Chemically Stable Group IV-V Transition Metal Carbide Thin Films in Hydrogen Radical Environments

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Abstract

Hydrogen is playing a crucial role in the green energy transition. Yet, its tendency to react with and diffuse into surrounding materials poses a challenge. Therefore, it is critical to develop coatings that protect hydrogen-sensitive system components in reactive-hydrogen environments. In this work, we report group IV-V transition metal carbide (TMC) thin films as potential candidates for hydrogen-protective coatings in hydrogen radical (H^{*}) environments at elevated temperatures. We identify three classes of TMCs based on the reduction of carbides and surface oxides (TMO_x). HfC, ZrC, TiC, TaC, NbC, and VC (class A) are found to have a stable carbidic-C (TM-C) content, with a further sub-division into partial (class A1: HfC, ZrC, and TiC) and strong (class A2: TaC, NbC, and VC) surface TMO_x reduction. In contrast to class A, a strong carbide reduction is observed in Co_2C (class B), along with a strong surface TMO_x reduction. The H*-TMC/TMO_x interaction is hypothesized to entail three processes: (i) hydrogenation of surface C/O-atoms, (ii) formation of CH_x/OH_x species, and (iii) subsurface C/O-atoms diffusion to the surface vacancies. The number of adsorbed H-atoms required to form CH_x/OH_x species (i), and the corresponding energy barriers (ii) are estimated based on the change in the Gibbs free energy (ΔG) for the reduction reactions of TMCs and TMO_x . Hydrogenation of surface carbidic-C-atoms is proposed to limit the reduction of TMCs, whereas the reduction of surface TMO_x is governed by the thermodynamic barrier for forming H_2O .

Introduction

Hydrogen plays an essential role in a multitude of applications and processes, varying from energy production to semiconductor manufacturing. For instance, hydrogen is used as fuel in fusion reactors,¹ hydrogen fuel cells,² and aerospace propulsion systems.³ Furthermore, hydrogen is also reported as a promising candidate for energy storage.⁴ In the semiconductor industry, hydrogen is utilized as an etchant and reducing agent, for example for removing excess Si for fabricating nanostructures,⁵ etching Sn contamination and reducing RuO_x in extreme ultraviolet (EUV) scanners,^{6,7} and reducing the surface oxides of group III-V semiconductors.⁸ While the high reactivity and small molecular weight of hydrogen make it a promising candidate for many applications, the inclination of hydrogen to react with and diffuse into the walls/components of the systems makes it difficult to work with.^{9–11} Hence, to fully exploit the potential of hydrogen, it is necessary to study novel coatings that can endure reactive-hydrogen environments and thereby protect hydrogen-sensitive layers.

Group IV-VI transition metal carbides (TMCs) exhibit high thermal stability and good hydrogen permeation barrier performance.^{12–16} Furthermore, literature indicates that group IV-V TMCs are stable in molecular hydrogen (H₂) environments.^{17,18} As such, TMCs may be interesting candidates for protective coatings in harsher environments containing chemically active hydrogen radicals (H^{*}) and ions at increased temperatures, for instance in fusion reactors and EUV scanners.^{19,20} To evaluate the feasibility of TMCs as protective coatings, it is necessary to first assess their chemical stability (reducibility) i.e., the removal of C-atoms bonded with transition metal (TM)-atoms (carbidic-C), in low-energy H^{*} environments. This understanding can then help to comprehend TMC reducibility in more energetic (complex) hydrogen environments (e.g., hydrogen plasma).

The reduction of TMCs in H^{*} environment at elevated temperatures is modeled involving three steps: hydrogenation, formation of CH_x species, and diffusion of subsurface C-atoms to the surface.^{21,22} Hydrogenation in pristine TMCs predominantly occurs on surface carbidic-C-atoms.^{12,23,24} However, the H-adsorption energy on surface carbidic-C atoms decreases as H-loading increases. When each surface carbidic-C-atom is occupied by one H-atom (H:C ratio = 1), H-adsorption on hollow sites (between two TM-atoms) becomes energetically more favorable.^{23,24} Nevertheless, the reported simulations only consider the hydrogenation of model systems in H₂ environments, the adsorption of more than one H-atom per surface carbidic-C-atom in a disordered (amorphous or polycrystalline) ambient-exposed TMC might be possible in H^{*} environment.

