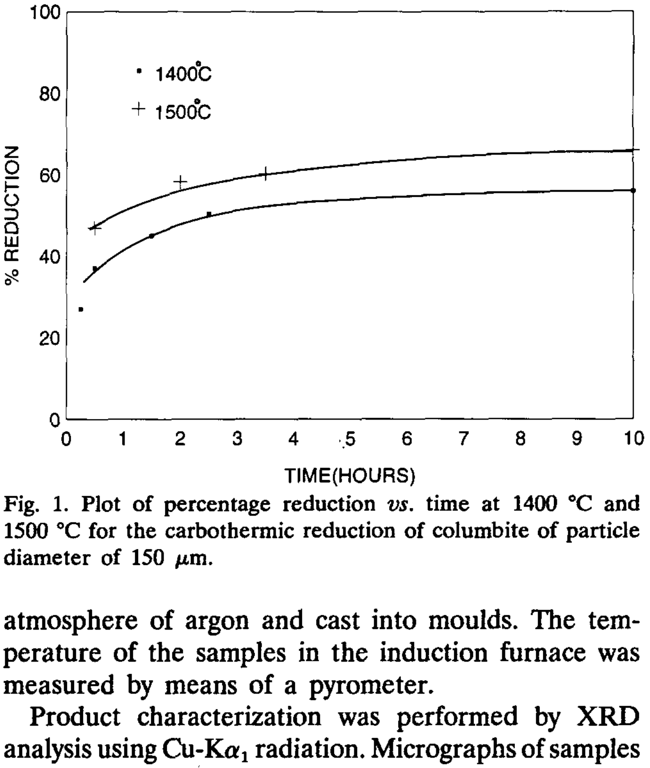

Fig. 1. Plot of percentage reduction *vs.* time at 1400 °C and 1500 °C for the carbothermic reduction of columbite of particle diameter of 150 μm.

atmosphere of argon and cast into moulds. The temperature of the samples in the induction furnace was measured by means of a pyrometer.

Product characterization was performed by XRD analysis using Cu-Kα_1 radiation. Micrographs of samples were obtained on a Reichert light microscope.

3. Results

Rate results for the carbothermic reduction of the coarser grade (150 μm diameter) columbite concentrate using carbon black at 1400 °C and 1500 °C are shown in Fig. 1. After about 30% reduction at 1400 °C and 45% reduction at 1500 °C, the reaction rate slowed down considerably. At this stage the rate became linear with time and even after 10 h a reduction of only 56% was achieved at 1400 °C and 62% at 1500 °C. When the finer grade (30 μm diameter) was used, the kinetics increased as would be expected and full reduction was achieved after 3 1/4 h as shown in Fig. 2. The effect of carbon black was also examined, results for which are also found in Fig. 2. The excess amount of the reducing agent increased the kinetics of reaction such that full reduction was observed after 3 h.

XRD analysis showed that in the initial stages (Fe, Mn)(Nb, Ta)$_2$O$_6$ was reduced to the disordered tapiolite (Fe, Mn, Nb, Ta)O$_2$ phase with minor amounts of ferromanganese and NbC–TaC solid solution being formed. No evidence of the ixiolite structure was found at either temperature. Formation of ferritic (α) ferromanganese with some retained austenite and (Nb, Ta)C then continued by reduction of the disordered tapiolite. The total metallic content after complete reduction was about 12%. The particles of fully reduced samples bonded together into a large aggregate which was indicative of ferromanganese melting.

Figure 3 is a micrograph of a sample obtained after reduction of the coarser concentrate at 1400 °C for 2 1/2 h showing evidence of nuclei of ferromanganese (white) containing carbides at the edges of the disordered tapiolite particles. From this some melting of the oxide phase (grey) is apparent as a continuous matrix of oxide particles is found. A micrograph of a fully reduced sample at 1500 °C is shown in Fig. 4. Complete wetting of the carbides by the metal was observed with (Nb, Ta)C particles (light grey) uniformly distributed in a very thin ferromanganese matrix (white).

