Crystal Grain Morphology Evolution over Ti, V, Nb and Ta Surface Heated in N₂ Gas Environment to 2000°C by Filtered Concentrated Solar Beam in a Solar Furnace at PROMES-CNRS

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In recent attempts of reacting *d*-group transition metals with N₂ gas under irradiation of concentrated solar beam at temperatures around 2000°C using a standard setup with graphite specimen holder, reaction products obtained were carbo-nitrides rather than targeted nitrides on account of yield of C₂ radical plume from the graphite crucible. To suppress the interference of C₂ radical possessing high carbon chemical activity *a*(C) in nitriding *d*-group transition elements in solar furnace, we investigated effectiveness of inserting colour filters in the solar beam path. Two readily available colour filters, Sky blue and Medium yellow filters, were tested for this purpose. As reported in our earlier publications, XRD (X-ray diffraction) phase identification results indicated that insertion of the Sky blue filter was effective for suppressing C₂ radical yield under solar beam radiation to synthesize carbo-nitride with comparatively high N content. On the other hand, insertion of the Medium yellow filter did not result in so remarkable effect for suppressing carburization as the one detected with the Sky blue filter. In the present work, aspects of microstructures developed for Ti, V, Nb and Ta surfaces heated to 2000°C under exposure to colour-filtered solar beam in N₂ gas environment are reviewed. The present experimental evidences indicated that, by insertion of the Sky blue filter, appreciable crystallite grain size refinement was realized for the synthesized M(C,N) with high N content while, by insertion of the Medium yellow filter, certain extent of influence on the morphological development, that varied depending on the substrate material, was unmistakably discernible.

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1. Introduction

In recent years, nitrides, as well as carbides and carbon-nitrides, of *d*-group transition metals have received increasing attention owing to their unique chemical and physical properties such as high hardness, good thermal stability, superior wear resistance, excellent corrosion resistance, and relatively high electrical conductivity, making them suitable for microelectronic applications, hard coatings, electrocatalysts, and medical devices.¹⁻⁴⁾

Recently, we reported a novel route of nitriding *d*-group transition metals under concentrated solar beam at temperatures around 2000°C.^{5,6)} For practical reasons, in the standard setup for performing solar heating experiments, graphite crucible must be used as the sample holder and, at temperatures as high as 2000°C, yield of C₂ radical plume from graphite crucible vaporization is inevitable.⁷⁾ On account of the formation of C₂ radical species with high carbon chemical activity *a*(C) in the gas surrounding the sample material in solar furnace reaction chamber, certain extent of carburization was unavoidable in nitriding experiments using N₂ gas atmosphere under solar beam irradiation to yield the reaction products consisting of carbo-nitrides rather than the target nitrides.^{5,6)}

At PROMES-CNRS where these nitriding experimental runs were carried out using concentrated solar beam as the

source of reaction heat, two colour filters were readily available, namely a Sky blue (068) and a Medium yellow (010) filters supplied from Lee (Hampshire, UK; <http://www.leefilters.com/>). Among these two filters, transmittance vs. wavelength curve of the Sky blue filter showed opaqueness to the C₂ Swan band emission at 517 nm⁷⁾ suggesting that inserting the Sky blue filter ought to suppress C₂ radical yield. Indeed, as previously reported,^{5,6)} extent of carburization for *d*-group metals was appreciably suppressed by the insertion of the Sky blue filter.

In the present work, effect of insertion of colour filters on the microstructure evolution of synthesized reaction product observed at the top surface exposed directly to the concentrated solar beam is reviewed.

With the insertion of the Medium yellow filter, effect for suppression of carburization was not so clearly discernible by XRD (X-ray diffraction) phase identification as in the case with the Sky blue filter. However, some effect on the microstructure was unmistakably noticeable with the Medium yellow filter as well as with the Sky blue filter.

2. Experimental

2.1 Sample materials

Specifications of the reagents used are listed in Table 1. The test pieces with disc shape of diameter 10 mm and thickness 4 mm were prepared by uniaxially pressing the metal powders at 400 MPa in a die at ambient temperature.

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Table 1 Specifications of reagents used.

Reagents	Purity (%)	Particle size (μm)	Supplier
Ti	99	<45	Ventron (Karlsruhe, Germany)
V	99	<45	Goodfellow (Cambridge, England)
Nb	99.5	<125	L. Light (Cambridge, England)
Ta	99.9	<75	Goodfellow (Cambridge, England)
C	—	<50	Merck AG (Darmstadt, Germany)
N ₂	99.998	—	Air Liquide (France)

2.2 Solar irradiation procedure

Details of the solar irradiation procedure were given elsewhere^{5,6} and thence only a brief description of essence of the procedure is given below.

