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Hydrothermal oxidation of bulk Ti_3SiC_2 in continuous water flow was studied at 500°–700°C under a hydrostatic pressure of 35 MPa. The oxidation was weak at 500°–600°C and accelerated at 700°C due to the formation of cracks in oxides. The kinetics obeyed a linear time-law. Due to the high solubility of silica in hydrothermal water, the resulting oxide layers only consisted of titanium oxides and carbon. Besides general oxidation, two special modes are very likely present in current experiments: (1) preferential hydrothermal oxidation of lattice planes perpendicular to the *c*-axis inducing cleavage of grains and (2) uneven hydrothermal oxidation related to the occurrence of TiC and SiC impurity inclusions. Nonetheless the resistance against hydrothermal oxidation is remarkably high up to 700°C.

I. Introduction

Ax phases exhibit a striking combination of the prominent properties of both ceramics and metals.^{1–3} They possess the general formula of $M_{N+1}AX_N$ (N = 1, 2 or 3), where M is a transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C or N. As an important member of this family, titanium silicon carbide (Ti₃SiC₂) displays numerous salient properties, such as good oxidation resistance, low density, high elastic modulus and strength, chemical stability, excellent thermal shock resistance, good machinability and high ratio of fracture toughness to strength.^{1–4}

Ti₃SiC₂ has obvious advantages over brittle ceramics such as silicon carbide because of good machinability,^{1,2,5} high damage tolerance,^{6,7} and reliability.⁸ Therefore, Ti₃SiC₂ has lately attracted great attention as a prospective material for energy-related systems. In the literature, some experiments evaluating the damage resistance of this ceramic under related conditions can be found. For example, Barnes *et al.*⁹ studied the corrosion behavior of Ti₃SiC₂ in circulating molten lead at 650° and 800°C for a possible cladding or structural material in a lead-cooled

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fast reactor. Nappé *et al.*¹⁰ investigated the behavior of Ti_3SiC_2 under nuclear and electronic irradiation for a cladding material for future fuels.

In addition to those environments, hydrothermal oxidation is a common category of oxidation involved in energy-related systems because high-temperature and high-pressure water is frequently handled. In contrast to the excellent high-temperature oxidation resistance, advanced ceramics, such as non-oxide materials like silicon carbide^{11–16} or silicon nitride^{17–19} and even alumina as an oxide,²⁰ are vulnerable to corrosion at relatively low temperatures during hydrothermal conditions.

Our recent work explored the hydrothermal oxidation behavior of $Ti_3SiC_2^{21}$ and $Ti_3Si_{0.9}Al_{0.1}C_2$ powders.²² The primary results showed that titanium, silicon, and aluminum were selectively extracted from the Ti_3SiC_2 and $Ti_3Si_{0.9}Al_{0.1}C_2$ substrates during hydrothermal oxidation, resulting in the formation of the corresponding oxides and carbon. The presence of carbon was attributed to the unique bonding and structural characteristics of Ti_3SiC_2 and $Ti_3Si_{0.9}Al_{0.1}C_2$.^{21,22}

In this work, for the first time, we extended the investigations to bulk Ti_3SiC_2 in steady-state conditions (flowing water) to study the hydrothermal oxidation kinetics, the composition and structure of the resulting layers. The systematic characterization of the hydrothermal oxidation of bulk Ti_3SiC_2 will greatly benefit its application in energy related systems, such as light water reactor.

II. Experimental Procedure

The bulk Ti_3SiC_2 was fabricated by the solid-liquid reaction synthesis and simultaneous *in situ* hot pressing process.²³ The grains size of the as-prepared bulk specimen was approximately 20 µm. Impurities including 5 wt% SiC, 5 wt% TiC, and minor amounts of graphite were macroscopically evenly distributed, but locally aggregated, in some regions, up to > 100 µm.

 $3 \times 4 \times 8$ mm³ rectangular bars were used for the hydrothermal oxidation experiments. These bars were ground on 1000 grit SiC papers, polished using diamond paste (grain size: 1 µm), chamfered and degreased in acetone.

Specimen bars were inserted into the gold-coated autoclave with a continuous water flow (SITEC Industrietechnologie GmbH, Chemnitz, Germany). A boxer type pump was used to maintain a controllable and constant flow-rate during the time of the experiments. At a flow rate of 15 mL/h, distilled water in the autoclave (30 mL) was replaced approximately every 2 h. The experiments were carried out at 500° to 700° C under a

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hydrostatic pressure of 35 MPa. Hydrothermal oxidation kinetics was evaluated by the mass change of the specimens, which was measured using an electric microbalance (Sartorius AG, Göttingen, Germany) with the precision of 0.1 μ g.

