

Carbide Phases Synthesised from C/Mo Powder Compacts at Specified Sub-Stoichiometric Ratios by Solar Radiation Heating to Temperatures between 1600°C and 2500°C

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There are a number of distinguishable carbide phases in the binary Mo-C system depending on C/Mo ratio as well as on temperature. In a preceding work published in this journal, carbide formation performance for graphite/molybdenum powder mixtures at specified levels of sub-stoichiometric C/Mo atom ratio ($C/Mo = 1/1, 3/4, 2/3$ and $1/2$) by exposure to concentrated solar radiation in a solar furnace at PROMES-CNRS in Odeillo (France) was reported at a target temperature 1900°C. In the present work, the similar carbide synthesis experiments were carried out at 1600°C as well as at temperature exceeding 2500°C. The target temperature setting was adjusted by controlling the downward deviation of the test piece top surface position from the exact focal spot of the parabolic mirror concentrator located above. In this solar furnace at PROMES-CNRS, temperature of the test piece was raised from ambient temperature to the target temperature within fractions of a second. Reaction products detected were hexagonal η - MoC_{1-x} and β - Mo_2C (high temperature sub-carbide phase) depending on the C/Mo ratio in the starting material as well as on the processing temperature. No evidence of formation of cubic α - MoC_{1-x} was detected by X-ray diffraction analysis for any test piece examined. [doi:10.2320/matertrans.M2009167]

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1. Introduction

In our preceding work,¹⁾ compacted powder mixtures of graphite and molybdenum at specified hypo-stoichiometric composition ratios, $C/Mo = 1/2, 2/3, 3/4$ and $1/1$, were heated to 1900°C in a solar furnace at PROMES-CNRS in Odeillo (France) to be converted to carbide MoC_{1-x} . Under the employed experimental condition with the target temperature 1900°C, yield of η - MoC_{1-x} was comparatively high for the specimen with the C/Mo atom ratio set at $2/3$ (close to the composition of the hexagonal η - MoC_{1-x}) as well as at $3/4$ (close to the composition of the cubic α - MoC_{1-x}) while β - Mo_2C phase was present insistently for any test piece examined. Yield of β - Mo_2C (high temperature sub-carbide phase) under the solar-synthesis condition with the target temperature 1900°C was specially high for the test piece started with $C/Mo = 1/1$ as well as for the test piece started with $C/Mo = 1/2$ while it was comparatively low with the test pieces started from $C/Mo = 2/3$ and $3/4$.¹⁾

In our earlier work on solar Mo carbide synthesis under condition of presence of excess free carbon at the end of the reaction,²⁾ identification for the XRD peaks of Mo_2C phase was done erroneously to be the α - Mo_2C phase (low temperature Mo_2C phase known to be stable at temperatures below 1430°C) in place of the β -phase. The origins of this shameful mis-interpretation in the identification for the Mo_2C phase in our earlier work²⁾ were as follows (cf. Table 1 in the preceding work¹⁾ composed on the basis of the available information³⁻⁵⁾):

- (1) The XRD peak for the η - MoC_{1-x} (101) at $2\theta = 34.93^\circ$ was identified erroneously as the overlapped peak with α - Mo_2C (002) peak ($2\theta = 34.43^\circ$),
- (2) Correspondingly, the β - Mo_2C (200) peak ($2\theta = 37.90^\circ$) was erroneously considered to be α - Mo_2C (002) peak ($2\theta = 37.96^\circ$).

Anyway, the results obtained in the earlier work²⁾ appeared to imply the possibility to synthesise single-phase η - MoC_{1-x} without co-existence of β - Mo_2C phase by adequate selection of reaction conditions in the solar radiation heating experiment. Non-stoichiometric composition range for the hexagonal η - MoC_{1-x} and that for the cubic α - MoC_{1-x} are known to be around $C/Mo = 0.70$.³⁻⁵⁾ Thus, in the preceding work,¹⁾ specimens with C/Mo atom ratios at $1/1, 3/4 (= 0.75), 2/3 (= 0.67)$ and $1/2$ were heated to 1900°C under concentrated solar beam radiation in the solar furnace at PROMES-CNRS aiming at identifying conditions leading to preferential formation of η - MoC_{1-x} phase. As reported in the preceding publication,¹⁾ under any chosen compositional condition at processing temperature 1900°C for duration 30 min, single-phase η - MoC_{1-x} was not synthesized and β - Mo_2C phase was always present, in some cases existing as single-phase without trace of η - MoC_{1-x} phase.

