

Behaviors of non-stoichiometric TiC_x ($x=0.5, 0.7, 0.9, 1.0$) under acid and high temperature environments

Cong Lei

leicong@gues.edu.cn

National Energy Large Scale Physical Energy Storage Technologies R&D Center of Bijie High- tech Industrial Development Zone

Liang Wang

National Energy Large Scale Physical Energy Storage Technologies R&D Center of Bijie High- tech Industrial Development Zone

Haisheng Chen

National Energy Large Scale Physical Energy Storage Technologies R&D Center of Bijie High- tech Industrial Development Zone

Research Article

Keywords: TiC_x powder, carbon vacancies, acid corrosion resistance, oxidation resistance

Posted Date: September 11th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10699859/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Behaviors of non-stoichiometric TiC_x ($x=0.5, 0.7, 0.9, 1.0$) under acid and high temperature environments

Cong Lei^{1,2}, Liang Wang^{1,3*}, Haisheng Chen^{1,3}

1 National Energy Large Scale Physical Energy Storage Technologies R&D Center of
Bijie High-tech Industrial Development Zone, Bijie 551700, China

2 School of Mechanical Engineering, Guizhou University of Engineering Science,
Guizhou, 551700, China

3 Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190,
China

* Corresponding author

E-mail address: leicong@gues.edu.cn

Abstract:

This study systematically investigates the influence of carbon vacancy on the stability of non-stoichiometric TiC_x ($x = 0.5, 0.7, 0.9, 1.0$) ceramics under strong acid and high temperature oxidation environments. TiC_x powders were synthesized via vacuum sintering using Ti powder and nano acetylene black, followed by crushing and sieving. The acid corrosion resistance was evaluated using HF-ethanol solution, the oxidation behavior was assessed through isothermal oxidation at 600°C in the air. XRD and SEM were employed to characterize phase compositions and microstructural evolutions. Results indicate that TiC_x powders with $x < 0.76$ exhibit an unstable cubic structure prone to HF corrosion, whereas those with $x > 0.76$ form a stable hexagonal structure with enhanced corrosion resistance. During oxidation, mass gain increases with increasing x value, $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ showing similar oxidation behavior to stoichiometric TiC. The oxidized $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ exhibit petal-like TiO_2 morphologies, while $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ display lamellar structures. This work provides experimental evidence and theoretical guidance for the component design and application of TiC_x ceramics in extreme environments.

Keywords: TiC_x powder; carbon vacancies; acid corrosion resistance; oxidation resistance

1 Introduction

Titanium carbide (TiC), as a typical transition metal carbide, is widely regarded as one of the key materials for extreme environmental applications due to its extremely high melting point ($\sim 3160^\circ\text{C}$), high hardness ($\sim 35\text{ GPa}$), excellent wear resistance, good chemical stability, and outstanding metal conductivity^[1-3]. It is commonly used in high-performance cutting tools, wear-resistant coatings, aerospace thermal structural components, and the nuclear industry^[4-6]. The crystal of TiC is a NaCl type face centered cubic structure, with an ideal stoichiometric ratio of 1:1^[7]. However, in the actual preparation process, vacancies in the carbon atomic sublattice are a common phenomena, resulting in a series of non-stoichiometric TiC_x , where $0.5 < x < 1.0$ ^[8-10]. It is worth noting that these carbon vacancies are not simple defects, they can significantly alter the physical and chemical properties of TiC_x such as hardness, melting point, conductivity, and chemical stability. Therefore, the study of non-stoichiometric TiC_x not only has theoretical significance, but also has important engineering value for accurately guiding its application in different harsh environments^[11-13].

In numerous demanding environments, strong acid and high temperature oxidizing conditions represent the most severe challenges for materials. In the chemical, metallurgical, and energy sectors, equipment components are often simultaneously exposed to high temperatures and corrosive media^[14-15]. Although stoichiometric TiC is known to exhibit certain acid resistance and oxidation resistance, the influence mechanism of non-stoichiometry on the stability of TiC_x under such environments remains unclear, and research conclusions are controversial^[16-17]. Some studies suggest that the presence of carbon vacancies disrupts the integrity of the crystal structure, potentially serving as active sites for preferential acid corrosion, thereby reducing its acid resistance. There is also a theory proposing that carbon vacancies alter the electron distribution on the surface of TiC_x , which may lead to different passivation behaviors under specific conditions^[18-19]. Similarly, during high temperature oxidation, carbon vacancies may provide pathways for the inward diffusion of oxygen atoms, accelerating oxidation, conversely, vacancies could also promote selective oxidation, leading to the formation of a denser, more protective oxide layer (such as TiO_2), thereby retarding further oxidation^[20-21]. The core of these controversies lies in how the carbon vacancy concentration systematically affects the corrosion kinetics and oxidation kinetics of TiC_x , as well as the underlying microstructural evolution mechanisms.