After hydrothermal oxidation, the reaction products were analyzed by X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). XRD was performed using a Bruker D8 Advance Microdiffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with a Co-sealed tube, an HOPG graphite primary monochromator and a 500 μ m monocapillary with 300 μ m pinhole. Raman spectroscopy was recorded using a Dilor Labram[®] 2 (Horiba Jobin Yvon GmbH, Bensheim, Germany) and Ar⁺-ion laser with the wavelength of 488.0 nm. Using a grating with 1800 lines/mm, a spectral resolution of ca. 1.7 cm⁻¹ was obtained. XPS were measured using a SPECS Phoibos100 electron energy analyzer and MgK α radiation (1253.6 eV, nonmonochromatized, 0.7 eV intrinsic line width). Typical pass energies were 50 eV for overview spectra and 10–20 eV for detail spectra, resulting in an overall energy resolution of 1 eV.

The thermodynamic reactions were calculated using the FactSage 5.4 Gibbs free energy minimization program.²⁴ The calculations were performed assuming a constant total pressure of 35 MPa and the gas phases were assumed to show ideal behavior.

The surfaces and cross-sections of the specimens were examined using a scanning electron microscope (LEO VP 1450, Carl Zeiss AG, Oberkochen, Germany, 15 kV acceleration current) equipped with an energy-dispersive spectroscopy (EDS) from Oxford (INCA energy 300, Oxford Instruments, Abingdon, U.K.). Before the examination, a thin platinum layer (ca. 35 nm) was sputtered onto the surfaces of the samples. SE-mode images were recorded using an Everhart-Thornley SE-detector (Carl Zeiss AG).

III. Results

(1) Kinetics

Figure 1 presents the weight gain per unit area as a function of exposure time for the Ti₃SiC₂ specimens hydrothermal oxidized in flowing water at 500° to 700°C under a hydrostatic pressure of 35 MPa. The kinetics obey a linear time-law, which differs from the parabolic kinetics shown in air oxidation of Ti₃SiC₂ at 500° to 900°C.²⁵ The weight gain is slight at 500° to 600°C (linear rate-constants: 1.2×10^{-2} and 2.5×10^{-2} µg/mm²/h, respectively) and is considerably accelerated at 700°C (linear rate-constant: 24.2×10^{-2} µg/mm²/h).



Fig. 1. Weight gain per unit area as a function of exposure time for the Ti_3SiC_2 specimens hydrothermal oxidized in flowing water at 500–700°C under a hydrostatic pressure of 35 MPa.

(2) Phase Analysis

Figure 2 shows XRD patterns of the Ti₃SiC₂ samples after hydrothermal oxidation. Anatase (TiO₂) is distinguished as the only reaction product at 500° to 600°C while anatase and rutile (both TiO₂ modifications) occur at 700°C. The diffraction peaks associated with rutile become much more intensive with oxidation time, owing to the phase transformation from anatase to rutile. This phase transformation was previously discovered in the hydrothermal oxidation of Ti₃SiC₂ and Ti₃Si_{0.9}Al_{0.1}C₂ powders,^{21,22} as well as the oxidation of Ti₃SiC₂ in air.²⁵ Silica (either crystalline or amorphous) was not detected in this work. In contrast to this, α -cristobalite (tetragonal SiO₂ modification) is present after hydrothermal oxidation of Ti₃SiC₂ and Ti₃ Si_{0.9}Al_{0.1}C₂ powders at 700°C.^{21,22} It is noteworthy that the diffraction peaks from the Ti₃SiC₂ substrate are visible even after 20 h at 700°C, indicating the formed oxide scales are quite thin (i.e., a few micrometers) at or below these conditions.