Each sample was heated by concentrated solar beam delivered by a vertical axis solar furnace optical system consisting of flat-surface mirror, louvered shutter, parabolic concentrator and sample holder set in Pyrex glass reaction chamber of capacity about 3 L. The colour filter was inserted between the louvered shutter and the parabolic concentrator. By insertion of any colour filter used, temperature drop at the reference pyrometric temperature monitoring spot was indiscernible from the temperature under the comparable configuration under absence of colour filter on account of the fact that heating effect under the solar beam was largely gained by the solar beam components in the IR (infra-red) range. All the solar beam-reflecting components were made of Ag and thence UV (ultra-violet) components in the solar beam were almost completely lost in the concentrated solar beam irradiating the test piece top surface. The flux density distribution at the focus of the solar furnace was Gaussian with a peak at about $16 \text{ MW}\cdot\text{m}^{-2}$.

Appearances of reaction chamber and sample holder are shown in Fig. 1 together with schematic setup configurations, A and B. The test piece top surface position (temperature measurement spot (a) over the graphite lid in the Setup A or the test piece top surface in the Setup B) was fixed at the exact focal spot of the concentrated solar beam and the heating process was controlled by stepwise opening of the shutter (shutter opening angle 90° refers to full opening). The louvered shutter was initially closed (opening angle 0°) and then it was opened instantaneously to angle 30° at the onset of the solar beam heating. This led to heating up of the temperature at the monitoring spot (a) in the Setup A (Fig. 1) to about 1000°C . This louvered shutter opening angle 30° was held for about 5 min to allow carburizing or nitriding reaction at this temperature as well as to prevent undesired disintegration of the consolidated disc specimen by eruptive degassing.

Under clear sky conditions yielding the natural solar intensity range $900\text{--}1000 \text{ W}\cdot\text{m}^{-2}$, the target temperature of 2000°C was reached with the shutter opening angle at around 75° after typically 10 min from the onset of the heating. We measured the surface temperature of the graphite lid at spot (a) in the Setup A (Fig. 1) with an optical pyrometer (HEITRONICS infra-red pyrometer Model KT15) that was calibrated taking into account that the emissivity ε for graphite to be 0.70 at $\lambda = 5 \mu\text{m}$ ⁸ and the light transmittance τ

Fig. 1 Appearances of reaction chamber and two crucible setups and schematic configurations of setup A and setup B. Temperature monitoring spot was (a) in the setup A and (b) in the setup B.

of the fluorine glass window at the top of the glass reactor chamber to be 0.92. The measured pyrometric temperature was displayed every 30 s in real-time over the display of the PC (personal computer) through EasyConfig control software.

In the Setup B experiment, temperature was measured at spot (b) over the graphite crucible in place of the test piece top surface center because the spectral emissivity ε of metal, Ti, V, Nb or Ta, was unknown. As the height of the temperature monitoring spot (b) in the Setup B was different from that of the temperature monitoring spot (a) in the Setup A, measured temperature in the Setup B at the point (b) was by 300°C lower than that at the spot (a) in the Setup A even under the comparable conditions.^{5,6} Thence, the measured pyrometric temperature under the Setup B experiment was merely considered as the control value assuming that the solar beam energy input at the test piece surface in the Setup B installed at the exact focal spot of the solar beam was comparable to that at the graphite lid surface in the Setup A that heated the graphite lid to the estimated temperature 2000°C .

In the Setup A, the test piece surface temperature must have been certainly lower than in the Setup B due to the indirect exposure to the solar radiation. Anyway, in either case, the test piece top surface was estimated to be heated up to $2000 \pm 100^\circ\text{C}$. This processing temperature was held for 30 min.

The Sky blue filter cuts more than 60% of the light with wave lengths between 500 and 700 nm while the Medium yellow filter cuts the wavelengths below 475 nm. Details of the filter characteristics and experimental setup employed are given elsewhere.^{5,6}

Table 2 Grouped test runs with measured test piece weight and N₂ gas pressure in the reaction chamber of about 3000 mL.