Adsorption of sufficient H-atoms on a surface carbidic-C-atom may lead to the formation

of volatile CH_x species. The thermodynamic feasibility of forming CH_x species is related to the change in the Gibbs free energy (ΔG) for the reduction reaction of TMCs.²⁵ For example, in H* environment at standard temperature and pressure, ΔG for forming CH_4 on TiC is negative, whereas ΔG for the formation of CH_x (x = 1, 2, 3) is positive.^{26,27} This implies that the reduction of TiC is energetically feasible only through the formation of CH_4 . Consequently, 4 H-atoms should adsorb on a surface carbidic-C-atom in TiC for the reduction reaction to occur.

The formation of volatile CH_x species leads to the formation of carbon vacancies on the surface. In order for the reduction reaction to proceed, subsurface C-atoms have to diffuse to these surface vacancies. Since the system of TMC/reduced TMC is likely similar to TMC/TM systems, where diffusion of C-atoms from the TMC layer to the adjacent TM-layer is reported at elevated temperatures,^{28–30} we expect that subsurface C-atoms will diffuse to the reduced TMC surface at elevated temperatures.

From calculations and literature, the formation of CH_x specie(s) and the diffusion of subsurface carbidic-C-atoms to the reduced TMC surface show to be energetically feasible processes at elevated temperatures. However, the number of H-atoms that can adsorb on a surface carbidic-C-atom (the first step in the model) is expected to be limited. Therefore we hypothesize that the reducibility of TMCs in H^{*} environments at elevated temperatures is determined by their hydrogenation.

It should be noted that TMCs are metastable in ambient conditions, and typically form an approximately 2-5 nm thick layer of transition metal oxide (TMO_x) and/or oxycarbide (TMO_xC_y), along with non-carbidic-C (C-C) on the surface.³¹ Non-carbidic-C may also form in TMC thin films during the deposition process, depending on the deposition conditions.^{32–36} Therefore, to comprehend the reducibility of TMCs, the interaction of H* with the surface TMO_xC_y/TMO_x and non-carbidic-C must also be taken into account.

The surface layer on ambient-exposed TMCs is typically O-rich, with predominating TM-O bonds. The reduction (removal of O-atoms bonded with TM-atoms) of surface oxides is expected to follow the same processes as in the reduction of TMCs. Hydrogenation of surface O-atoms and diffusion of subsurface O-atoms toward the surface vacancies are expected to be energetically favorable processes.^{37,38} Nevertheless, the thermodynamic energy barrier for forming volatile species (e.g., H_2O) in the reaction environment is believed to impede the reduction of surface oxides.^{38–40} Consequently, we hypothesize that the reduction of the surface oxide layer on ambient-exposed TMCs is primarily governed by the thermodynamic barrier for forming H_2O .

The interaction of H^{*} with non-carbidic-C depends mainly on its hybridization state (sp³-C and sp²-C).^{41,42} We expect that the rate of chemical erosion of non-carbidic-C in TMCs will depend on the type of C and defect sites.⁴³⁻⁴⁵

In this work, we report on the interaction of H^{*} with TMC thin films at elevated temperatures. The behavior of TMCs upon H^{*}-exposure is divided into two main classes, based on the observed variation in the carbidic-C fraction. A further subdivision is recognized, based on the reduction of native oxides on the TMC surfaces during H^{*}-exposure. We explain the observed behavior based on ΔG calculations for the reduction reactions involved. We hypothesize that the hydrogenation of surface carbidic-C-atoms limits TMC reduction, while the thermodynamic barrier for forming H₂O on TMO_x governs the reducibility of TMC surface oxides.

Material Selection and Thermodynamic Calculations

We chose TiC, ZrC, HfC, VC, NbC, TaC, Co₂C, and Ni₃C thin films for this study. Group IV-V TMCs are potential candidates for high-temperature hydrogen-protective coatings. In contrast, Co₂C and Ni₃C, known to reduce under H₂ loading,^{46,47} are studied to provide counterexamples for our hypothesis.