Raman spectroscopy is highly sensitive to carbon and, therefore, a valuable tool to identify carbon allotropes^{26,27} and interpret structural characteristics.²⁸ This is why structural characterizations of carbon were carried out using Raman spectroscopy (Fig. 3). The Raman spectra clearly verify strong bands of the graphite band (G-band) and the disordered/nanocrystal-line carbon band (D-band),^{11–15} which provides the evidence for the presence of carbon. Due to carbon consumption by reaction with water,^{15,21,22} the amounts of as-formed carbon decrease with reaction time at 700°C (Fig. 3(j)-(1)). It can be seen from Fig. 4 that the positions of G-bands are constant and independent of experimental conditions, while D-bands display a significant down-shift with oxidation temperatures and time. In Fig. 3, the D-bands are asymmetric and another two peaks at 1179 and 1287 cm⁻¹ are assigned by fitting using two Gaussian-Lorenz mixed curves. Previous studies about hydrothermal oxidation of SiC suggested these broad peaks in the D-band region originated from the contribution of sp^3 carbon.^{11–14} This analysis cannot unambiguously be confirmed from Raman spectroscopy alone, because the Raman scattering cross section of sp^3 carbon is much lower than sp^2 carbon unless the laser wavelength lies in the ultraviolet range.^{29,30}



Fig. 2. X-ray diffraction patterns of the $T_{13}SiC_2$ samples after hydrothermal oxidation at 500°–700°C at 35 MPa. CoK α radiation was employed. PDF No.: anatase/021-1272, rutile/021-1276, and $T_{13}SiC_2/$ 040-1132.



Fig. 3. Raman spectra of bulk Ti_3SiC_2 after hydrothermal treatment at 500°C for (a) 6, (b) 20, (c) 42, and (d) 100 h; 600°C for (e) 6, (f) 20, (g) 42, and (h) 100 h; and 700°C for (i) 6, (g) 20, (k) 42, and (l) 95 h under the pressure of 35 MPa.

This is why we also applied XPS for closer investigating the sp^2/sp^3 ratio. ^{31–35} Figure 5 shows the typical C1s spectrum for the Ti₃SiC₂ sample hydrothermal oxidized at 500°C for 100 h. The C1s peak appears at 285.6 eV with a full width at half maximum (FWHM) of 2.0 eV, which considerably exceeds that of graphite (1.3 eV) and diamond (1.4 eV).^{31–33} The asymmetric broadening to higher binding energy and the small shoulder together with high FWHM suggest that at least two components contribute to this peak. Considering the actual physical interpretation, three components are employed for the fitting. The first component at 285.3 eV (FWHM = 1.4 eV) corresponds to sp^2 carbon, and the second at 286.4 eV (FWHM = 1.3 eV) originates from sp^3 carbon. The third at 288.4 eV comes from C-O contamination due to air exposure of the sample surface.^{32–35} This result is quite similar to the work on synthesizing sp^2/sp^3 hybrid diamond-like carbon,^{31–35} and confirms the results of Raman spectroscopy.



Fig. 4. Wavenumbers of the G- and D-band at various experimental conditions obtained via Raman spectroscopy (cf. Fig. 3). Note the down-shift of the D-band at higher temperatures/longer exposure times.



Fig. 5. Typical X-ray photoelectron spectroscopy C1s spectrum for the Ti_3SiC_2 sample hydrothermal oxidized at 500°C for 100 h. The fitted curve is the red solid line; the measured C1s peak is the black dot line.

(3) Scale Morphology and Composition

Figure 6(a) to (c) depict typical surface morphologies of the Ti_3SiC_2 specimens hydrothermally oxidized at 600° to 700°C. Short hydrothermal exposure at/below 600°C yields a crack-free oxide scale (Fig. 6(a)). However, cracks do appear once temperature is up to 700°C, and become pronounced with longer exposure time (Fig. 6(b) and (c)). These cracks provide pathways for water transportation to the carbide interface and facilitate further hydrothermal oxidation, which is responsible for the acceleration oxidation at 700°C. Similar cracks were previously observed in intermediate-temperature oxidation of Ti_3SiC_2 ,²⁵ Ti_3AlC_2 ,³⁶ and Ti_2AlC^{37} in air.

Figure 7(a)–(c) display the cross-sections of the specimens hydrothermally oxidized at 700°C and the corresponding EDS line scan. The images at 500° to 600°C are similar to Fig. 7(a), so they are not shown here for briefness. It can be seen from Fig. 7(a) that thin oxide layer is formed after 20 h at 700°C, which consists with the presence of matrix peaks in XRD measurements (Fig. 2). Thick oxide layer can cover the substrate, for example, after 95 h at 700°C (Fig. 7(b)), but it is not dense, and therefore does not provide protection. Thus linear kinetics is expected.

As indicated by the line scan in Fig. 7(c), the scale is rich in Ti and O but deficient in Si. The concentration of C remains constant without significant difference between substrate and scale. These results are fully consistent with XRD (Fig. 2) and Raman spectroscopy (Fig. 3).