Group	run	M	w_i (g)	w_f	Δw	p_i (Torr)	$p(2000^\circ\text{C})$	p_f	Δp	phases present (by XRD)
I: setup A with graphite lid no filter	07	Ti	0.4835	0.6059	0.1224	399.5	588.3	374.5	−25.0	<i>fcc</i> Ti(C,N)
	10	V	0.8626	1.0634	0.2008	405.5	NA	363.8	−41.7	<i>fcc</i> V(C,N)
	11	Nb	1.2026	1.3352	0.1326	402.8	590.2	378.2	−24.6	<i>fcc</i> Nb(C,N)
	12	Ta	1.4883	1.5833	0.095	398.6	559.0	378.2	−18.6	<i>fcc</i> Ta(C,N)
II: setup B no graphite lid no filter	15	Ti	0.4818	0.5950	0.1132	406.1	548.3	389.2	−16.9	<i>fcc</i> Ti(C,N)
	16	V	0.8984	1.0932	0.1948	401.7	572.0	369.1	−32.6	<i>fcc</i> V(C,N)
	17	Nb	1.2004	1.3275	0.1271	399.2	561.3	374.0	−25.2	<i>tetragonal</i> Nb ₄ (C,N) ₃
	18	Ta	1.4895	1.5465	0.057	401.7	600.9	397.9	−3.8	<i>hexagonal</i> Ta ₂ (C,N) + <i>fcc</i> Ta(C,N)
III: setup B no graphite lid Sky blue.068	21	Ti	0.4725	0.5940	0.1215	408.6	539.6	390.0	−18.6	<i>fcc</i> TiN
	22	V	1.1866	1.4598	0.2732	401.7	473.6	346.0	−55.7	<i>fcc</i> VN
	26	Nb	1.2171	1.3592	0.1421	401.5	524.1	369.5	−32.0	<i>tetragonal</i> Nb ₄ N ₃
	23	Ta	1.5035	1.6046	0.1011	404.9	521.9	383.0	−21.9	<i>hexagonal</i> Ta ₂ N + <i>fcc</i> TaN
IV: setup B no graphite lid Medium yellow.010	29	Ti	0.7019	0.8804	0.1785	402.0	530.5	371.7	−30.3	<i>fcc</i> Ti(C,N)
	33	Nb	1.4458	1.6040	0.1587	403.3	540.7	370.0	−33.3	<i>tetragonal</i> Nb ₄ (C,N) ₃
	32	Ta	1.4652	1.5214	0.0562	404.9	576.3	401.7	−3.2	<i>hexagonal</i> Ta ₂ (C,N) + <i>fcc</i> Ta(C,N)

w_i : initial test piece weight (g),

w_f : final test piece weight (g),

$\Delta w = w_f - w_i$,

p_i : initial N₂ gas pressure (Torr),

$p(2000^\circ\text{C})$: maximum measured N₂ gas pressure at the reaction temperature (Torr),

p_f : final N₂ gas pressure (Torr),

$\Delta p = p_f - p_i$,

NA: not available; $p(2000^\circ\text{C})$ for Run 10 was carelessly forgotten to register,

note 1) Phases present at the top surface of each test piece was identified by XDR using CuK α radiation.

note 2) Principal phase in the test piece top surface was represented by **bold letters**.

note 3) Noting the reported evidences of suppressed carburization under insertion of Sky blue filter,^{5,6)} phases synthesized in the Group III experiments are represented as nitride in place of carbo-nitride in the other experiments.

To our knowledge, it was the very first time that colour filters were deliberately inserted in the optical system of the solar furnace to cut yield of C₂ radical species, aiming at retarding the carburization reaction competing with the nitriding reaction. The effect of the Sky blue filter towards retardation of carbide formation was quite impressive. This aspect seemed to be rational noting that the wavelength of emission from C₂ radical was reported to be 517 nm⁷⁾ which fell in the wavelength range (between 500 and 700 nm) that was cut efficiently by the Sky blue filter.

The Pyrex glass reactor with capacity 3 L was filled with high purity N₂ gas to a pressure of 400 ± 3 Torr (≈ 55 kPa) at ambient temperature after at least twice evacuating and flushing the chamber with N₂ gas. At the reaction temperature of about 2000°C, the measured N₂ gas partial pressure $p(2000^\circ\text{C})$ reached up to 600 Torr (80 kPa) (run 18 for Ta) and 475 Torr (63 kPa) (run 22 for V) depending on the amount of N₂ gas being absorbed into the test piece. The weight change of the test pieces was also recorded.

2.3 Specimen characterization

The reaction products were characterized by XRD (X-ray diffraction) using a Geigerflex D/MAX IIIC diffractometer (Rigaku Internat. Corp., Japan) and CuK α radiation. The microstructure at the test piece top surface exposed directly to the concentrated solar beam was inspected by scanning electron microscopy (SEM; Philips FEG XL30, The Netherlands).

3. Results and Discussion

3.1 Carbo-nitride phases in the reaction products in different experimental groups

Table 2 summarizes the XRD phase identification results reported in the preceding work⁵⁾ as well as values of the measured experimental parameters in the respective test runs.