In order to select H*-exposure conditions, we consider typical application temperatures for hydrogen permeation barriers for fusion reactors, ranging from 300 °C to 800 °C.^{48,49} In comparison, components in EUV lithography devices operating in the H^{*} environment may experience temperatures of up to 700 °C at the background pressures of 0.02 mbar to 0.05 mbar.^{20,50,51} For this study, we therefore selected an exposure temperature of 700 °C and a pressure of 0.02 mbar to operate in an industrially relevant range. Note that only Co₂C and Ni₃C have been exposed to H^{*} at a lower temperature of 250 °C, since they are reported to decompose at 300-350 °C and 415 °C, respectively.^{46,47}

The hydrogenation of surface carbidic-C-atoms is hypothesized to limit the reduction of TMCs in H^{*} environments. We simulate the thermodynamic feasibility of forming CH_x species on selected TMCs under the performed experimental conditions based on ΔG for the reduction reaction (Figure 1).^{26,27} Only the formation of CH₄ is spontaneous on HfC, ZrC, TiC, and TaC (thus 4 H-atoms should absorb on a carbidic-C atom for the reduction reaction to occur), while CH₃ formation is also spontaneous on NbC and VC. Furthermore, ΔG for forming CH₂ on Co₂C and Ni₃C is nearly at the thermodynamic equilibrium. Hence, considering the number of adsorbed H-atoms per carbidic-C-atom required to form volatile specie (CH_x) and the corresponding energy barrier, a trend in the reducibility of selected TMCs is expected (as indicated by the arrow in Figure 1).

Note that the simulations performed at a lower temperature (500 K) for Co_2C and Ni_3C exhibit a steeper slope (Figure 1). This suggests that the formation of CH_x on TMCs is thermodynamically more favorable at a lower temperature. However, in this temperature range, the reduction process is likely constrained by the diffusion of subsurface C/O-atoms to surface vacancies.^{38,52}



Figure 1. ΔG for the reduction of TMCs per molecule of CH_x (x = 1, 2, 3, 4) calculated at 0.02 mbar and 1000 K (for HfC, ZrC, TiC, TaC, NbC, and VC) and at 500 K (for Co₂C and Ni₃C). A trend in the reducibility (removal of carbidic-C-atoms) of TMCs is expected (indicated by arrow), with HfC being the least reducible and Ni₃C being the most reducible.

The thermodynamic energy barrier for forming H_2O on ambient exposed TMCs (i.e., the TMO_x top layer) is expected to govern the reduction of oxide species on TMC surfaces that may form on the surfaces of TMC samples in ambient or during H*-exposure. Figure 2 shows ΔG for the reduction reaction of TMO_x by forming H₂O under the performed experimental conditions.^{26,27} For HfO₂ and ZrO₂, ΔG for the reduction of oxides (TMO_x \rightarrow TM) is positive, suggesting that oxides on HfC and ZrC should be stable. For TiO₂, ΔG for partial reduction to TiO is negative, while full reduction to Ti has positive ΔG , suggesting that surface oxides on TiC should be less stable that than on HfC and ZrC. ΔG for partial and full reduction of other oxides is negative, based on which it is expected that surface oxides on TaC, NbC, VC, Co₂C, and Ni₃C samples are likely to undergo spontaneous reduction.



Figure 2. ΔG for the reduction of TMO_x per molecule of H₂O calculated at 0.02 mbar and 1000 K (for HfO_x, ZrO_x, TiO_x, TaO_x, NbO_x, and VO_x) and at 500 K (for CoO_x and NiO_x). ΔG for the complete reduction of all TMO_x is negative except for HfO₂, ZrO₂, and TiO₂. Thus, the oxides on the surfaces of TaC, NbC, VC, Co₂C, and Ni₃C are expected to undergo a spontaneous reduction, in contrary to the oxides on the surfaces of HfC, ZrC, and TiC during H*-exposure.