In addition to the general oxidation, other two modes were exhibited during hydrothermal oxidation of bulk Ti_3SiC_2 , which were never found in air oxidation. Figure 8(a) and (b) show the cross-section morphology of Ti_3SiC_2 hydrothermal oxidized at 500°C for 42 h and the corresponding elemental mapping. Phases appearing dark grey in Fig. 8(a) penetrate deep into the matrix, and they are parallel to each other. Their elemental distribution is deficient in Si and rich in both O and Ti (Fig. 8(b)), indicating titanium oxide. Based on above results, we speculate that hydrothermal oxidation can tear Ti_3SiC_2 grains apart and attack the weak-spots of this material: the layered configuration. This means that a single Ti_3SiC_2 grain is oxidized firstly along planes perpendicular to the *c*-axis. Further experiments like EBSE or TEM are required to fully confirm this deduction. In addition, it has been observed that the weak



Fig. 6. Scanning electron microscopic images (SE-mode) showing typical surface morphologies of the Ti_3SiC_2 specimens hydrothermal oxidized at (a) 600°C for 20 h, (b) 700°C for 6 h, and (c) 700°C for 95 h.

layered configuration can induce delamination of grains after mechanical deformation. $^{\rm l-3}$

Another weak spot in the Ti_3SiC_2 matrix was identified as TiC and SiC impurities. Figure 9 displays a typical morphology of interfaces between impurities and the Ti_3SiC_2 substrate. Oxidizing species can deeply penetrate along the interfaces consuming the TiC or/and SiC inclusions, which suggests that bulk Ti_3SiC_2 may exhibit a somewhat better resistance than both TiC and SiC impurities under hydrothermal oxidation. This oxidation scheme is only observed at 700°C in our experimental conditions. In absence of comparative kinetics data of bulk TiC and bulk SiC under the same conditions, this phenomenon can not simply be applied to a general situation that bulk Ti_3SiC_3 possess better hydrothermal oxidation resistance than bulk TiC and bulk SiC. Therefore, we are planning to perform the hydrothermal oxidation of bulk TiC and SiC under the same conditions to further compare, on the basis of quantitative data, the hydrothermal oxidation kinetics of Ti_3SiC_2 , SiC and TiC.

No doubt this is an interesting and important phenomenon although we cannot currently explain it. For TiC, no hydrothermal oxidation kinetics data are reported up to now. In case of the hydrothermal oxidation of SiC, it has been well recognized that the resulted silica is not protective because of its high solubility in hydrothermal water, and then SiC presents weight





Fig. 7. Cross-sections (SE-mode scanning electron microscopy) of the specimens hydrothermal oxidized at 700° C for (a) 20 h, (b) 95 h, and (c) energy-dispersive spectroscopy line scan taken from the white line in Fig. 7(b).



Fig.8. (a) Cross-section morphology of Ti_3SiC_2 hydrothermal oxidized at 500°C for 42 h; (b) Elemental mapping of the white rectangular region in Fig. 8(a).

loss.^{12,13,16} Thus, for SiC impurity, the higher solubility of silica than titania in hydrothermal water is probably responsible for this phenomenon; and for TiC impurity, we envisage defect structures from carbon deficiency as well as low density and small grains size, etc. to affect the hydrothermal oxidation behavior of TiC_x impurities in the matrix. Kraft *et al.*¹² investigated the hydrothermal oxidation of

Kraft *et al.*¹² investigated the hydrothermal oxidation of CVD SiC fibers under the pressure of 200 MPa, and the linear rates, if using the unit of weight, were 9.12×10^{-2} , 1.15 and 13.38 µg/mm²/h at 500, 600 and 700 respectively. Barringer *et al.*¹³ studied the hydrothermal oxidation of high purity CVD SiC at 500°C and 25 MPa, and the linear rate was calculated as 6.3×10^{-3} µg/mm²/h. For sintered SiC under much more moderate conditions (360°C) the linear rate was calculated as 2.8×10^{-2} µg/mm²/h.¹⁶ Comparing the data obtained here, Ti₃SiC₂, as a sintered and impurity containing ceramic, presents amazing hydrothermal oxidation resistance.