A second set of experiments was carried out by the *in situ* reduction of columbite at 1500 °C in an excess of iron to form MMCs based on cast iron containing 20 wt.% (Nb, Ta)C. A cast iron matrix was obtained with flakes of carbon and a good distribution of fine

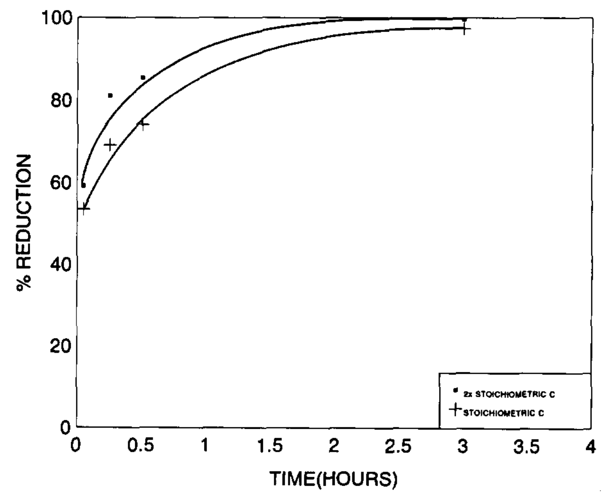

Fig. 2. Rate plot for the carbothermic reduction of columbite of 30 μm particle diameter at 1500 °C.

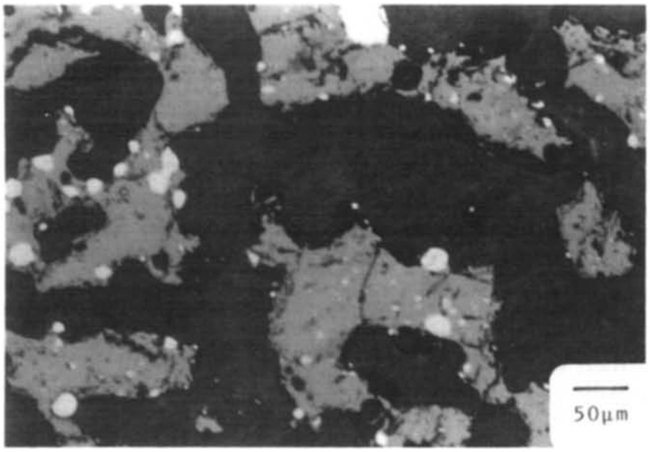

Fig. 3. Micrograph after 2 1/2 h of reaction at 1400 °C showing (Fe, Mn) nuclei with carbides (white) and tapiolite (grey).

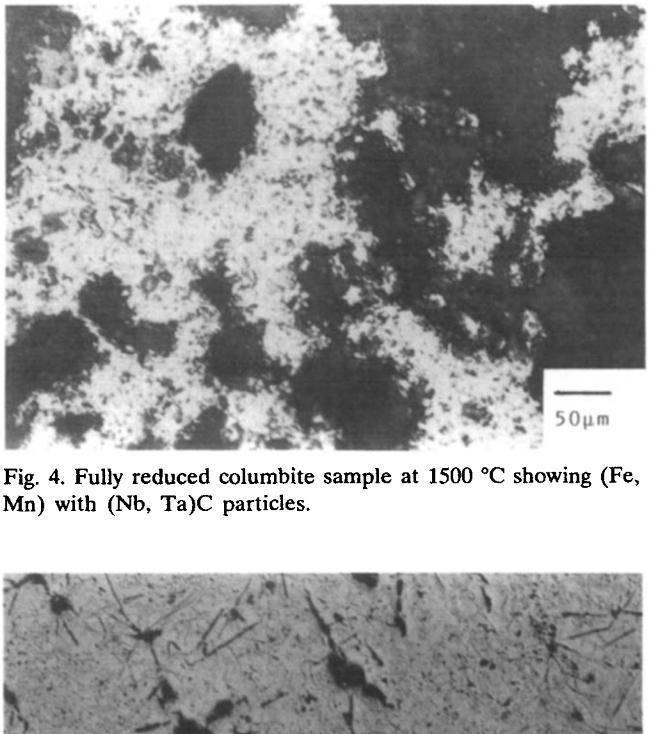

Fig. 4. Fully reduced columbite sample at 1500 °C showing (Fe, Mn) with (Nb, Ta)C particles.