Methodology

TMC thin films were deposited onto diced Si(100) wafers via DC co-sputtering using TM and C targets. The deposition rates of the magnetrons were calibrated using X-ray reflectometry (XRR) aiming at 20 nm (only for calibration) thick layers to deposit TM and C atoms in a stoichiometric ratio. This ratio was set at 1:1 for group IV-V TMCs, and adjusted to 2:1 and 3:1 for Co₂C and Ni₃C samples, respectively. The base pressure of the deposition chamber before each deposition is in the lower range of 10^{-8} mbar. Ar (99.999%) with a flow rate of 25 sccm was used as the sputtering gas. Working pressure during the deposition was measured to be approximately 9×10^{-4} mbar, while the corresponding deposition rate was approximately 0.07 ± 0.01 nm/sec. 5 ± 0.5 nm thick TMC films were deposited. The thickness was chosen such that the entire depth of the TMC layer can be probed using theta probe Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS), which uses a monochromatic

Al-K α radiation source. During the measurements, spectra are collected at take-off angles (θ) ranging from 26.75° to 71.75°, with respect to the surface normal, providing a probing depth ranging from approximately 5 to 1.5 nm, respectively with a spot size of ≈ 400 m.



Figure 3. Schematic of methodology. (a) TMC samples were deposited via co-sputtering of TM and C targets. Thin $\text{TMO}_x/\text{TMO}_x\text{C}_y+\text{C-C}$ and ad. C layers formed on the samples surfaces during ambient storage. (b) TMC samples were annealed at elevated temperatures. (c, d) After that, samples were exposed to H^{*} twice. Samples were moved between the annealing/H^{*}-exposure and AR-XPS chambers under a vacuum of low 10^{-9} mbar.

The as-deposited samples were stored in the ambient for approximately a week before the AR-XPS measurements were performed. The measurements revealed the formation of TMO_xC_y/TMO_x along with non-carbidic-C and adventitious carbon (ad. C) on the surface (Figure 3a). In order to saturate all the thermally induced processes before high-temperature H*-exposures, the samples were annealed in a vacuum chamber for 2 h (Figure 3b) at the same temperature as would subsequently be used for H*-exposures (Figure 3c and 3d). Note that the same chamber/setup is used for H*-exposures, ensuring consistency of temperature settings. The base pressure of the vacuum chamber is in the lower range of 10^{-8} mbar, while the maximum pressure of the chamber during annealing was measured to be in the lower range of 10^{-7} mbar. The temperature of the sample was measured via an N-type thermocouple which was mounted on the surface of the sample. After annealing, the samples were cooled down to approximately 100 °C in vacuum, before they were transferred in-vacuo to the XPS chamber. AR-XPS measurements were performed on the annealed samples. The corresponding measurements are referred to as pre-exposed (pre-exp) in the text and figures and are used as the reference. These XPS measurements mainly revealed the desorption of surface hydrocarbons which the samples accumulated during ambient storage.

The pre-exposed samples were then transferred in-vacuo back to the chamber where they were exposed to H^{*} at elevated temperature (Figure 3c). H^{*} are generated by thermally cracking H₂ via a W filament, which is heated to approximately 2000 °C. The samples were positioned approximately 5 cm from the W filament. The working pressure during the H^{*}-exposure was 0.02 mbar, and the corresponding H^{*} flux on the sample surface was calculated to be $10^{21\pm1}$ m⁻²s⁻¹.^{53,54} The samples were exposed to H^{*} for 2 h, providing a H^{*} fluence of $7x10^{24\pm1}$ m⁻², which is an industry-relevant total exposure flux.^{51,55} After H^{*}-exposure, the samples were cooled down to approximately 100 °C and then transferred to the XPS chamber. The corresponding XPS measurements are referred to as 1st H^{*}-exposed (1st H^{*}-exp).