Currently, most studies focus on stoichiometric TiC or TiC_x with a specific x value^[22-23]. There remains a lack of a systematic research framework for comparatively investigating the properties of TiC_x ceramics with varying carbon vacancy concentrations under continuous harsh conditions. In particular, strong acid corrosion resistance and high temperature oxidation resistance are essential for comprehensively evaluating the application potential of TiC_x ceramics^[24]. Hydrofluoric acid (HF) is one of the few strong acids capable of effectively corroding TiC, HF solution is adopted as the corrosion medium to assess the chemical inertness of the materials. Meanwhile, isothermal oxidation tests, which monitor the mass variation of powders with different x values, serve as a classic approach to evaluate their oxidation resistance.

This study aims to systematically clarify the influence rules and underlying mechanisms of carbon vacancy concentration on the stability of TiC_x ceramics under strong acid and high temperature oxidation environments. Using Ti powder and acetylene black as raw materials, a series of bulk $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ ceramics were fabricated by precisely regulating the molar ratio of C to Ti. The corresponding powders were then obtained via crushing and sieving. By establishing the intrinsic relationship among compositions, structure and properties, this work is expected to provide solid experimental evidence and theoretical guidance for the component design, controllable preparation and application expansion of TiC_x ceramics serving in specific extreme environments.

2 Experimental procedure

2.1 Preparation of non-stoichiometric TiC_x ceramic powders

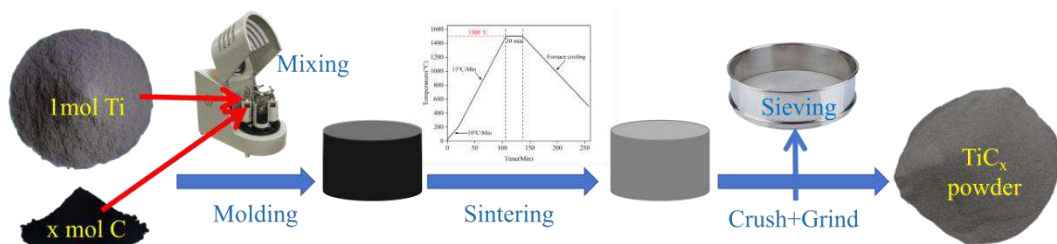


Figure 1 Schematic diagram of the process for preparing TiC_x ceramic powder

TiC_x ($0.5 < x < 1.0$) ceramic powders were prepared using acetylene black (C) powder with an approximate particle size of 50 nm (Tianjin Tianyi Century Chemical Products Technology Development Co., Ltd) and Ti powder of 45 μm with 99.9% purity (CHINA GRINM GROUP CORPORATION LIMITED) as the initial components. According to

the Ti/C stoichiometric ratios of 1:0.5, 1:0.7, 1:0.9 and 1:1, four groups of powder mixtures were formulated with a total mass of 100 g for each batch, and the corresponding mass fractions are listed in Table 1^[25-26].

The mixed powders were loaded into a stainless steel jar of a high energy planetary ball mill, together with 500 g stainless steel balls. The mass ratio of steel ball to powder were 5:1. The sealed jar was evacuated and then subjected to ball milling at a rotational speed of 300 r/min for 5 hours . After milling, the blended powders were collected via sieving.

Subsequently, the milled powder with mass 20 g was placed into a graphite crucible and sintered in a vacuum furnace. The entire sintering process was conducted under vacuum atmosphere. The furnace was heated from room temperature to 1500 °C at a heating rate of 10 °C/min, and the isothermal holding time at the target temperature was 30 minutes. Upon completion of the sintering procedure, the samples were naturally cooled to room temperature.