In the Setup A with graphite lid (Group I experiment), synthesized phase from any examined M (= Ti, V, Nb or Ta) was carbonitride M(C,N) with face centred cubic (*fcc*) structure whereas, in the Setup B without graphite lid under absence of colour filter (Group II) experiment, Nb yielded tetragonal Nb₄(C,N)₃ and Ta yielded reaction product consisted of two phases, hexagonal Ta₂(C,N) and *fcc* Ta(C,N). These evidences suggest that the chemical activity $a(\text{C})$ of carbon varied appreciably depending on the experimental setup.

In the Group I experiment with loosely closed graphite lid, gas phase in the crucible interior surrounding the test piece must have been saturated with C₂ radical plume and thence $a(\text{C})^{\text{I}}$ must have been certainly higher than $a(\text{C})$ in the other experimental setups with no graphite lid (Groups II, III and IV).

For carbo-nitride UC_{1-x}N_x with exact stoichiometric composition, Katsura and co-workers⁹⁻¹⁴⁾ reported that the composition x under co-presence of C with a given activity $a(\text{C})$ tended to rise with N₂ gas partial pressure $p(\text{N}_2)$ or x in N₂ gas with a given $p(\text{N}_2)$ tended to diminish with rising $a(\text{C})$.

Fig. 2 Typical top surface appearances of the Ti specimens after solar heating to 2000°C in N₂ gas environment. (a) run 07 in setup A, (b) run 15 in setup B with no filter, (c) run 21 in setup B with Sky blue filter, (d) run 29 in setup B with Medium yellow filter.

To look into this aspect to evaluate $a(C)$ in respective experimental Groups comparatively, visual inspection was made for colours of the reaction products from Ti specimens in respective test runs (Run 07 in Group I; Run 15 in Group II; Run 21 in Group III; Run 29 in Group IV). It is well known²⁻⁴⁾ that *fcc* TiN and *fcc* TiC are fully miscible to form carbonitride Ti(C,N) with *fcc* structure and that colour and luster of TiN are practically comparable to those of Au but the colour of Ti(C,N) tends to blacken with decreasing N content. Observation showed that the colour of Ti(C,N) test piece surface tended to fade from golden (TiN) to black (TiC) in the order of

$$\text{Run 21 (III)} > \text{Run 15 (II)} \approx \text{Run 29 (IV)} > \text{Run 07 (I)} \quad (1)$$

implying that $a(C)$ in the four experimental Groups increased in the order of

$$a(C)^{\text{III}} < a(C)^{\text{II}} \approx a(C)^{\text{IV}} < a(C)^{\text{I}} \quad (2)$$

as the experiments were done under comparable $p(\text{N}_2)$ and reaction temperature T .

Accepting this, formation of the tetragonal Nb₄(C,N)₃ in the experimental Group II was speculated to be induced by the decreased $a(C)^{\text{II}}$ from $a(C)^{\text{I}}$ under insufficiently high $p(\text{N}_2)$ to synthesize *fcc* NbN instead of slightly N-deficient tetragonal Nb₄N₃.

Validity of order of $a(C)$ in respective experimental Groups as given in eq. (2) appeared to be supported also by comparison of colour of Nb specimens between Run 26 (III) and Run 33 (IV). The Nb test piece surface after the Run 26 (III) was more yellowish implying higher N content than that after Run 33 (IV) ensuring the order $a(C)^{\text{III}} < a(C)^{\text{IV}}$ as presented in eq. (2).

3.2 Morphological characteristics of the test piece top surfaces

SEM appearances of the test piece top surfaces are reproduced in Fig. 2 (Ti), Fig. 3 (V), Fig. 4 (Nb) and Fig. 5 (Ta). In the following, characteristic features of the test piece surface exposed directly to the concentrated solar beam are reviewed for respective sample materials.

3.2.1 Ti

When we look at Fig. 2 comparing the Ti specimen surface appearances after different test runs, it is evident that the surface after the Run 07 (Group I with graphite lid) (a) and that after the Run 29 (Group IV with Medium yellow filter) (d) showed presence of Ti(C,N) grains with comparatively large size, probably representing the crystal grains present in the initial Ti powders (Table 1) while crystallites with refined grain size emerged after the Run 15 (Group II with no graphite lid nor colour filter) (b) and the Run 21 (Group III with Sky blue filter) (c).

As reviewed earlier in 3.1, $a(c)$ was the lowest for the Run 21 with Sky blue filter and the reaction product synthesized in this test run was identified to be virtually pure TiN or Ti(C,N) with very low C content (Table 2). This morphological feature seems to be explainable in terms of either sublimation growth¹⁵⁾ or combustion synthesis^{16,17)} mechanism.