 1^{st} H*-exposure of group IV-V TMC samples showed surface cleaning (i.e., reduction of surface oxides and chemical erosion of non-carbidic-C). This resulted in a lesser attenuation of photoelectrons at the surface level, while subsurface C-atoms may have also diffused to the surface O-vacancies. Together, these phenomena caused an apparent increase in TMC fraction in the XPS probing depth. In contrary, for the Co₂C sample, the intensity of C1s spectra dropped to almost the noise range. Furthermore, a substantial increase in the intensity of Si2p spectra was noted in the Ni₃C sample (Figure S11). The increase in the Si2p spectra intensity was due to the severe dewetting of the sample, which was confirmed via atomic force microscopy (AFM, Figure S12). Therefore, XPS spectra of the Ni₃C sample are not discussed in detail.

In order to avoid ambiguities regarding the stability of carbidic-C in group IV-V TMC samples, the samples were exposed to H* again under the same conditions (Figure 3d). The XPS measurements on the samples after 2nd H*-exposure are referred to as 2nd H*-exposed (2nd H*-exp).

Changes in the stoichiometry of the samples due to H*-exposure(s) are evaluated based

on the core-level TM, C1s, and O1s XPS spectra. The core-level TM and C1s spectra of preand post-H^{*} exposed samples taken at $\theta = 34.25^{\circ}$ are discussed in the results and discussion section, while corresponding fitted peaks positions are provided in the supplementary information (Table S1-7). Furthermore, a comparison of XPS spectra (TM, C1s, O1s, and Si2p) taken over the range of θ , before and after H*-exposure(s) for each sample is also provided in the supplementary information (Figure S4-11). To quantify carbidic-C and O loss upon H*-exposure(s), the ratios between at.% of carbidic-C and at.% of TM (carbidic-C/TM); and at.% of O and at.% TM (O/TM) in the samples were calculated over the range of θ . The at.% of carbidic-C in the samples was calculated by considering the cumulative area under the carbidic-C peaks (TMC and $\text{TMO}_x C_y$) in C1s spectra and the corresponding sensitivity factor. The whole area under the O1s spectra was considered to calculate the O-fraction in the samples. Except for the TaC sample, the at.% of the TM in the samples was also calculated by taking the whole area under the core level XPS-spectra of the TM. Due to overlapping binding energies for the Ta4f and O2s spectra, the cumulative area under the main peaks of TaC, TaO_xC_y/TaO_x , and Ta_2O_5 doublets along with the corresponding sensitivity factor was considered for calculating the Ta-fraction in the TaC sample. Changes in the carbidic-C/TM ratios upon H*-exposure(s) are discussed in the Results and Discussion section, while O/TM ratios are provided in the supplementary information (Figure S1-3).

Results and Discussion

The relative change in carbidic-C/TM and O/TM ratios in the samples after 1^{st} and 2^{nd} H*-exposure with respect to the pre-exposed samples are highlighted in Figure 4. TMCs are categorized into three classes based on the change in chemical composition caused by H*-exposure(s). Class A is characterized by an initial increase in carbide signals after 1^{st} H-exposure, due to the removal of non-carbidic surface species, followed by no further apparent change upon 2^{nd} H*-exposure (Figure 4a). This class is further subdivided into classes A1

and A2, based on the amount of surface oxides removed during the 1st H*-exposure, which is either small (A1) or large (A2) (Figure 4b). In the results, a final class B is recognized, where during the 1st H*-exposure strong/complete reduction of carbidic and oxidic species was observed (Figure 4). In the subsequent subsections, we discuss each class separately.



Figure 4. Relative change in the post-H*-exposed samples with respect to the pre-exposed samples at $\theta = 34.25^{\circ}$. (a) Relative change in carbidic-C/TM ratio and (b) Relative change in O/TM ratio. TMCs are categorized into three classes. The HfC, ZrC, TiC, TaC, NbC, and VC samples (class A) showed no sign of carbide reduction. Surface oxides on the TaC, NbC, and VC samples (class A2) showed stronger reduction than that on the HfC, ZrC, and TiC samples (class A1) upon 1st H*-exposure. The drop in carbidic-C/Co and O/Co ratios following 1st H*-exposure was due to the reduction of carbides and oxides in the Co₂C sample (class B).