Finally, the sintered products were sequentially crushed, ground and sieved to obtain 200 mesh TiC_x ceramic powders. The resultant samples were designated as TiC_{0.5}, TiC_{0.7}, TiC_{0.9} and TiC_{1.0} powders were prepared using the same method as TiC_{0.5}, respectively.

Table 1 Raw material ratio of TiC_x ceramic powder

	Ti/g	C/g
TiC _{0.5}	88.86	11.14
TiC _{0.7}	85.07	14.93
TiC _{0.9}	81.59	18.41
TiC _{1.0}	79.96	20.04

2.2 Strong Acid Corrosion

To evaluate the acid corrosion resistance of TiC_x ceramic with different stoichiometric ratios, HF-ethanol solution was used as the corrosive agent to treat the powder samples. Firstly, 20 g of HF-ethanol corrosion solution was prepared, with a mass ratio of HF to ethanol of 1:5. Then, 10 g each of prepared TiC_{0.5}, TiC_{0.7}, TiC_{0.9} TiC_{1.0}, as well as the commercially purchased TiC powder (~45 μm, CHINA GRINM GROUP CORPORATION LIMITED) ceramic powder samples were weighed and placed into

PTFE containers. Subsequently, the containers with the ceramic powders and corrosion solution were placed in an ultrasonic machine and subjected to ultrasonic corrosion treatment at room temperature for 10 minutes to ensure full contact and reaction between the powder and the corrosive solution. After the reaction, the supernatant in the container was completely removed using a pipette. Then, absolute ethanol was added to the residual powder for rinsing, and this process was repeated five times to thoroughly remove the residual acid solution and reaction products from the powder surface. The cleaned powder was transferred to a petri dish and dried in a constant temperature forced-air drying oven at 40°C for 5 hours to ensure complete drying. Finally, the dried powder samples were vacuum-sealed and stored for subsequent analysis.

XRD was used to analyze the phase composition of the powders before and after corrosion, SEM was employed to observe the evolution of the microstructure.

2.3 Oxidation Resistance Detection and Analysis

To investigate the high temperature oxidation resistance of TiC_x ceramic, isothermal oxidation experiments were conducted in this study. Firstly, 10.00 g each of the prepared $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$, $\text{TiC}_{1.0}$, as well as the commercially purchased TiC powder ceramic powder samples were accurately weighed and evenly placed into high-purity alumina crucibles. Subsequently, the crucibles were placed in the constant temperature zone of a box-type oxidation furnace preheated to 600 °C. The oxidation experiments were carried out in static air. To obtain precise oxidation levels, the crucibles were rapidly removed from the furnace at oxidation times of 1 h, 2 h, 5 h, 10 h, 20 h, and 30 h, and the total mass of the crucible and powder was weighed using an analytical balance with an accuracy of 0.1 mg, recording the mass at each time point. The total mass of the powder after oxidation was obtained by subtracting the initial mass of the alumina crucible from the total mass after oxidation.

For the powder samples subjected to 30 hours of oxidation, XRD was employed to analyze the phase composition of the oxidized powders and identify the types of oxidation products. SEM was used to observe the microstructure of the oxidized powders, analyzing the structure, density, and formation of defects such as cracks in the surface oxide layer, thereby correlating these features with the oxidation resistance performance.