IV. Discussion

(1) Reaction Products and Hydrothermal Oxidation Reactions

Crystalline silica was not detected by XRD (Fig. 2) after hydrothermal oxidation, and the EDS line scan (Fig. 7(c)) clearly showed the deficiency of Si in the oxide layers. Also, amorphous silica was not detected using Raman spectroscopy. The absence of silica is attributed to its high solubility in hydrothermal water.^{38–40} The extrapolation of these literature data to the



Fig.9. Cross-section morphology of Ti_3SiC_2 hydrothermal oxidized at 700°C for 95 h.

experimental parameters of this work suggests the dissolution rate of silica is over 500 times faster than that of TiO_2 .^{38–41} The dissolved silica could not precipitate in the final products because it was exported from the autoclave with the continuous water flow. In the studies of Ti_3SiC_2 and $Ti_3Si_{0.9}Al_{0.1}C_2$ powders,^{21,22} the situation was different because gold capsules used to contain sample powders/water provided closed environments. Thus the dissolved silica precipitated in the capsules as cooled to ambient temperature. For SiC fibers,¹² non-dense and spalling silica layers were observed after hydrothermal oxidation because of the high solubility of silica.

Gaseous compounds also were produced during the hydrothermal oxidation process. The temperature dependent partial pressures of the volatile compounds are calculated at a H₂O: Ti₃SiC₂ molar ratio of 900:1 considering that there is sufficient water in the system (Fig. 10). The dominating volatile species are H₂O, H₂, CO₂, CO, and CH₄. It should be noted that methane significantly decreases with temperatures.

Based on the results of XRD, Raman, XPS and thermodynamic calculations, the hydrothermal oxidation reactions of bulk Ti_3SiC_2 was described as follows: Ti_3SiC_2 was firstly



Fig. 10. Temperature dependent partial pressures of the volatile compounds at a H₂O:Ti₃SiC₂ molar ratio of 900:1 under the pressure of 35 MPa. The amount of water is estimated using: density of 0.087 g/cm³ (700°C, 35 MPa), volume of 30 mL. The amount of Ti₃SiC₂ is estimated using: density of 4.53 g/cm³, volume of 6.8 mm³. Only reacted Ti₃SiC₂ is considered, and we used 50 μ m as the thickness of reacted Ti₃SiC₂.

oxidized to TiO_2 and SiO_2 with the survival of carbon, and a mixture layer of TiO_2 , SiO_2 , and carbon was formed on the surface. This corresponded to the reactions

$$Ti_3SiC_2 + 8H_2O = 3TiO_2 + SiO_2 + 2C + 8H_2$$
(1)

and

$$Ti_3SiC_2 + 8H_2O = 3TiO_2 + SiO_2 + C + CH_4 + 6H_2.$$
(2)

The formed SiO₂ dissolved into water and TiO₂ remained. Simultaneously, the resulting carbon was consumed by reaction with water. Because CO₂ possessed higher partial pressures than CO (Fig. 10), the carbon consuming reactions¹⁵ were

$$C + 2H_2O = CO_2 + 2H_2$$
(3)

$$C + H_2O = \frac{1}{2}CO_2 + \frac{1}{2}CH_4$$
 (4)

The significant decrease of methane with higher temperatures indicated that reactions (1) and (3) were preferred above 550° C, and reactions (2) and (4) were favored below 550° C. Consequently, as the equilibrium state was achieved after the consumption of the entire sample, the predominating reactions between water and Ti₃SiC₂ were:

above 550°C:

$$Ti_3SiC_2 + 12H_2O = 3TiO_2 + SiO_2 + 2CO_2 + 12H_2$$
 (5)

below 550°C:

$$Ti_3SiC_2 + 9H_2O = 3TiO_2 + SiO_2 + \frac{1}{2}CO_2 + \frac{3}{2}CH_4 + 6H_2$$
(6)

(2) Carbon Formation During Hydrothermal Oxidation

The mechanism for carbon formation has been discussed in detail in previous studies.^{21,22} Briefly, carbon was produced by extraction of titanium and silicon out of the carbide. Both thermodynamics and kinetics factors contributed to the formation of carbon, and kinetics played an essential role on this process.^{21,22} From thermodynamics, the reason was the affinity of metals to water and oxygen was higher than that of carbon.^{15,42,43} From kinetics, carbon formation was related to the unique layered structure and weak Ti–Si bonding of Ti₃SiC₂.^{1–3,44–49}