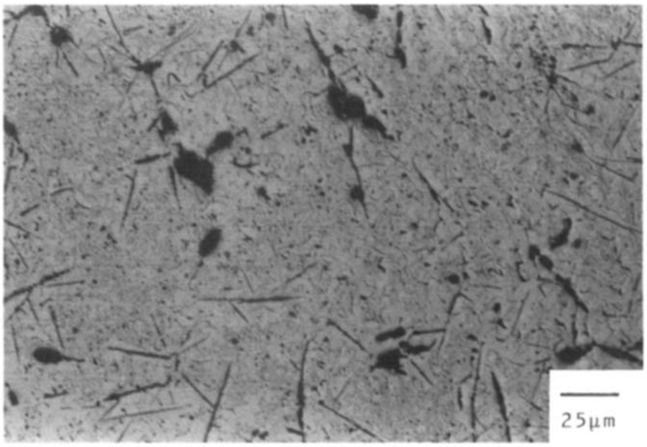

Fig. 5. (Nb, Ta)C reinforced cast iron.

(Nb, Ta)C of average grain diameter of 5–10 µm (Fig. 5). The addition of Ni during the *in situ* processing of the MMC led to a profound change in the microstructure as shown in Fig. 6. The carbon flake structure broke up to some extent, though much finer flakes are in evidence. The carbides present were coarser and seemed to be associated with the carbon.

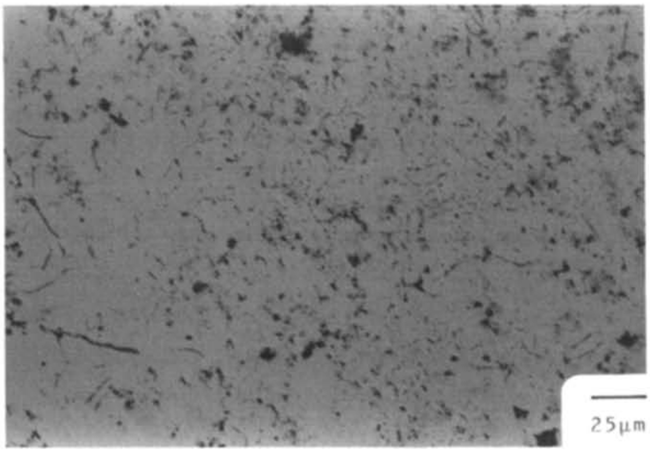

Fig. 6. (Nb, Ta)C particles in a cast iron matrix containing 10% Ni.

4. Discussion

The carbothermic reduction of columbite takes place in two distinct steps. The initial reaction is the reduction of columbite to the suboxide tapiolite

$$\begin{aligned}&(\mathrm{Fe, Mn})(\mathrm{Nb, Ta})_2\mathrm{O}_6+(2+2y)\mathrm{C}\longrightarrow\\&\quad(\mathrm{Fe, Mn})_y(\mathrm{Nb, Ta})_{1-y}\mathrm{O}_2+(1-2y)(\mathrm{Fe, Mn})\\&\quad+2y(\mathrm{Nb, Ta})\mathrm{C}+2\mathrm{CO}\end{aligned}$$

which accounts for 33 1/3% reduction (or 33 1/3% of the total expected weight loss). This is followed by

$$\begin{aligned}&(\mathrm{Fe, Mn})_y(\mathrm{Nb, Ta})_{1-y}\mathrm{O}_2+(3-y)\mathrm{C}\longrightarrow\\&\qquad y(\mathrm{Fe, Mn})+(1-y)(\mathrm{Nb, Ta})\mathrm{C}+2\mathrm{CO}\end{aligned}$$

Appropriate heat treatments also revealed that ixiolite was being transformed to the disordered tapiolite. The reaction mechanism where the carbide forms from the dioxide (in this case tapiolite) is comparable to the reduction of Nb_2O_5 which forms NbC via the dioxide NbO_2 [9].

NbC and TaC are isomorphous having a face-centred cubic (f.c.c.) structure with very similar *d*-spacings. The X-ray patterns were closely examined by expanding their axes in order to determine whether the two carbides were forming as separate phases or as a solid solution (Nb, Ta)C. A unit cell dimension of 0.4462 nm (4.462 Å) was measured which showed no variation with reduction time. This suggested that the composition of the solid solution remained constant throughout each experiment. This composition, as calculated from a mass balance, is roughly 52% NbC and 48% TaC.

