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Ultra-rapid processing of refractory carbides; 20 s synthesis of molybdenum carbide, Mo_2C

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The microwave synthesis of molybdenum carbide, Mo_2C, from carbon and either molybdenum metal or the trioxide has been achieved on unprecedented timescales; *Ex-* and *in-situ* characterisation reveals key information as to how the reaction proceeds.

The development of new synthetic techniques is arguably as important as the synthesis of novel materials and the two aspects are often intimately connected. Microwave (MW) heating, as such an emerging technique, offers many advantages over more conventional heating methods including enhanced energy efficiency, rapid processing times and unique heating profiles.[1–5] Irradiaton is a rapid and volumetric process and within the last two decades MW synthesis methods have received much attention with the majority of developments reported in solution-based synthesis.[6,7] Recently however, interest has grown in the field of solid state MW synthesis where the dielectric properties of the reaction components have been exploited to dictate heating.[8] This approach can however introduce synthetic constraints since at least one precursor must couple efficiently with microwaves. In some cases a MW susceptor is required if the volume of the sample is small and/or the dielectric properties are unfavourable at low temperature.[9]

Molybdenum carbide, Mo_2C, like other refractory carbides, has high hardness and strength coupled with good thermal and electrical conductivity as well as a high chemical stability and melting point.[10] Found in steel alloys and as a tool/blade coating, it is often favoured over the more expensive tungsten carbide, WC.[11] The molybdenum–carbon system comprises three known stoichiometric compositions: MoC, Mo_3C_2 and Mo_2C. Mo_2C forms two known phases: orthorhombic α-Mo_2C and hexagonal β-Mo_2C. Mo_2C also exhibits superconductivity, although there is some inconsistency in the reported superconducting transition temperature, T_c. Early work and later specific heat measurements agree that T_c lies between 2.4 and 3.2 K for β-Mo_2C,[12,13] however values between 3.45 and 7.2 K have also been reported.[14] These discrepencies are thought to be due to the synthetic procedure as well as the carbon stoichiometry; the electron–phonon coupling and hence T_c is especially sensitive to the latter. It is possible that reported Mo_2C phases with higher T_c in fact contain hexagonal or cubic polymorphs of MoC_{1-x}.

Recently we described how tungsten carbide, WC, could be synthesised from the elements in <1 min using high power MW methods.[15] Here we report the ultra-rapid synthesis of superconducting hexagonal β-Mo_2C starting from either Mo powder or the metal trioxide, MoO_3. The high power MW synthesis performed in a TE_{10n} single mode cavity yields single-phase carbide in a fraction of a minute and by using *in-* and *ex-situ* methods we have developed an understanding of the way in which these ultra-rapid reactions proceed.

A series of synthesis experiments were performed in both multi-mode (Delonghi Domestic Microwave Oven (DMO), 800 W, 2.45 GHz model number E8021TP-B1) and single-mode cavity systems (TE_{10n}, WR430).[15] using pelletised mixtures of C with Mo (**1**) or MoO_3 (**2**) powders.† *In-* and *ex-situ* methods were used to follow the reactions and characterise the products.‡ Analysis of the products **1** and **2** revealed pure β-Mo_2C at various times and powers: 90 s at 800 W in the DMO and 20 s at 3 kW in the single mode cavity being the optimum conditions for both experiments. Fig. 1 indicates the phases present at 5 s time intervals for the reaction yielding **1**. Direct conversion from the metal and carbon powders to the product is observed. In the formation of **2**, initial reduction to the dioxide takes place before the product is formed and at no point is elemental Mo observed by PXD. Conventionally, the two steps in eqn (1) are performed separately.

$$2\ MoO_3 + 7\ C \rightarrow 2\ MoO_2 + 2\ CO + 5\ C \rightarrow Mo_2C + 6\ CO \qquad (1)$$

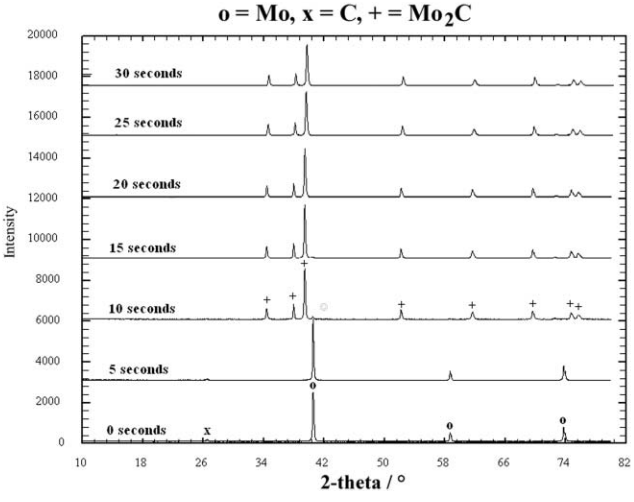

Fig. 1 PXD patterns taken *ex-situ* from the Mo + C reaction (to yield **1**), performed at 3 kW. Patterns are shown for each 5 s time interval.