3 Results and discussion

3.1 TiC_x powders

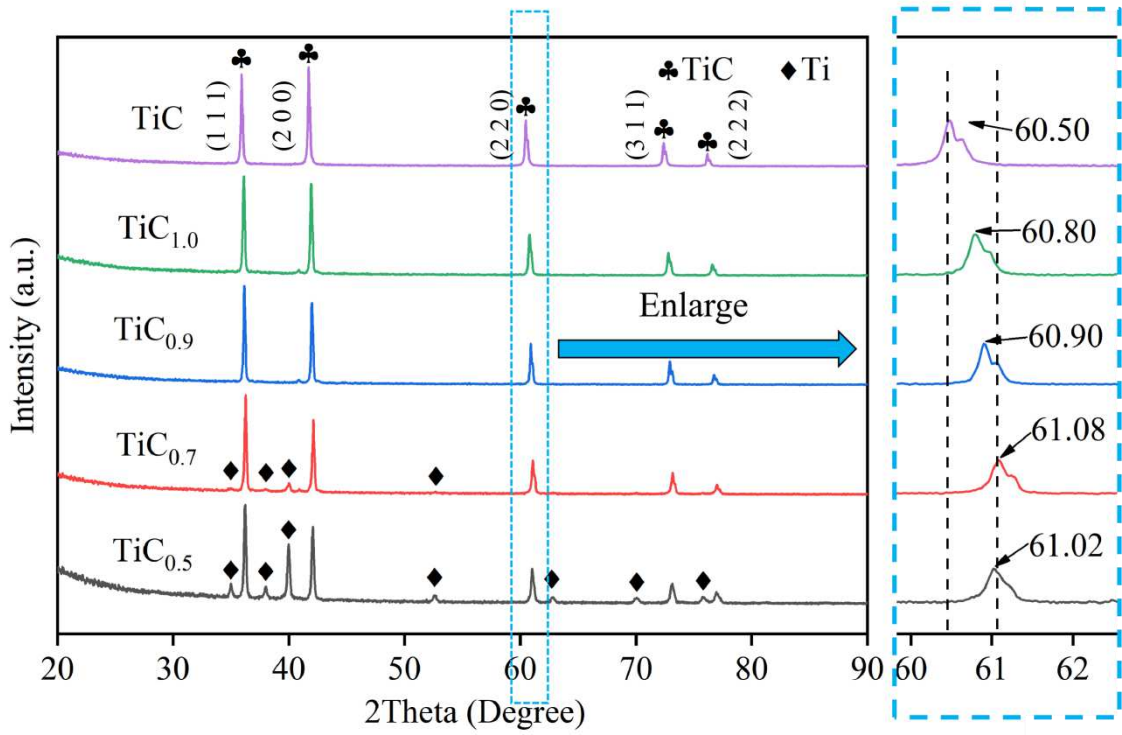


Figure 2 XRD patterns of TiC_x ceramic powders

Figure 2 shows the XRD patterns of $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ ceramic powders, along with the commercially purchased TiC powder, with the right side displaying a local magnification of the diffraction peak at the (2 2 0) plane of TiC . From the diffraction patterns, it can be observed that the positions and morphologies of the main peaks of the self-prepared TiC_x ceramic powders are identical to those of the reference powder, indicating that the reaction has essentially completed and the ceramic phase has formed. However, in the patterns of $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$, the presence of a Ti phase was detected, and the intensity and number of diffraction peaks of Ti in $\text{TiC}_{0.5}$ are significantly higher than those in $\text{TiC}_{0.7}$, whereas no residual Ti diffraction peaks were detected in the patterns of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$.

This indicates that under the conditions of 1500 °C and a holding time of 30 minutes, Ti did not fully participate in the reaction for the compositions of $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$. For the patterns of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$, although no residual Ti diffraction peaks were detected, it can be seen from the magnified diffraction peaks that the x value of the formed TiC_x did not reach 1, suggesting that a longer time or higher temperature is required to fully form TiC . The TiC_x powders we prepared are still non-stoichiometric. Combined with the Bragg equation $a = d^* \sqrt{h^2 + k^2 + l^2}$ and the empirical formula relating the lattice parameter to the x value, the actual x values of the powders are 0.66, 0.68, 0.86, and 0.87,

respectively^[22,27]. This also indicates that there must be residual unreacted C in $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$.