In the Group III experimental condition with the Sky blue filter, $a(C)^{\text{III}}$ in the gas phase must have been insufficiently low to promote carburization and thence, during initial stage of heating by opening the louvered shutter from 0 to 30°, the sample surface temperature instantaneously rose to 1000°C from ambient temperature, eruptive TiN forming reaction emitting massive reaction heat took place and, as the consequence, partial sublimation of Ti must have been

Fig. 3 Typical top surface appearances of the V specimens after solar heating to 2000°C in N₂ gas environment. (a) run 10 in setup A, (b) run 16 in setup B with no filter, (c) run 22 in setup B with Sky blue filter, (d) run 22 in setup B with Sky blue filter.

Fig. 4 Typical top surface appearances of the Nb specimens after solar heating to 2000°C in N₂ gas environment. (a) run 11 in setup A, (b) run 17 in setup B with no filter, (c) run 26 in setup B with Sky blue filter, (d) run 33 in setup B with Medium yellow filter.

induced alongside direct conversion of Ti to *fcc* TiN in solid state through diffusion of N fed from surrounding N₂ gas environment. Sublimated Ti might have been converted quickly to TiN by reaction with N₂ molecules in the gas phase and precipitated back onto the surface as discrete crystallites of TiN. During holding at louvered shutter

opening angle 30° for 5 min, homogenization process of the formed TiN progressed steadily to the equilibrium state. This mechanism appears to explain rationally the observed non-edgy morphology of refined TiN crystallites distributing discretely over comparatively large crystalline granular TiN [Fig. 2(c)].

Fig. 5 Typical top surface appearances of the Ta specimens after solar heating to 2000°C in N₂ gas environment. (a) run 12 in setup A, (b) run 18 in setup B with no filter, (c) run 23 in setup B with Sky blue filter, (d) run 32 in setup B with Medium yellow filter.

Table 3 Selected values of thermodynamic parameters for Ti, V, Nb and Ta presented in NIST-JANAF Thermochemical Tables.¹⁸⁾

Parameter	Element			
	Ti	V	Nb	Ta
crystal-liquid transition temperature (K)	1939	2190	2750	3258
glass-liquid transition temperature (K)	1460	1430	1750	2150
$\log K_f(M(g))$ at 2300 K	-3.514	-16.536	-8.773	-10.401
$\log K_f(M(g))$ at 1300 K	-11.437	-37.328	-21.537	-24.043
$\Delta G_f(M(g))$ at 1300 K (kJ·mol ⁻¹)	284.7	929.0	536.0	598.4
$\Delta H_f(M(g))$ at 1300 K (kJ·mol ⁻¹)	461.6	1187.4	733.0	780.1

standard state pressure is taken to be at 0.1 MPa.

$K_f(M(g))$: equilibrium constant for reaction forming monatomic gaseous M from condensed M in crystalline form,

$\Delta G_f(M(g))$: Gibbs free energy change on sublimation reaction to yield monatomic gaseous M from condensed M in crystalline form,

$\Delta H_f(M(g))$: enthalpy change on sublimation reaction to yield monatomic gaseous M from condensed M in crystalline form.

To verify validity of the above speculation, selected values of thermodynamic parameters for Ti as well as for V, Nb and Ta listed in NIST-JANAF Thermochemical Tables¹⁸⁾ are reproduced in Table 3. The selected parameters listed in Table 3 are as follows;

(crystal-liquid transition temperature): temperature at which solid M in crystalline state is subjected to melting known commonly as equilibrium melting point (in K),

(glass-liquid transition temperature): temperature at which solid M in amorphous state is subjected to melting (in K),

($K_f(M(g))$): equilibrium constant for reaction yielding monatomic gaseous M from condensed M in crystalline form,

($\Delta G_f(M(g))$): Gibbs free energy change on sublimation reaction to yield monatomic gaseous M from condensed M in crystalline form (in kJ·mol⁻¹),

($\Delta H_f(M(g))$): enthalpy change on sublimation reaction to yield monatomic gaseous M from condensed M in crystalline form (in kJ·mol⁻¹).

In Table 3, values for $\log K_f$, ΔG_f and ΔH_f at $T = 1300$ K as well as $\log K_f$ at $T = 2300$ K are listed. In the present experimental procedure, heating of the test piece with concentrated solar beam was done quickly from ambient temperature to about 1000°C (= 1273 K) by opening the shutter from opening angle 0 to 30° instantaneously and held for 5 min at the shutter opening angle 30°. Thence, several reactions determining the surface morphology of the test piece were considered to take place at around $T = 1300$ K. Therefore, values of the key thermodynamic parameters are compared among Ti, V, Nb and Ta at $T = 1300$ K. As the target processing temperature was 2000°C (= 2273 K), values for $\log K_f$ at $T = 2300$ K are also listed in Table 3 although for comparison purpose although, when $T = 2000^\circ\text{C}$ was reached, it was quite likely that metallic phase was fully converted to carbo-nitride phases in solid state.