To look into the formation condition of η - MoC_{1-x} in further detail, we carried out the solar irradiation heating experiments for the powder compacts with C/M atom ratios, $1/1, 3/4, 2/3$ and $1/2$, at 1600°C and also at “2500°C”, in the present work. In fact, the so-called “2500°C” test was undertaken by placing the test piece top surface at the exact focal spot of the parabolic mirror concentrator without encasing the test piece in graphite crucible unlike in the

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standard solar irradiation experiment. The background idea of this experimental setup was to apply all the heat of the concentrated solar beam exclusively to the test piece by minimising the dissipation of the heat to the surrounding sample holder. Naturally, near-black body radiation for the pyrometric temperature measurement condition was not fulfilled for the “2500°C” test. Thus, the designated temperature 2500°C for the “2500°C” test represents merely the situation that the nominal measured radiation temperature was no less than 2500°C and thence the real test piece temperature must have been by 100–200°C higher than the measured temperature by optical pyrometer, quite probably exceeding the melting temperature 2600°C of α -MoC_{1-x} phase³⁻⁵⁾ noting the evidences indicating partial melting of the top surface of most of the test pieces.

The present experimental results showed that single-phase η -MoC_{1-x} was prepared only from the C/Mo = 3/4 specimen processed at “2500°C” and all the other specimens contained β -Mo₂C. No evidence of formation of α -MoC_{1-x} was detected by XRD in any specimen examined.

2. Experimental

The experimental setup used to perform the carbide synthesis experiments in the solar furnace at PROMES-CNRS was described in detail elsewhere.^{1,2,6-8)} The compacted pellets of C/Mo atom ratios set to be 1/2, 3/4, 2/3 and 1/1 with diameter 8 mm and height 5 mm were prepared by uni-axially pressing the powder mixtures at 450 MPa. Mo powder (99.9% pure, mean particle size 2 μ m) was supplied from Goodfellow, Ltd. (Cambridge, England) and graphite powder (< 50 μ m) from E.Merck AG (Darmstadt, Germany). The compacted pellet specimen was placed in a specially designed crucible for the exposure to the concentrated solar beam (see Figs. 1 and 2 in Ref. 6) for the crucible). The reaction chamber (Pyrex glass; 5 l capacity) was flushed twice with inert Ar gas with grade U (nominal purity 99.999% with O₂ no higher than 5 ppm and H₂O also no higher than 5 ppm) before being filled with 460 mbar (4.6×10^4 Pa) Ar gas at ambient temperature. It should be noted that the PROMES-CNRS facilities lies about 1500 m from the sea level and the atmospheric pressure there is normally *ca.* 850 mbar (8.5×10^4 Pa).

Like in the earlier experimental works performed at PROMES-CNRS,^{1,2,6-8)} the sample holder was brought into the hot spot of the solar furnace by sliding manually the reaction chamber over a pair of guiding rails. Within fractions of a second, the specimen temperature rose from ambient temperature to the target processing temperature. This ultra-fast heating rate at the onset of the concentrated solar beam radiation experiment is the unique characteristic of the solar furnace at PROMES-CNRS at Odeillo. In the earlier solar-carbide synthesis experiments done at PSA (Tabernas), it took about a few minutes to heat the specimen from ambient temperature to the target temperature depending on the rate of opening of the louvered shutter.^{9,10)}

In cases of the experiments performed at the target temperatures, 1600°C and 1900°C, the radiation temperature of the specimen material was measured through the triple vertical slits of width 1 mm cut in the graphite crucible using

an optical pyrometer (Model 95 of Pyrometric Instrument Company, Inc., Bergenfield, N.J., USA) through a view window from the side of the Pyrex glass reaction chamber.

On the other hand, the experiments at the nominal target temperature “2500°C” were undertaken by configuring the test piece top surface to be set at the exact focal spot of the parabolic mirror concentrator as pointed out earlier in the text. After the 2500°C test, the test piece top part showed deformation as the consequence of “macroscopic” melting whereas only evidence of “microscopic” or partial melting was detected for the test pieces processed at target temperature lower than 1900°C.^{1,2)}

After 30 min holding at the target temperature, the sample holder was taken away from the hot spot of the solar furnace and the specimen material was cooled down under flowing Ar gas. After about 30 min, the Pyrex glass reaction chamber was opened to take out the specimen cooled down near ambient temperature. Then, the specimens were characterized by means of XRD and scanning electron microscopy (SEM).