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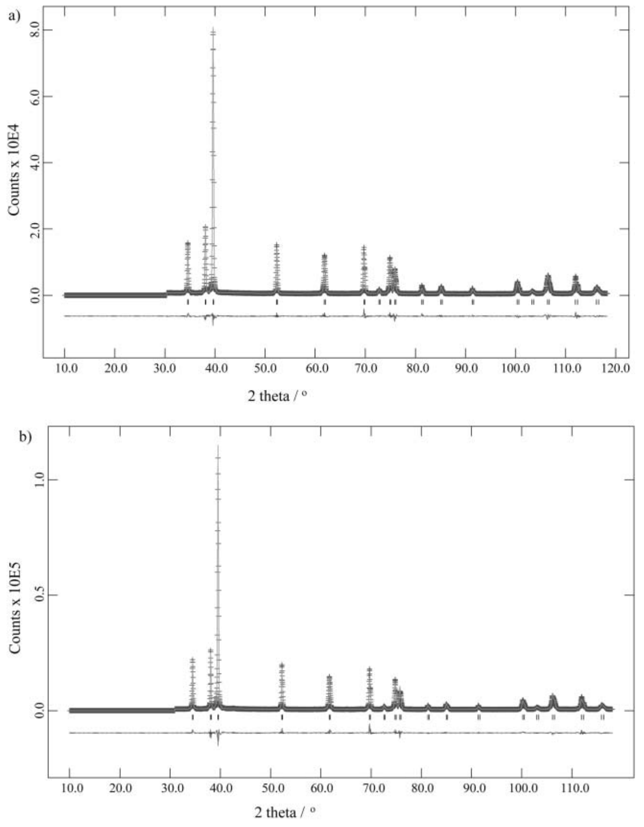

Fig. 2 Observed (plusses), calculated (solid line) and difference (below) profile plot for the Rietveld refinement against PXD data of (a) **1** and (b) **2** (both produced in 20 s at 3 kW). Tick marks denote Mo_2C reflection positions.

The profile plots shown in Fig. 2 indicate the single-phase product (**1**) obtained from the elemental powders (hexagonal $P6_3/mmc$, $a = 3.0049(1)$ Å, $c = 4.7377(1)$ Å, $V = 37.046(2)$ Å^3, $Z = 1$; $R_p = 0.0576$, $R_{wp} = 0.0715$, $\chi^2 = 6.923$) and that (**2**) afforded from the oxide, MoO_3 (hexagonal $P6_3/mmc$, $a = 3.0089(1)$ Å and $c = 4.7340(1)$ Å, $V = 37.116(1)$ Å^3, $Z = 1$; $R_p = 0.0646$, $R_{wp} = 0.0861$, $\chi^2 = 9.587$). Lattice parameters from both **1** and **2** are in good agreement with those for β-Mo_2C in the literature.[18]

No obvious amorphous component in the product is detected by PXD and TGA under oxygen (Q600 TA instruments, sample heated at 2° min^{-1} from 25 to 1000 °C) reveals only a weight gain corresponding to the oxidation of Mo_2C at 500 °C (to MoO_3, as confirmed by PXD). EDX yielded an Mo : C ratio of 2.2(4) : 1 for **1** and 2.0(1) : 1 for **2**, with no other elements present in both cases. Analysis for Mo and C by XRF and combustion respectively yielded a Mo : C ratio of 2 : 0.99(1) for both **1** and **2**, strongly suggesting the formation of stoichiometric Mo_2C.

SQUID magnetometry reveals a superconducting onset temperature, T_c of 3.5 K and a superconducting volume fraction of 97% for **1** (Fig. 3). A very similar T_c onset of 3.4 K and a superconducting volume fraction of 97.7%, was observed for **2**. These T_c values are very close to the upper limit value originally reported for β-Mo_2C by Meissner and Franz in their measurements of the bulk carbide.[12] The high volume fractions coupled with PXD and analytical evidence clearly suggest that superconductivity is intrinsic to the (stoichiometric) MW-synthesised bulk β-phase.