Judging from the value of $\log K_f(M(g))$ for Ti at $T = 1300$ K in Table 3, vapour pressure $p(\text{Ti})$ of Ti must have

been the highest among the four examined elements at this T and thence, during 5 min holding at 1000°C with the shutter opening angle 30°, significant sublimation of Ti and subsequent re-precipitation of TiN must have taken place besides direct conversion of Ti to TiN that would certainly yield considerable reaction heat to lead to instantaneous temperature rise to a level well above 1300 K.

It is also intriguing to note in Table 3 that the glass-liquid transition temperature of any given M is by 500–1000 K lower than the equilibrium melting point of the same M implying that solid M in glassy state might be converted to liquid phase at T by far lower than the equilibrium melting point of the solid M in crystalline form.

Therefore, if amorphization of M took place during the initial stage of the solar heating by any chance, emergence of liquid phase might have occurred at T considerably lower than the equilibrium melting point of the M.

During the eventual 30 min holding at the nominal processing temperature 2000°C, homogenizing process might have taken place steadily but the violent carbo-nitriding process with considerable exothermic reaction heat must have been largely completed during the initial 5 min holding period at 1000°C.

Liu *et al.*¹⁶⁾ undertook combustion synthesis of TiN from starting materials, Ti powders (99% pure) and N₂ gas (99.9%), by igniting with electric current and found that the reaction products were consisted of TiN crystals with varying morphologies including quasi-spherical grains, well-developed faceted cubic or pyramidal crystals and dendritic crystals. In the work of Liu *et al.*,¹⁶⁾ temperature during the combustion reaction was not measured. Judging from presence of dendritic crystals and of quasi-spherical grains in the reaction product, maximum temperature in their combustion synthesis process must have reached to a level sufficient to yield localized liquefaction although presence of the faceted crystal grains appeared to suggest the solid state conversion of Ti to TiN.

With reference to classification of Liu *et al.*,¹⁶⁾ surface morphology of Fig. 2(c) developed in the Group III experiment using the Sky blue filter looks comparable to the quasi-spherical grains as exhibited in Fig. 3(a) in their publication.

In contrast to the situation with the Sky blue filter [Fig. 2(c)], initial grain size of Ti metal powders appeared to be practically retained in Ti(C,N) synthesized in the Runs 07 [Fig. 2(a)] and 29 [Fig. 2(d)]. In these runs with comparatively high $a(C)$, carburization progressed during heating at the instantaneous opening of the louvered shutter from 0 to 30° besides competing nitriding reaction but progress of the carbo-nitriding reaction might have been not so violent as the nitriding reaction involved with sublimation/precipitation process in the Run 21 with comparatively low $a(C)$ ^{III}. Therefore, carbo-nitriding reactions in Runs 07 and 29 must have progressed without liquid phase formation.

The morphological characteristics observed in Fig. 2(b) for the Ti(C,N) specimen top surface prepared by the Run 15 under condition with no graphite lid nor colour filter looked somewhat similar to that observed in Fig. 2(c) for TiN prepared by the Run 21 with Sky blue filter. Thus, during the carbo-nitriding reaction in the Run 15, liquid phase formation

process might have taken place over the compacted Ti specimen surface but not in the Run 21 [Fig. 2(c)].

These evidences seemed to imply that, although $a(C)$ ^{II} and $a(C)$ ^{IV} in eq. (2) were evaluated to be comparable to one another on the basis of XRD phase identification results (Table 2), effective $a(C)$ ^{II} might have been slightly lower than $a(C)$ ^{IV} suggesting $a(C)$ was somewhat raised by the presence of Medium yellow filter. This aspect deserves further experimental verification.

3.2.2 V

SEM appearances of the V sample surfaces prepared by different test runs are compared in Fig. 3; (a) Run 10 (Group I), (b) Run 16 (Group II), (c) and (d) Run 22 (Group III). For V, test run corresponding to Group IV experiment was not realized simply because we ran out of V specimen material during our planned stay at PROMES-CNRS over 3 weeks.