The kinetics of reduction were extremely slow when the coarser grade of columbite was used. Initially columbite is reduced to tapiolite and this step appears to take place relatively fast. Further reaction occurs at the contact points between tapiolite and carbon black. According to Guha and Kolar [10], Fe and NbC form a simple eutectic at 1310 °C with a composition of 91% Fe. The product at 1400 °C and 1500 °C is likely to consist of solid (Nb, Ta)C and a molten solution of Fe–Mn–Nb–Ta–C as confirmed by microscopy. Reaction, therefore, is expected to proceed by diffusion of carbon black through the product solid and liquid solutions. Diffusion of carbon through the product layer can be expected to be relatively fast since C can dissolve in Fe. However, if the reactant particle size is fairly coarse its surface area will be small. As a result, there will be only a limited contact between the oxide and carbon black for reaction to occur and very few product nuclei will result. By using a finer columbite powder the surface area of the concentrate will be higher and therefore the points of contact between the reactants increase and more product nuclei appear through which carbon black may diffuse to encounter more of the oxide. Thus, by decreasing the particle size of the starting oxide, a much faster rate of reaction is observed.

At the temperatures of investigation, the product is partially molten due to the formation of a liquid solution of Fe–Mn–Nb–Ta–C. Melting is observed at the interface between the metal and the carbide, and as a result full wetting of the carbide by the matrix is observed. The final microstructure consists of (Nb, Ta)C spheroids dispersed in a thin, continuous matrix of ferromanganese. However, the final product is not fully dense and further treatment is required. This can consist of cold-pressing the product followed by heat treatment at about 1400 °C.

When the reacting mixture was diluted with Fe and an excess of carbon black, a well-distributed structure of (Nb, Ta)C in cast iron was obtained. However, on replacing 10% of Fe with Ni, the carbide particles became larger and the amount of carbide present in the microstructure was less and the distribution was not uniform. The solid solubilities of NbC and TaC in iron have been reported to be 1 wt.% and 0.5 wt.% respectively and 3 wt.% and 5 wt.% in nickel [4]. The addition of Ni can therefore be expected to reduce the amount of carbide precipitation as more NbC and TaC will dissolve in the matrix. For the same reason, some regions in the microstructure are carbide-rich while others are metal (Fe–Mn–Ni–Nb–Ta–C solution)-rich. This gives rise to a strong association between carbon and (Nb, Ta)C as they are both rejected by the solidifying liquid. As a result, the carbon flakes become disrupted and become much finer. Evidence that carbon begins to take up a more spheroidal form is also found. The non-uniform distribution of carbides in the matrix is likely to result in poor mechanical properties. The presence of Ni is also likely to generate austenite though no retained austenite was observed.

The impurity content in the columbite was too low to expect any significant effects on the final product. Also, Ti and V form f.c.c. carbides which form solid solutions with NbC and TaC. The only impurity metal of significant levels in the starting material is W (0.41%) which is a strong carbide former and although WC is simple hexagonal, it too forms f.c.c. solid solutions with TiC and NbC [11]. On the contrary, Co and Ni do not form stable carbides and are likely to be dissolved in the ferromanganese matrix.

5. Conclusions

This investigation has shown that it is possible to produce flake graphite cast iron MMCs by the carbothermic reduction of columbite. A (Nb, Ta)C solid solution was formed which was completely wetted by the matrix. The carbide particle size was of the order of 5–10 μm and it was well distributed within the metal matrix. The addition of 10% Ni to the MMC disrupted the flake carbon structure and gave rise to spheroids. In addition to this, the carbide particle size increased and (Nb, Ta)C became less uniformly spread. It was therefore deduced that addition of Ni would have a detrimental effect on the mechanical properties of the MMC because this produced a non-uniform carbide dispersion.

The reduction of columbite by carbon black was dependent on temperature and reactant particle size. The production of cemented carbides by direct reduction of columbite is possible, though it appears that further treatment may be required to produce a fully dense material.

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