(Class A1) No Effective Carbide Reduction along with Partial Reduction of Surface Oxides

Figure 5 shows the XPS core-level TM and C1s spectra of the HfC, ZrC, and TiC samples taken at $\theta = 34.25^{\circ}$, along with the carbidic-C/TM ratio calculated over the angular range of AR-XPS measurements. After the 1st H*-exposure, the intensity of the oxide doublets decreased due to the reduction of surface oxides (Figure 5a, 5d, 5g, and S1). Simultaneously,

an increase in the intensity of TMC doublets and carbidic-C peaks was observed (Fig. 5a, 5b, 5d, 5e, 5g, and 5h). This increase in the TMC fraction in the XPS probing depth is due to the reduction of surface oxides and the chemical erosion of non-carbidic-C. Accordingly, the carbidic-C/TM ratios increased (Figure 5c, 5f, and 5i). The higher increase in the carbidic-C/TM ratio in the TiC sample compared to the HfC and ZrC samples is due to the stronger reduction of surface oxides on the TiC sample than that on the HfC and ZrC samples as predicted based on the Δ G evaluations (Figure 2, and S1).

Furthermore, a discrepancy in the chemical erosion of non-carbidic-C in the samples upon 1st H*-exposure is also observed. Non-carbidic-C fraction in the C1s spectra of the HfC and ZrC samples was identified (Figure 5b and 5e), while in the TiC sample, non-carbidic-C was completely etched after 1st H*-exposure (Figure 5h). The difference in the rate of chemical erosion of non-carbidic-C in the samples could be due to the difference in the hybridization state (sp²-C and sp³-C) of the non-carbidic-C and the extent of carbide/oxide passivation on the non-carbidic-C.^{32,34,36,45} Nevertheless, further investigations are required to understand the H*-induced chemical erosion of the non-carbidic-C phase in TMC systems.

Upon 2nd H*-exposure, no significant changes were observed in the C1s spectra and the carbidic-C/TM ratios (Figure 5). This suggests that the carbide fraction in HfC, ZrC, and TiC is non-reducible under the performed experimental conditions. Based on the thermodynamic calculations, only the formation of CH₄ on HfC, ZrC, and TiC is thermodynamically feasible (Figure 1). Therefore, the stability of carbidic-C in the samples suggests that H-adsorption on surface carbidic-C-atoms is insufficient - less than 4 H-atoms per surface carbidic-C-atom, which is consistent with our hypothesis (Figure 1). Furthermore, the stronger reduction of surface oxides on the TiC sample in comparison with the HfC and ZrC samples (Figure SI1) is explained by ΔG for the reduction reaction of pristine oxides, where reducing TiO₂ to TiO (as well as TiO₂ to Ti) is thermodynamically favourable, while reducing HfO₂ to Hf and ZrO₂ to Zr is energetically unfavorable (Figure 2).



Figure 5. XPS core level TM and C1s spectra taken at $\theta = 34.25^{\circ}$ along with carbidic-C/TM ratio as a function of θ in the pre-exposed (in black), 1st time H*-exposed (in blue), and 2nd time H*-exposed (in red) HfC (a-c), ZrC (d-f), and TiC (g-i) samples. (a) Hf4f spectra, (b) C1s spectra of the HfC sample, (c) carbidic-C/Hf ratio, (d) Zr3d spectra, (e) C1s spectra of the ZrC sample, (f) carbidic-C/Zr ratio, (g) Ti2p spectra, (h) C1s spectra of the TiC sample, and (i) carbidic-C/Ti ratio. An increase in the carbidic-C/TM ratio following 1st H*-exposure is due to the removal of non-carbidic surface species. No significant change in the C1s spectra and carbidic-C/TM ratio upon 2nd H*-exposure suggests that the carbidic fraction in the HfC, ZrC, and TiC samples is non-reducible. Furthermore, surface oxides on the TiC sample showed a stronger reduction than that on the HfC and ZrC samples.

(Class A2) No Effective Carbide Reduction along with a Strong Reduction of Surface Oxides

In contrast to the partial reduction of surface oxide observed on TiC, ZrC, and HfC, surface oxides on TaC, NbC, and VC underwent strong reduction upon H*-exposure (Figure 4b).