Phase identification was made by XRD analysis using a Geigerflex D/MAX IIIC diffractometer (Rigaku International Corp., Japan) with CuK α radiation. For this purpose, as-synthesized specimens were stuck to a glass sheet surface and scanned over a range of 2θ from 25° to 45° at a scanning speed of 2°2 θ ·min⁻¹. To ensure flatness of the test piece surface exposed to XRD characterization, top surface of the test piece processed at “2500°C” showing deformation as the consequence of macroscopic melting had to be polished lightly.

The morphology of the specimen surface was inspected using a Field Emission Philips XL 30 FEG SEM operated with acceleration voltage 10 to 15 kV.

3. Results and Discussion

The XRD profiles obtained for the test pieces processed to the target temperature 1600°C are reproduced in Fig. 1 and those for the test pieces processed to the target temperature “2500°C” in Fig. 2. Table 1 summarises the phases detected in the top and the bottom surfaces in the specimens at respective target temperatures. In Table 1, the data acquired at 1900°C are integrated taken from the preceding report.¹⁾ The data for the “2500°C” test pieces are incomplete (lacking the data for C/Mo = 2/3 test piece) and thus might be considered merely as the reference data for comparison purpose.

Following features are noticed in Table 1.

- (i) All the test piece top and bottom surfaces contained β -Mo₂C phase besides η -MoC_{1-x} phase in the reaction product except for the C/Mo = 3/4 test piece top surface processed at “2500°C” which was identified to be composed solely of the η -MoC_{1-x} phase.
- (ii) The top and the bottom surface of the C/Mo = 1/2 test piece processed at 1600°C were with β -Mo₂C single phase.
- (iii) Free metallic Mo was detected in the two specimens; the bottom surface of the C/Mo = 2/3 test piece processed at 1600°C and the top surface of the C/Mo = 1/2 test piece processed at “2500°C”.

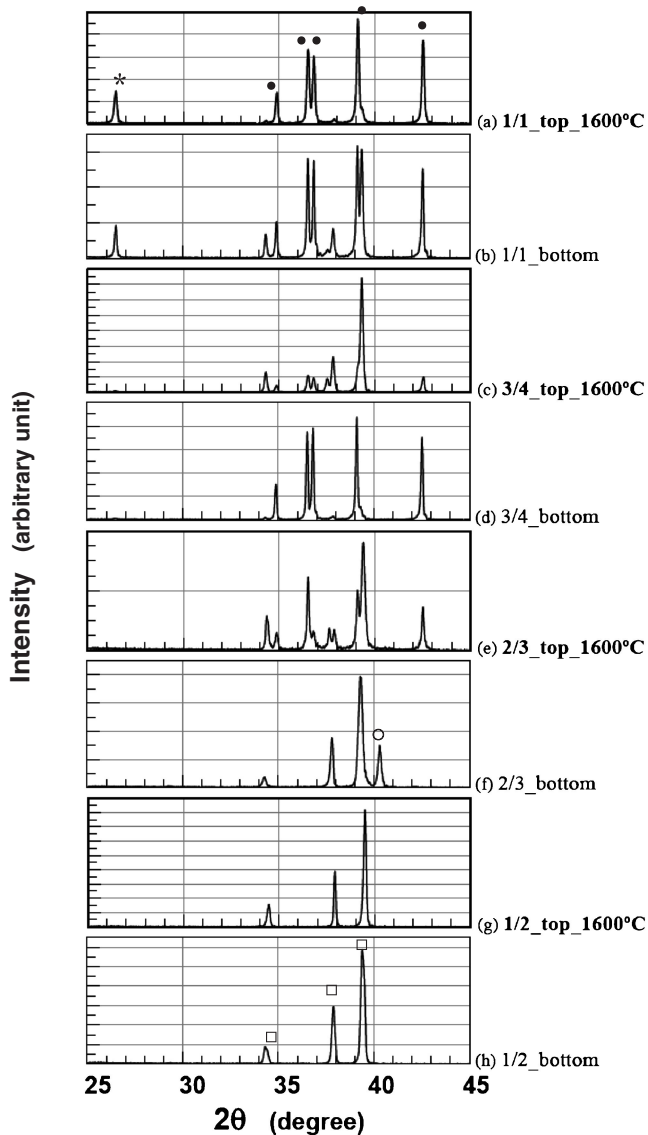


Fig. 1 The XRD patterns ($\text{CuK}\alpha$) of the top and the bottom surfaces of the pellets of graphite/molybdenum powder mixtures with C/Mo atom ratios, 1/1, 3/4, 2/3 and 1/2, heated to 1600°C in the solar furnace with the initial ultra-fast heating rate. (●) $\eta\text{-MoC}_{1-x}$, (□) $\beta\text{-Mo}_2\text{C}$, (○) Mo, (*) graphite.