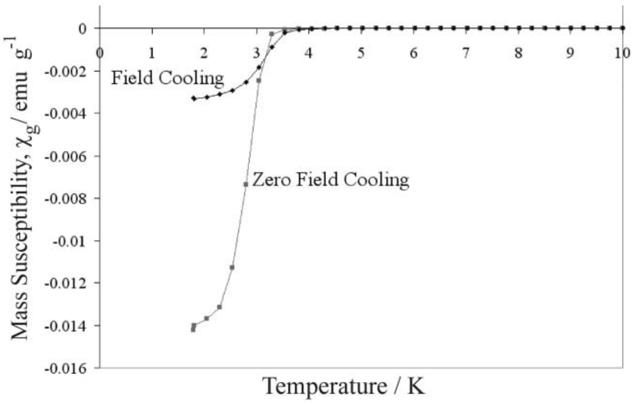

Fig. 3 Plot of mass susceptibility, χ_g, against temperature, for superconducting Mo_2C (sample **1**), showing a T_c onset at 3.5 K.

In order to try and understand the progress of the reaction and the mechanism by which the reactants couple with the incident microwaves, non-invasive, *in-situ* temperature measurements were recorded for the synthesis of β-Mo_2C from elemental powders (**1**). *Ex-situ* dielectric measurements were also performed at 293 K on (partially) reacted samples at various timepoints in the course of formation of **1**. Although the dielectric properties are temperature dependent, these *ex-situ* measurements describe semi-quantitatively the trend expected at the higher temperatures recorded during the reaction. Fig. 4 shows the results of these experiments indicating direct relationships between temperature, loss tangent, tan δ, (tan $\delta = \varepsilon''/\varepsilon'$ where ε' is the dielectric constant and ε'' is the dielectric loss) and β-Mo_2C phase fraction.

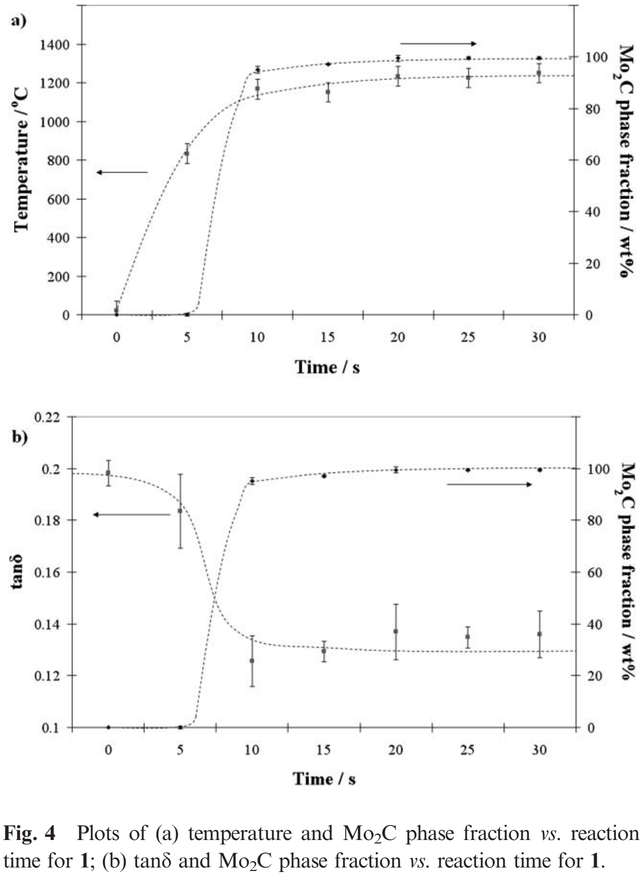

Fig. 4 Plots of (a) temperature and Mo_2C phase fraction *vs.* reaction time for **1**; (b) tanδ and Mo_2C phase fraction *vs.* reaction time for **1**.

Formation of the product is negligible below 5 s, however the rate of change of change of temperature at this point is rapid. From 5–10 s β-Mo_2C formation is observed with a commensurate and significant change in gradient of the temperature curve. At 10 s the composition of the sample is close to 100 wt% β-Mo_2C and at this point the temperature begins to stabilise. Considering the dielectric data, little difference in the real part of the permittivity, ε', was observed over the course of the reaction, however a noticeable decrease in the imaginary part, ε'', was observed as the reaction progressed. Hence we observe an overall decrease in the loss tangent, tan δ, over the period of the reaction (20 s and beyond).