The intensity of oxides doublets in the TaC, NbC, and VC samples dropped to almost the noise range after 1st H*-exposure (Figure 6a, 6d, 6g, and S2). The strong reduction of surface oxides on the samples is consistent with the ΔG values, where the complete reduction (TMO_x \rightarrow TM) of TaO_x, NbO_x, and VO_x is thermodynamically favourable (Figure 2). Accordingly, a stronger surface oxide reduction resulted in a higher increase in the TMC fraction in the XPS probing depth in the TaC, NbC, and VC samples than in the HfC, ZrC, and VC samples (Figure 5 and 6).

Similar to class A1 TMCs, a discrepancy in the chemical erosion of non-carbidic-C is noted in the TaC, NbC, and VC samples (Figure 6b, 6e, and 6h). Therefore, further research is necessary to comprehend the chemical erosion of non-carbidic-C in TMC systems.

No change in the chemical composition of the TaC, NbC, and VC samples was noted upon 2nd H*-exposure (Figure 6), indicating that similar to HfC, ZrC, and TiC, the carbidic fraction in the TaC, NbC, and VC samples is also non-reducible under the performed experimental conditions. According to our hypothesis, the stability of carbidic-C in the TaC, NbC, and VC samples is due to limited H-adsorption on surface carbidic-C atoms. Based on the Δ G calculations, CH₄ formation is spontaneous on TaC, while in addition to CH₄, the formation of CH₃ is spontaneous on NbC and VC (Figure 1). Therefore, the observed stability of carbidic-C suggests that hydrogenation in the TaC, NbC, and VC sample is limited to fewer than 3 H-atoms per surface carbidic-C atom.



Figure 6. XPS core level TM and C1s spectra taken at $\theta = 34.25^{\circ}$, along with carbidic-C/TM ratio as a function of θ in the pre-exposed (in black), 1st time H*-exposed (in blue), and 2nd time H*-exposed (in red) TaC (a-c), NbC (d-f), and VC (g-i) samples. (a) Ta4f spectra, (b) C1s spectra of the TaC sample, (c) carbidic-C/Ta ratio, (d) Nb3d, (e) C1s spectra of the NbC sample, (f) carbidic-C/Nb ratio, (g) V2p spectra, (h) C1s spectra of the VC sample, and (i) carbidic-C/V ratio. A strong reduction of surface oxides was noted on the TaC, NbC, and VC samples, which resulted in a strong increase in the TMC fraction in the XPS probing depth upon 1st H*-exposure. No change in the stoichiometry of the samples was observed upon 2nd H*-exposure, indicating that carbidic-C fraction in the TaC, NbC, and VC samples is non-reducible.

(Class B) Carbide Reduction along with Strong Reduction of Surface Oxides

In contrast to class A TMCs, the Co_2C sample underwent strong carbide reduction. Figure 7 shows the Co2p and C1s XPS spectra of the Co_2C sample along with carbidic-C/Co ratio,

before and after the H^{*}-exposure. The Co2p XPS spectra are not deconvoluted due to the lack of references on Co[°] asymmetric characteristics and satellite features of distinct oxidation states of Co. Nevertheless, a significant increase in the intensity of Co2p at lower binding energies following H^{*}-exposure indicates a strong reduction of the sample (Figure 7a). Likewise, the drop in the intensity of the CoC_x peak in the C1s spectra and the carbidic-C/Co ratio suggests a strong carbide reduction (Figure 7b and 7c). Furthermore, a strong reduction of surface oxides was confirmed by the decrease in the O/Co ratio following H^{*}-exposure (Figure S3).