Typical SEM appearances of the top surface of the test pieces processed at 1600°C are summarised in Fig. 3 and those processed at “2500°C” in Fig. 4.

It is noticed in Fig. 3 that the top surface of the test pieces processed at 1600°C yielded hexagonal $\eta\text{-MoC}_{1-x}$ phase as the principal phases judging from appearance showing epitaxial growth of hexagonal columns (see Figs. 3(c), (f) and (i)). It is also noticed in Fig. 3 that fraction of the porosity in the test piece tended to diminish with the decreasing C/Mo atom ratio on going from 1/1 to 1/2. Figure 3 also shows that clear gaps were visible among the neighbouring grains. No such hexagonal surface morphology was detected for the SEM appearances of the C/Mo = 1/2 test piece top surface processed at 1600°C (Fig. 3(j)–(l)) that yielded single-phase $\beta\text{-Mo}_2\text{C}$ phase (Fig. 1(g)).

In fact, it is a bit peculiar that $\eta\text{-MoC}_{1-x}$ phase emerged as the principal phase at the top surface of the test pieces

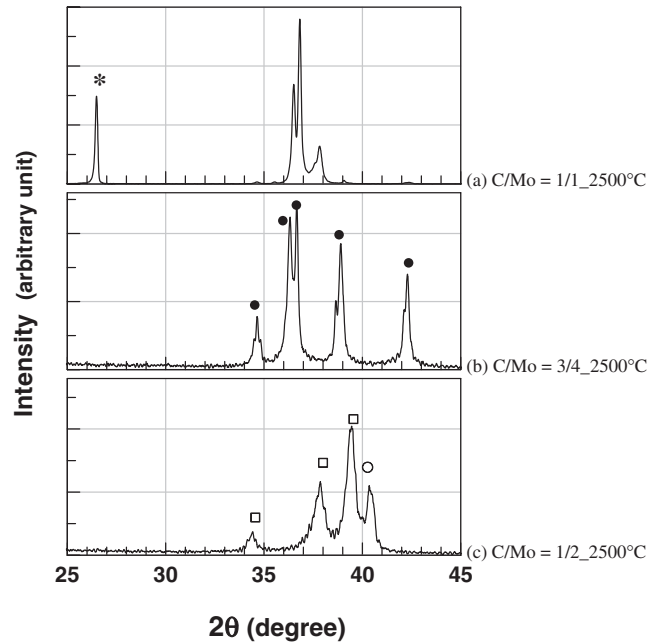


Fig. 2 The XRD patterns ($\text{CuK}\alpha$) of the top surfaces of the pellets of graphite/molybdenum powder mixtures with C/Mo atom ratios, 1/1, 3/4 and 1/2, heated to 2500°C or higher at a focal spot in the solar furnace with the initial ultra-fast heating rate. (●) $\eta\text{-MoC}_{1-x}$, (□) $\beta\text{-Mo}_2\text{C}$, (○) Mo, (*) graphite.

Table 1 List of Mo carbide phases detected by XRD in the test pieces prepared under different conditions of processing temperature and of C/Mo atom ratio in the starting material. The results for the test pieces treated at 1900°C were taken from our preceding work.¹⁾

C/Mo	surface	1600°C			1900°C Ref. 1)			“2500°C”		
		β	η	else	β	η	else	β	η	else
1/1	top	△	○	g	○	△	g	△	○	g
	bottom	○	○	g	○	○	g	NA	NA	NA
3/4	top	○	△	×	○	○	g	×	○	×
	bottom	△	○	×	○	△	g	NA	NA	NA
2/3	top	○	○	×	○	△	×	NA	NA	NA
	bottom	○	×	Mo	△	○	g	NA	NA	NA
1/2	top	○	×	×	○	×	×	○	×	Mo
	bottom	○	×	×	○	△	g	NA	NA	NA