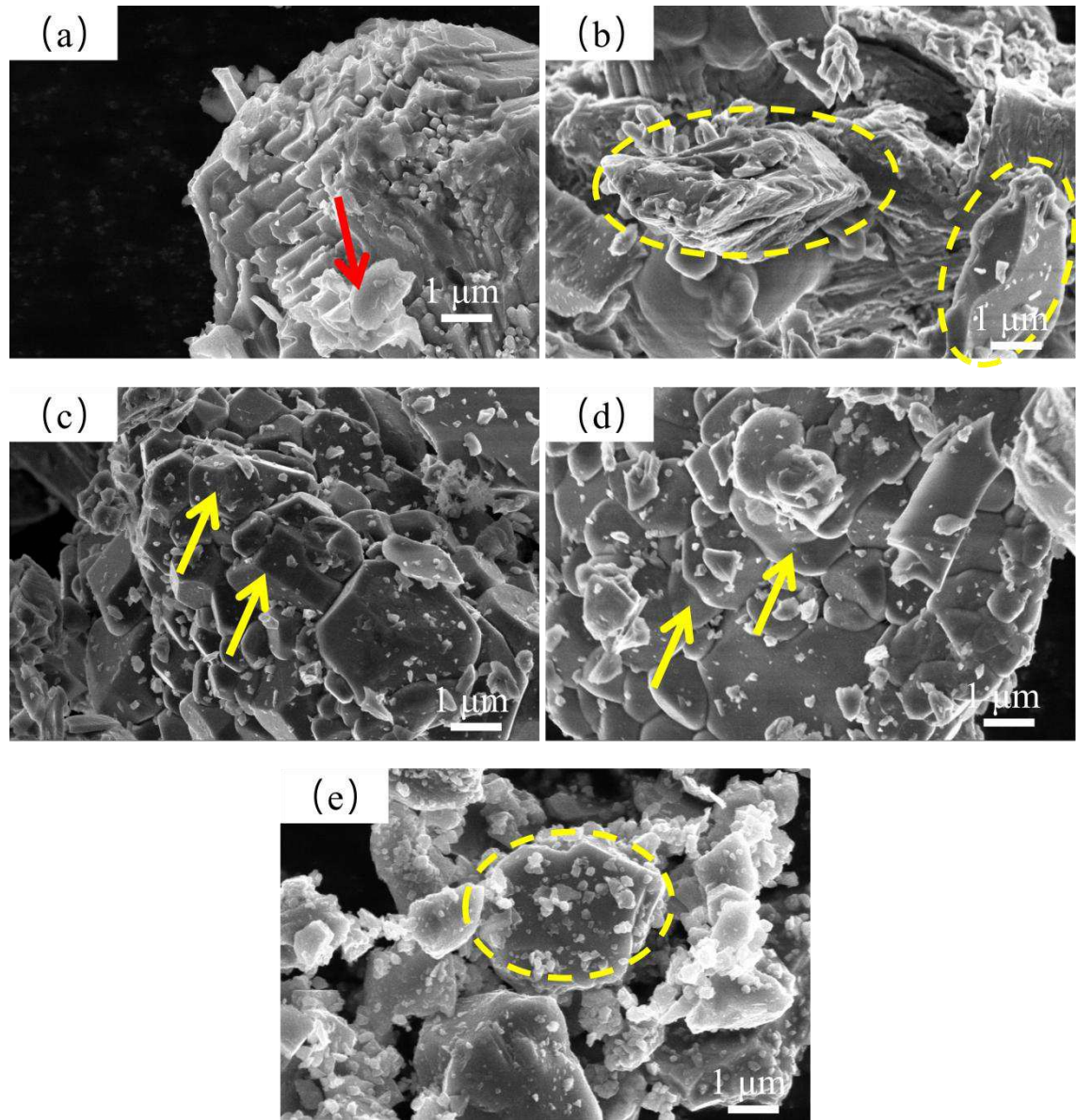


Figure 3 Micromorphology of TiC_x ceramic powder, (a) $\text{TiC}_{0.5}$, (b) $\text{TiC}_{0.7}$, (c) $\text{TiC}_{0.9}$, (d) $\text{TiC}_{1.0}$, (e) TiC

Figure 3 shows the particle morphology of the $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$, $\text{TiC}_{1.0}$ and TiC powder. The yellow arrows and circles indicate the TiC ceramic particles. In Figure 3(a), in addition to the TiC ceramic particles, residual Ti particles can also be observed, as indicated by the red arrows. In terms of ceramic morphology, $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ exhibit larger sizes formed by the stacking and growth of small-sized grains. This grain growth reduces grain boundaries, decreases the specific surface area, and thus minimizes the associated defects.