It is seen in Figs. 3(c) and 3(d) that refined VN crystallites formed over the test piece surface under the Group III experimental condition with Sky blue filter. These appearances look similar to those for the Ti specimen processed under the comparable condition shown in Fig. 2(c) implying the involvement of sublimation growth mechanism for VN synthesis as well as for TiN synthesis under the Group III experimental condition with suppressed $a(C)$ ^{III}. However, crystal refinement for V under the Group III condition [Figs. 3(c) and 3(d)] took place more homogeneously than that for Ti under the comparable condition [Fig. 2(c)]. Possible explanation for slightly different morphologies between TiN [Fig. 2(c)] and VN [Figs. 3(c) and 3(d)] might be made on the basis of the fact that neither sub-carbide nor sub-nitride phase would form with Ti (IVa-group d -transition element) but sub-carbide V₂C as well as sub-nitride V₂N might form with V and other two Va-group d -transition elements, Nb and Ta, examined in this work besides mono-carbide VC and mono-nitride VN.^{1–4,19)}

Free energy of formation $\Delta G_f(M_2N)$ of sub-nitride M₂N must be less negative than that $\Delta G_f(MN)$ of mono-nitride MN of the same M and $\Delta G_f(VN)$ must be less negative than $\Delta G_f(TiN)$ because affinity between M and N must be stronger for M = IVa-group elements (Ti, Zr, Hf) than for M = Va-group elements (V, Nb, Ta).

On the instantaneous opening of the louvered shutter from 0 to 30° and during the subsequent holding at the shutter opening 30° for 5 min, V₂N formation rather than VN formation must have progressed. Similar intermediate sub-carbide formation was observed for another Va-group element, Ta, during synthesis of carbide under heating with concentrated solar beam.²⁰⁾ The formed sub-carbide V₂C in meta-stable state was eventually converted to stable mono-carbide VC after prolonged holding at the high temperature.²⁰⁾

Under the present reaction condition of the Group III experiment with suppressed $a(C)$ ^{III} under presence of the Sky blue filter, sub-nitride V₂N in meta-stable state might have formed initially and then it was converted to stable VN during subsequent heating process.

If such was the case, crystal grain size refinement observed for the V specimen surface in Figs. 3(c) and 3(d) in the Group III experiment must be the consequence of crystal lattice transformation from non-cubic sub-nitride V₂N to *fcc*

mono-nitride VN unlike re-precipitation of sublimated Ti [Fig. 2(c)].

Likewise, the crystal grain size refinement detected for the V(C,N) under the Group I experiment [Fig. 3(a)] must be interpreted in terms of crystal lattice transformation from non-cubic sub-carbide V_2C formed during the intermediate 5 min holding at 1000°C to *fcc* mono-carbo-nitride V(C,N) during heating to 2000°C.

Under the Group II experimental condition with comparatively high $a(C)^{II}$, synthesized V(C,N) was with relatively large crystal grain size [Fig. 3(b)]. This surface morphology of V(C,N) somewhat looks like the faceted crystalline geometries by Liu *et al.* for TiN [cf. Figs. 3(b) and 3(d) and Fig. 6 in Ref. 16].

Under the balance between $a(C)^{II}$ and $p(N_2)$ in the Group II experimental condition, conversion of hexagonal $V_2(C,N)$ phase to eventual V(C,N) with *fcc* structure as well as the initial conversion of V to $V_2(C,N)$ was speculated to take place by competitive absorption of C and N. Under condition with competitive absorption of C and N into V in solid state in the Group II experiment, crystallite grain size refinement as observed in preferential N dissolution for V in the Group III experimental condition or in preferential C dissolution for V in the Group I experiment might have been inhibited. Validity of this speculation must be verified by further experimental work.

3.2.3 Nb

Microstructure evolution modes observed for Nb samples in Fig. 4 look quite different from those observed for the same Va-group metal V in Fig. 3 or for Ti (IVa-group metal) in Fig. 2 under corresponding conditions of $a(C)$ and $p(N_2)$ as well as of T . It is specially remarkable in Fig. 4(c) for $M = Nb$ to notice that the crystal grain size refinement effect under the Group III experimental condition with suppressed $a(C)^{III}$ observed for Ti [Fig. 2(c)] and V [Figs. 3(c) and 3(d)] was not detected.

This distinguishable mode of lacked crystal grain refinement detected specifically for Nb in the Group III experiment might be appreciated in terms of strong trend of formation of tetragonally distorted crystal structure $\delta-Nb_4N_3$ under N-deficient condition realized under insufficiently high $p(N_2)$ to yield *fcc* mono-nitride NbN.^{2-4,20,21)}

The mode of morphological development for Nb in the Group IV experiment [Fig. 4(d)] also looks very different from that for Ti [Fig. 2(d)]. The surface appearance of Fig. 4(d) suggests that surface melting took place prior to eventual formation of tetragonal $Nb_4(C,N)_3$ in the Group IV experiment with the Medium yellow filter. In fact, trace of dendrite-like surface pattern is detected in the central zone of the large grain in the right hand side in Fig. 4(d). For development of dendritic crystal, liquid phase formation must have been preceded.