○: detected

△: detected but weak

×: not detected

NA: data not available

g: graphite (002) peak detected

Mo: Mo metal (110) peak detected

β : $\beta\text{-Mo}_2\text{C}$ phase

η : $\eta\text{-MoC}_{1-x}$ phase

with C/Mo equal to or higher than 2/3 processed at 1600°C noting that stability range of $\eta\text{-MoC}_{1-x}$ phase is defined to be no less than 1655°C in the available equilibrium phase diagrams.^{3–5)} The similar result was obtained by our earlier attempt of synthesising Mo carbide starting from C/Mo powder mixtures with excess carbon (C/Mo = 1.5) at 1600°C using a solar furnace at PSA (Plataforma Solar de Almería, Tabernas (Spain))¹¹⁾ as well as in our more recent work using the solar furnace at PROMES-CNRS.²⁾ At the time of work at PSA about a decade ago, we tentatively interpreted the observed peculiarity in terms of some kind of photochemical effect.¹¹⁾ However, we are still unable

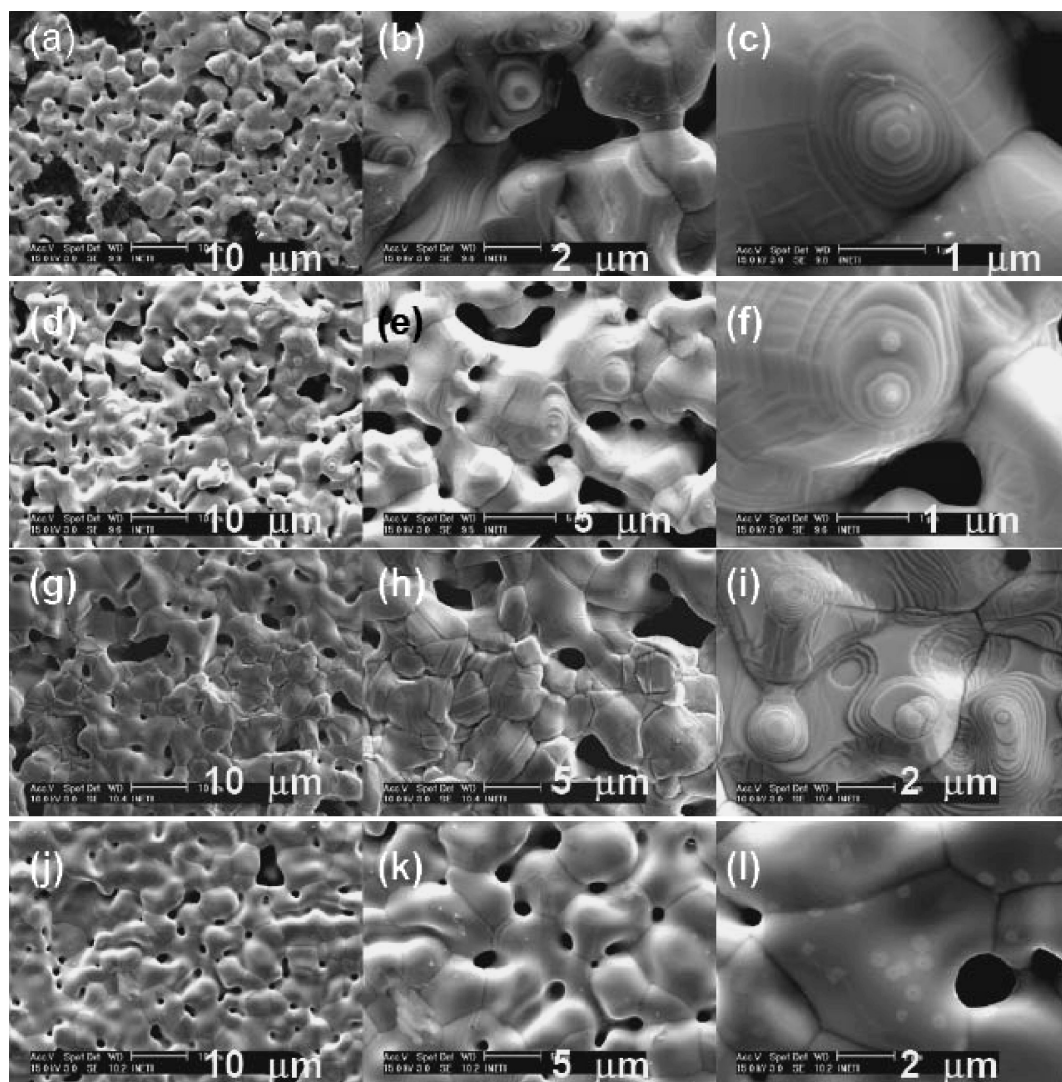


Fig. 3 Typical SEM appearances of the top surfaces of the C/Mo = 1/1, 3/4, 2/3 and 1/2 specimens heated to 1600°C. (a)–(c): C/Mo = 1/1, (d)–(f): C/Mo = 3/4, (g)–(i): C/Mo = 2/3, (j)–(l): C/Mo = 1/2.