The Raman spectra demonstrated the positions of G-band to be independent of experimental conditions, but the D-band displayed down-shift with temperatures and time (Figs. 3 and 4). This down-shifting behavior is known to result from smaller domain sizes and was reported, for example, by Cancado *et al.*⁵⁰ Their results showed that the domain size of carbon was decreased accompanied with the downshift of the D-band and the constant position of the G-band. Another size-depending parameter is the D/G band ratio, which is inversely proportional to the domain size of carbon.^{50,51} Plotting both (Fig. 11), the shift of the D-band and the D/G band ratio, we see a linear correlation between these two size-sensitive parameters. A semi-quantitative equation for determining domain size of carbon (L_a) is⁵¹

$$L_a(nm) = (2.4 \times 10^{-10}) \lambda_{laser}^4 \left(\frac{I_D}{I_G}\right)^{-1},$$
(7)

where λ_{laser} is the laser wavelength in nm unit, $\frac{I_D}{I_C}$ is the intensity ratio between D- and G-bands. Based on this equation, the domain size of carbon obtained in this work ranges between 17 and 28 nm. Although it is difficult to clearly state the relative



Fig. 11. Wavenumbers of D bands as a function of the intensity ratio of D/G bands.

experimental error of these values, the general trend of smaller domain sizes is unambiguously verifiable by both (1) the D/G intensity ratio and (2) the D-band downshift.

Figure 12 illustrates the relationship between the D/G band ratio and experimental conditions. This figure points out that the domain size of carbon decreases with temperatures and time. This is owing to more severe reactions between carbon and water happens at higher temperatures and longer time, which reduce carbon domain sizes.

The formed carbon showed both sp^3 and sp^2 hybridization. Considering the low temperatures and pressures of the reactions, hydrothermal oxidation of Ti₃SiC₂ is likely to produce sp^3 carbon in analogy to studies on SiC.^{11–14}

Currently we are attempting to optimize the experimental conditions, such as using diamond seeds and metal catalysts, to increase the amounts of sp^3 carbon. Further research about this topic is necessary, because the formation mechanism of sp^3 carbon in the course of hydrothermal decomposition of Ti₃SiC₂ is not clearly understood.

The production of sp^3 carbon from SiC was explained similar to diamond formation at low pressures by CVD.^{11–14} The formation of hydrogen played an import role because in CVD diamond synthesis hydrogen dissociated into atoms to etch preferentially sp^2 bonded carbon, which facilitated retention of sp^3 carbon and nucleation of diamond.^{11–14}

(3) Cracks Formed in Oxide Layers

The formation of cracks in the oxide scales contributed to the acceleration of hydrothermal oxidation of Ti_3SiC_2 at 700°C.



Fig. 12. Relationship between the intensity ratio of D/G bands and the experimental conditions.

Anatase transformed to rutile at high temperatures due to the higher stability of rutile.^{52,53} This phase transformation resulted in tensile stresses in oxides because the density of rutile (4.26 g/cm^3) is larger than that of anatase (3.84 g/cm^3) . The generation of tensile stresses could crack the oxides.^{2,25,36,37} From XRD (Fig. 2)/SEM (Fig. 6) results, only anatase TiO₂ was detected at 500° to 600°C and no cracks were present in the oxides. Once temperature was up to 700°C, however, cracks were formed in the oxide layers accompanied with this phase transformation. Also, this phase transformation induced crack formation in the oxide scale during air oxidation of Ti_3SiC_2 ,²⁵ Ti_3AlC_2 ,³⁶ and Ti₂AlC.³⁷

V. Conclusions

Hydrothermal oxidation of bulk Ti₃SiC₂ was investigated at 500° to 700°C under a hydrostatic pressure of 35 MPa in a continuous water flow. The reaction obeyed a linear law. The hydrothermal oxidation rate was slow below 700°C and dramatically accelerated at 700°C due to the formation of cracks in oxides. The phase transformation from anatase to rutile (two TiO₂ modifications) was responsible for the formation of cracks. Titanium and silicon were selectively extracted from Ti₃SiC₂ during hydrothermal oxidation, resulting in the formation of the corresponding oxides and sp^2/sp^3 hybrid carbons. However, due to the high solubility of silica in hydrothermal water, the formed oxide layers only contained titanium oxides and carbon. Besides general oxidation, two special modes very likely demonstrate in current experiments: (1) preferential hydrothermal oxidation of lattice planes perpendicular to the *c*-axis inducing cleavage of grains, (2) uneven hydrothermal oxidation because of the occurrence of TiC and SiC impurity inclusions. Because the oxidation processes will certainly accelerate further with increasing temperature we expect an application limit in the order of 700°C for this material, which is, for many uses, a quite good value.

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