Comparison of the results in Fig. 4 highlights a palpable link between dielectric properties, phase fraction and temperature. A noticeable reduction in tanδ is observed between 5 and 10 s coinciding with the rapid formation of the β-Mo_2C phase and the sharp change in gradient of the temperature curve. The absorbed power per unit volume is directly proportional to the dielectric loss factor in addition to the electric field strength inside the material squared. Over the initial 10 s period the temperature rises to over 1600 K but from this point forward, the rate of heating is very low. From the combined sets of data, one can thus define two unambiguous heating regimes; the first in which MW dielectric heating mediates the reaction and the second in which heating is dominated by conventional conduction.

The highest rate of heating occurs before most of the Mo and C has produced β-Mo_2C and one can thus infer that the exothermic formation of β-Mo_2C ($\Delta H_{f,\,298} = -46.05 \pm 2.9$ kJ mol^{-1})[19] is not a major contributor to the initial rapid heating although the heat from combustion of excess C (to CO) is probably of some significance even over this short timescale. Manifestly, the dielectric properties of the components play a central role in the reaction, with self-termination resulting from the loss of components, C and Mo, with superior MW absorbing properties. That the initial interaction of the mixture with the applied microwaves is so favourable is not unexpected given that various forms of carbon couple strongly to microwaves[3] and one might expect finely divided metals such as molybdenum to contribute to heating ohmically in a high frequency electric field.[2,3,20] Hence, as in the W–C system,[15] the accelerated self terminating formation of the carbide produces phase-pure product with no decomposition, melting, oxidation or safety issues that would arise from thermal runaway. These observations raise the possibility of industrial scale-up. Given optimisation of the cavity, the overall reaction time ($\approx$20 s), initial enhanced heating and the final self-termination imply that one could engineer a continuous, flow process to rapidly produce large amounts of crystalline, single phase Mo_2C. Moreover, the option to employ MoO_3 (as opposed to Mo) in a MW-mediated carbothermal reduction and carburisation has significant economic implications.

In summary, a pure phase of β-Mo_2C has been synthesised on an unprecedented timescale by reacting either the respective metal trioxide or the elemental metal powder with carbon. A powerful combination of *ex-* and *in-situ* methods have provided vital evidence towards the understanding of the MW reaction mechanism for carbide synthesis. Control over this ultra-rapid, self-terminating reaction offers a real prospect for the industrial scale up of MW carbide processing.

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Notes and references

† A stoichiometric 2 : 1 ratio of Mo (BDH, >99% pure) and C (BDH, >99.5%, <50 μm particle size) were ground together using a pestle and mortar. The powder was pressed using a hand press and 8 mm dye to produce a 2 g pellet, which was set in 0.35 g of graphite powder – as a MW susceptor/load – in a 10 mm open top quartz tube (with the upper face of the pellet visible). The tube was placed in a silica beaker and packed with ground silica sand. The experiments were repeated replacing Mo with MoO_3 powder (>99%, Aldrich, 2 MoO_3 + 7 C). No spontaneous reaction was observed without the graphite load for these small sample volumes. Temperature was measured *in situ* using an optical pyrometer (LAND System4 Thermometer M1 600/1600 °C; ±1 °C accuracy) with a 5 mm diameter spot centred on the exposed pellet surface.

‡ The elemental composition was investigated using SEM/EDX (FEI Quanta 600 SEM), XRF (for Mo) (Panalytical PW1480) and combustion analysis (for C) (LECO CS-444). Phase composition was assessed *ex-situ* by powder X-ray diffraction (PXD; Philips X-pert θ–2θ diffractometer; Cu-Kα radiation for $5 \leqslant 2\theta \leqslant 120°$ for *ca.* 12 h with a step size of 0.02° 2θ). Quantitative phase fraction data and crystallographic parameters were obtained by Rietveld refinement against PXD data for each dataset (using GSAS and EXPGUI packages[16,17]). Magnetic measurements were taken with a SQUID magnetometer (Quantum Design MPMS 5T). Dielectric measurements were performed at 293 K, *ex-situ* using a cavity perturbation method. Results were obtained at a frequency of 2.47 GHz to enable comparison with the MW treatments which were carried out at 2.45 GHz.

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