With reference to Table 3, glass-liquid transition temperature of Nb is as low as 1750 K whereas the equilibrium melting point of Nb is 2750 K. Thus, amorphization of Nb took place by any chance in the initial stage of rapid heating with concentrated solar beam up to the intermediate stagnation temperature 1000°C (= 1273 K), surface melting of the Nb test piece might be accepted but 1000°C is nearly by 500°C lower than the glass-liquid transition temperature

of Nb and, even taking into account heat evolved on conversion of Nb to $Nb_4(C,N)_3$, it seems difficult to imagine emergence of massive molten surface layer over the Nb test piece.

In the earlier works,²²⁻²⁵⁾ we pointed out that some phases of carbide of *d*-group transition elements synthesized using concentrated solar beam as the reaction heat source did not always coincide exactly with the available equilibrium phase diagrams in literature¹⁻⁴⁾ defined in terms of conventional thermodynamic parameters such as temperature T and chemical activity $a(C)$ of C alone and thenceforth it was felt desirable to take into account contribution from some other factors such as some wave frequency component in the solar beam towards selective promotion or suppression of specific reaction process.

Some of the present experimental evidences such as the one exhibited in Fig. 4(d) for Nb remind us of necessity of taking into account such additional factor in solar materials processing.

As pointed out earlier in the text in 3.1, $a(C)^{IV}$ was estimated to be comparable to $a(C)^{II}$. Nevertheless, the morphological characteristics of tetragonal $Nb_4(C,N)_3$ synthesized under the Group II experimental condition [Fig. 4(b)] looks totally different from those of tetragonal $Nb_4(C,N)_3$ synthesized in the Group IV experiment [Fig. 4(d)] showing no evidence of massive surface melting in the Group II experiment. These evidences suggest intriguing effect of insertion of Medium yellow filter on materials processing under solar beam radiation. That is, whereas the synthesized carbo-nitride phase, tetragonal $Nb_4(C,N)_3$, with or without Medium yellow filter was indistinguishable in terms of XRD, their morphological features were not comparable to one another. There is no straightforward explanation readily available but it seems certain that this effect must be investigated systematically in future work.

3.2.4 Ta

Top surface appearances for Ta specimens obtained under varying solar beam radiation conditions are summarized in Fig. 5.

As seen in Figs. 5(b) and 5(d), morphological characteristics of two-phase specimen consisted of $Ta_2(C,N)$ and Ta(C,N) synthesized by the Group II experiment and those of two-phase specimen synthesized by the Group IV experiment were somewhat comparable to each other unlike the situation with Nb (Fig. 4) implying that no appreciable effect of Medium yellow filter insertion was detectable for Ta unlike for Nb.

It is intriguing to noticed that morphologies seen in Figs. 5(b) and 5(d) are strikingly resembling to the faceting morphology presented in Fig. 7 in the publication by Liu *et al.*¹⁶⁾

Like for Nb (Fig. 4), additional factor related to solar beam wave frequency in addition to conventional thermodynamic parameters must be taken into account in order to interpret rationally the detected surface morphologies for Ta specimens (Fig. 5) although the details are still demanded to be investigated by future elaboration.

It is also worthwhile pointed out that SEM appearances of the Ta specimens in Fig. 5 show single-phase nature whereas

XRD characterization results summarized in Table 2 suggested two-phase nature. Such apparent inconsistency must be interpreted in terms of composition gradient along the height reported earlier for solar-synthesized specimens on account of inevitable temperature gradient in the solar heating experiments.²⁶⁾

4. Concluding Remarks

Morphological characteristics of top surface of carbo-nitrides of Ti, V, Nb and Ta synthesized at 2000°C in N₂ gas environment using graphite crucible sample holder were reviewed in relation to filtering of solar beam with colour filters. Temperature drop caused by insertion of Sky blue or Medium yellow filter was verified to be negligibly small implying that heating effect with concentrated solar beam was gained mainly by solar beam wave components in IR range.

Top surface morphology of the obtained carbo-nitrides varied, in some cases, being dependent on the inserted colour filter even when XRD characterization of phases did not show any distinctive effect of colour filter insertion on the phase formation.

With the Sky blue filter insertion, yield of C₂ plume appeared to be efficiently suppressed to retard carburizing reaction in N₂ gas atmosphere. On the other hand, effectiveness of the Medium yellow filter insertion on the C₂ plume yield suppression was not detectable but there was certainly some effect of the Medium yellow filter insertion on the morphological characteristics of the reaction product.

As the acquired experimental evidences in this preliminary work are still too scarce to draw any definitive conclusion regarding effect of colour filtering for carbo-nitride synthesis under solar beam radiation, we now believe firmly that this aspect is worthwhile investigated systematically in future.

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