to verify the involvement of photochemical effect or not to appreciate the observed peculiarity and accordingly we still have no clear-cut explanation on this aspect. We feel it desirable to undertake solar heating experiment using coloured filter to cut away some frequency range of solar beam to look into this aspect. We proposed another tentative interpretation suggesting that the excessively fast heating rate realised at the onset of the heating in the solar furnace at PROMES-CNRS might be the possible cause for this.²⁾ Anyway, neither of these tentative interpretations^{2,11)} is considered to be convincing conclusive explanation for why η -MoC_{1-x} phase yielded in solar carbide synthesis for Mo at 1600°C. Thus, this aspect must be elucidated by future work.

In our earlier publication,¹¹⁾ hexagonal η -MoC_{1-x} phase was cited as α -MoC_{1-x} and cubic α -MoC_{1-x} as β -MoC_{1-x}, respectively, accepting the older nomenclature for these carbide phases used by Storms³⁾ rather than newer one.^{4,5)} Thus, special attention must be taken in this respect on reading our earlier publication¹¹⁾ for the purpose of comparing with the discussions presented herein as well as in our preceding publication.¹⁾

From the SEM pictures in Fig. 3, unit powder diameter of the Mo was largely in the single-digit micron-meter (μ m) order in accordance with the nominal powder size specification of around 2 μ m. The graphite particles size also appeared to be in the single-digit μ m range, while the nominal size specification was simply < 50 μ m, judging from the size of the pores that were considered to emerge as the diffusion of graphite to the neighbouring metallic Mo to yield Mo carbide phases.

To verify the above aspect concerning the SEM particle size inspection results, particle size distributions of the raw materials were measured using CILAS 1064 liquid granulometer. The mean particle size d_{50} was determined to be $8.0 \pm 0.6 \mu$ m for Mo powders and $6.9 \pm 0.4 \mu$ m for graphite powders.

Although no XRD evidence of formation of cubic α -MoC_{1-x} phase was detected under any examined experimental condition, careful SEM inspection of the melted top surface of the C/Mo = 3/4 test piece processed to a temperature exceeding 2500°C showed localized development of square surface pattern as exhibited in Fig. 5(b) that might be considered as the evidence of formation of