The Ni₃C sample underwent dewetting upon H*-exposure, as mentioned in the Methodology. We expect that this dewetting is caused by the strong reduction of carbides and surface oxides. This interpretation is supported by the previous studies. For instance, Leng et al. noted the reduction of Ni₃C nanoparticles in H₂ below its decomposition temperature (≈ 415 °C in Ar).⁴⁷ Additionally, Alburquenque et al. observed the dewetting of NiO thin film when reduced in H₂ at 450 °C.⁵⁶

The thermodynamic energy barrier for forming CH₂ on Co₂C is negligible (close to zero) in comparison with HfC, ZrC, TiC, TaC, NbC, and VC. Hence, fewer adsorbed H-atoms (2-4) per surface carbidic-C-atom are required to reduce Co₂C through CH_x formation than HfC, ZrC, TiC, TaC, NbC, and VC (3-4 H-atoms). The observed reduction of Co₂C suggests that the adsorption of at least 2 H-atoms per surface carbidic-C-atom is energetically feasible on the Co₂C sample under the performed experimental conditions. Moreover, the strong reduction of surface oxides observed in the Co₂C sample, similar to the TaC, NbC, and VC samples, is due to the thermodynamically favourable reduction of CoO (Figure 2).



Figure 7. Co2p and C1s XPS spectra taken at $\theta = 34.25^{\circ}$, along with carbidic-C/Co ratio as a function of θ in the pre-exposed (in black) and 1st time H*-exposed (in blue) Co₂C sample. (a) Co2p spectra, (b) C1s spectra, and (c) carbidic-C/Co ratio. A strong reduction of carbides and surface oxides was noted.

Conclusion

Ambient-exposed HfC, ZrC, TiC, TaC, NbC, and VC thin film are exposed to H^{*} at 700 °C, while Co₂C sample is exposed to H^{*} at 250 °C. In the HfC, ZrC, TiC, TaC, NbC, and VC samples, an initial reduction of surface oxides/oxycarbides is observed upon H^{*}-exposure. After that, no further change in the chemical composition of the samples is noted. The results show that the carbide fraction in the HfC, ZrC, TiC, TaC, NbC, and VC samples is non-reducible. In contrast, the Co₂C sample showed strong carbide and oxide reduction. Furthermore, a discrepancy in the reducibility of surface oxide on the TMC samples is noted, i.e., oxides on the TaC, NbC, VC, and Co₂C samples showed stronger reduction than the oxides on the HfC, ZrC, and TiC samples.

We propose that the number of H-atoms that can adsorb on surface carbidic-C atoms (hydrogenation) limits TMC reduction in H^{*} environments. Based on the Δ G calculations, HfC, ZrC, TiC, and TaC should undergo reduction by forming CH₄, while NbC and VC can also reduce by CH₃ formation. Notably, the non-reducible samples carbidic content indicates that H-adsorption on surface carbidic-C atoms is insufficient to form CH₄ or CH₃ so fewer than 3 H-atoms absorb per surface carbidic-C atom. Furthermore, the observed reduction

of Co₂C aligns with our hypothesis, as it can reduce by forming CH₂, necessitating only 2 H-atoms per surface carbidic-C atom to form a volatile CH_x specie.

In addition to that, we explain the observed discrepancy in the reducibility of surface oxides based on the thermodynamic barrier for forming H₂O on the surface oxides. Since Δ G for complete reduction of TaO_x, NbO_x, VO_x, and CoO is negative, the oxides on the surfaces of the TaC, NbC, VC, and Co₂C samples undergo strong reduction. Whereas thermodynamically complete reduction of HfO_x, ZrO_x, and TiO_x is not feasible, hence, oxides on the surfaces of the HfC, ZrC, and TiC samples show only partial reduction.

The results indicate that group IV-V TMCs are chemically stable in H^{*} at an elevated temperature. Hence, they can be a potential candidate for protective coatings in H^{*} environments. Moreover, the study also highlights the fact that surface cleaning (reduction of surface oxides and chemical erosion of non-carbidic-C) of TMCs occurs during H^{*}-exposure, suggesting that H^{*}-exposure may be used to improve/maintain the surface response of group IV-V TMCs.

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Supporting Information Available

 Supplementary information includes O/TM ratios, a comparison between the core level TM, C1s, O1s, and Si2p XPS spectra of the pre- and post-H*-exposed samples as a function of θ, the fitted peak positions in the core level TM and C1s XPS spectra of the pre- and post-H*-exposed sample taken at $\theta = 34.25^{\circ}$, and AFM of the Ni₃C sample.

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TOC Graphic