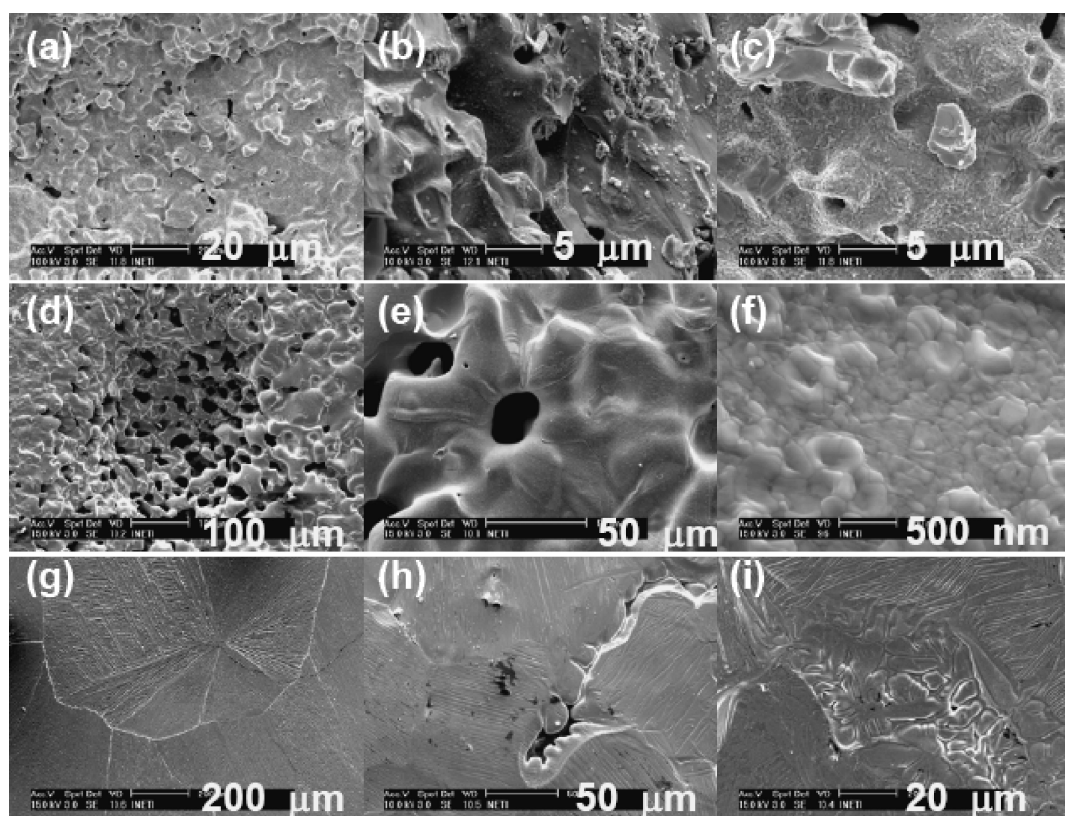


Fig. 4 Typical SEM appearances of the top surfaces of the C/Mo = 1/1, 3/4 and 1/2 specimens heated to 2500°C or higher. (a)–(c): C/Mo = 1/1, (d)–(f): C/Mo = 3/4, (g)–(i): C/Mo = 1/2.

cubic α -MoC_{1-x} phase at least temporarily. Judging from the typical surface appearances of this same test piece exhibited as Figs. 4(d)–(f) and the failure to detect any XRD peak identifiable as α -MoC_{1-x}, the volume fraction of the formed α -MoC_{1-x} must have been insignificant compared with that of η -MoC_{1-x} or have been lost by dissociation to η -MoC_{1-x} during cooling on account of insufficiently slow rate of quenching down to ambient temperature. Failed detection of XRD peak identifiable as α -MoC_{1-x} in this test piece might be also the consequence of slight extent of surface polishing of the test piece to ensure flatness of the surface before the XRD characterisation to lead to loss of the surface layer containing the α -MoC_{1-x}.

Metallic Mo was detected at the bottom surface of the C/Mo = 2/3 test piece processed at 1600°C (Fig. 1(f)) as well as at the top surface of the C/Mo = 1/2 test piece heated to a temperature higher than 2500°C (Fig. 2(c)). The former must represent the un-reacted Mo on account of relatively low temperature of the reaction at the test piece bottom side compared with that at the top side of the same test piece but the latter might represent the expelled metallic Mo during cooling out of the once formed β -Mo₂C.

In Fig. 2(b), satellite peak is detectable at $2\theta = 38.8^\circ$ but, as far as the binary Mo-C system is concerned (cf. Table 1 in Ref. 1)), there is no compound to yield XRD peak at this position. Satellite peak is also detectable in Fig. 2(b) at $2\theta = 42.1^\circ$ which might represent the remnant of cubic α -MoC_{1-x} phase judging from non-typical localised SEM appearances in Fig. 5 showing cubic morphology.

Insistent presence of sub-carbide phase, β -Mo₂C, even in the test pieces started at the C/Mo atom ratios higher than 1/2 at any examined processing temperature was quite intriguing. The similar situation was experienced for the W-C system.⁶⁻⁸⁾ Probable cause for the preferential formation of the sub-carbide phase and its insistent presence during heating to a higher temperature at gross C/M ratio in the test piece higher than 1/2 might be interpreted with reference to the electron band theory calculation results reported by Hugosson *et al.*^{12,13)} claiming that, for M_mC_n type carbide phases for M = Mo and W, the electronic energy difference among different carbide phases is quite small and thence, once some carbide phase was formed during the processing condition, it would remain insistent without being converted to another phase with truly stable state in thermodynamic terms even when the conditions were shifted to the range under which the other carbide phase would be stable thermodynamically.

Under the condition of ultra-fast heating rate realised at the onset of the heating in the solar furnace at PROMES-CNRS in Odeillo, sub-carbide Mo₂C would form preferentially during initial stage of heating by diffusion of graphite into Mo metal lattice (judging from SEM pictures summarised in Figs. 3 and 4). In the test pieces with C/Mo ratio greater than 1/2, direct physical contact between the formed Mo₂C and the residual graphite might be lost and, if such was the case, even if graphite was present in macroscopic sense in the entire test piece, further conversion of the once formed Mo₂C to η - or α -MoC_{1-x} phase would not proceed because of the lost direct contact

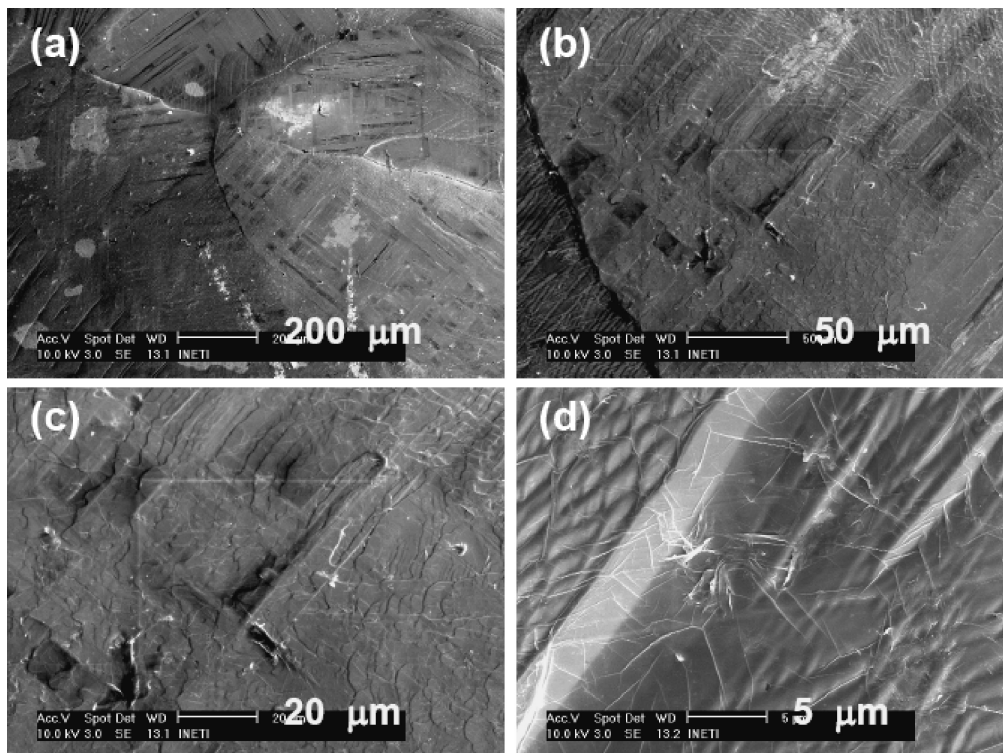


Fig. 5 Non-typical localized SEM appearances detected over the top surface of the C/Mo = 3/4 specimen heated to 2500°C or higher showing square surface pattern, rather than hexagonal, indicative of possible formation of cubic α -MoC_{1-x} phase.

between the formed β -Mo₂C particles and the residual graphite.

Such preferential formation of sub-carbide phase during the solar carbide synthesis was experienced for M = V (Va group metal) under condition of presence of excess free carbon in the reaction product.¹⁴⁾ For the binary V-C system, the mono-carbide phase VC is incomparably more stable thermodynamically than the sub-carbide phase V₂C and correspondingly the once formed V₂C was fully converted to VC by prolonged heating¹⁴⁾ in contrast to the situations with M = Mo and W in which M₂C insisted to remain in the reaction product even after prolonged heating to 90 min.⁶⁻⁸⁾

4. Conclusions

From the experimental evidences acquired in the present work together with those obtained in the earlier works,^{1,2)} following conclusions were drawn concerning the formation conditions for carbide phases of Mo under solar radiation heating with ultra-fast initial heating from ambient temperature to the processing temperature between 1600°C and 2500°C:

- (1) Under any examined condition, formation of β -Mo₂C phase was preferential.
- (2) Single-phase hexagonal η -MoC_{1-x} was prepared only from C/Mo = 3/4 test piece processed at 2500°C or higher.
- (3) Single-phase β -Mo₂C was synthesised from C/Mo = 1/2 test piece at the processing temperature 1600°C.
- (4) No XRD evidence of formation of cubic α -MoC_{1-x} phase was detected under any examined condition

(Table 1; Figs. 1 & 2) whereas SEM surface inspection for the melted top surface of the C/Mo = 3/4 test piece showed evidence of formation of some cubic phase (Fig. 5(b)) implying the necessity of very high rate of quenching to ambient temperature from the reaction temperature in order to retain the once formed cubic α -MoC_{1-x} phase at ambient temperature.

- (5) Very careful control over the C/Mo ratio in the starting material as well as processing temperature must be taken to synthesise single-phase Mo carbide with desired constitution.

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