3.2 Corrosion resistance

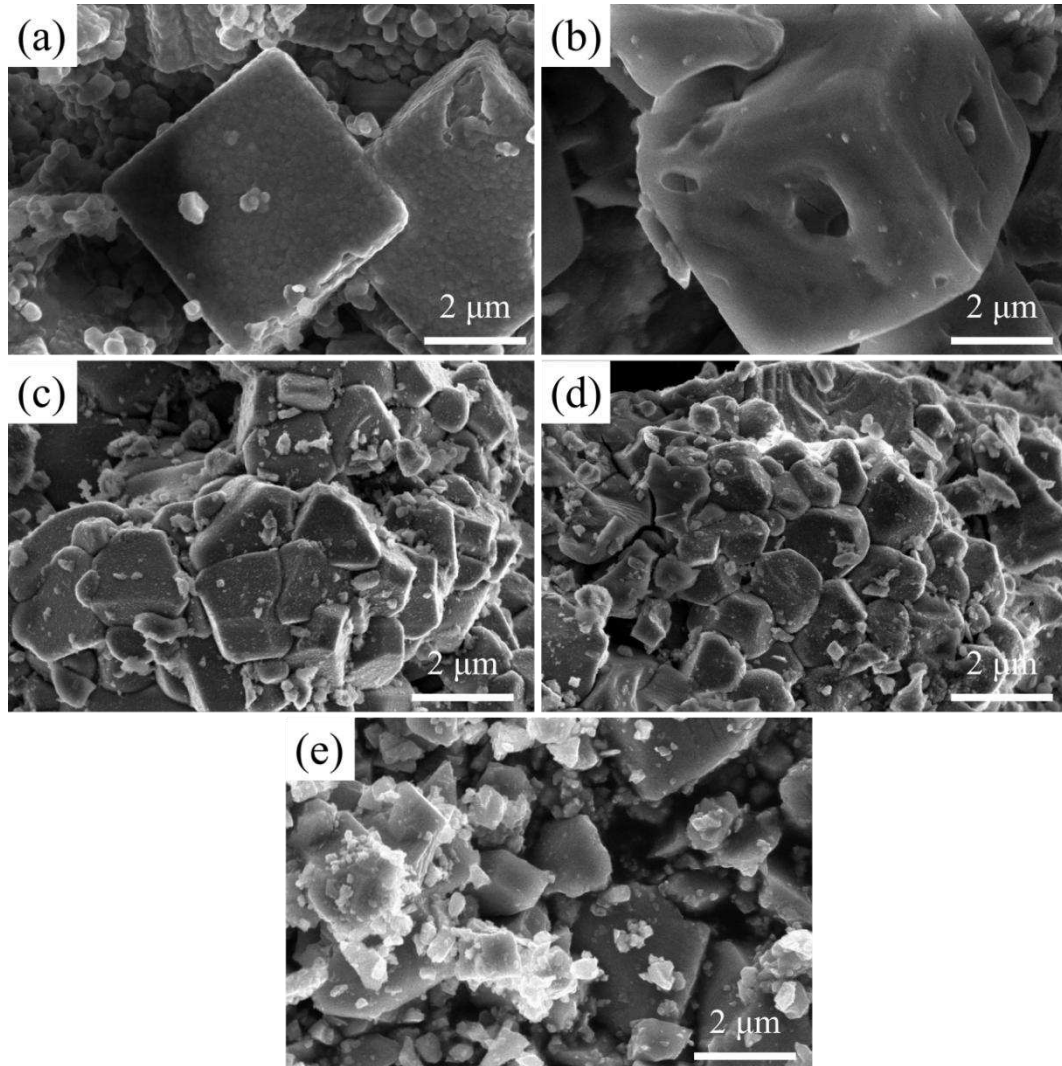
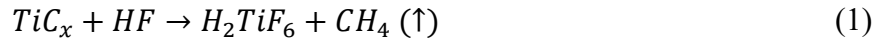


Figure 4 Micromorphology of etched TiC_x ceramic powder, (a) $\text{TiC}_{0.5}$, (b) $\text{TiC}_{0.7}$, (c) $\text{TiC}_{0.9}$, (d) $\text{TiC}_{1.0}$, (e) TiC

Figure 4 shows the micro morphology of $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$, $\text{TiC}_{1.0}$ and TiC powder, after strong acid corrosion. In terms of grain morphology, the ceramic grains of $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ are mainly cubic crystals, while the ceramic grains of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ are mainly hexagonal crystals. In our previous study^[26], it has been concluded that when the x value of TiC_x is less than 0.76, the ceramic grains exhibit an unstable structure, in which the carbon content is insufficient to completely transform the crystal structure of titanium, thus the grains retain a cubic shape. In the composition ratios of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$, the stoichiometric ratio of C to Ti exceeds 0.76, so the formed TiC_x reaches the condition for a stable crystal structure. Moreover, since carbon is interspersed among the grains of TiC_x , hindering grain growth, the grain size of TiC_x decreases with the increasing proportion of

C, as shown from Figure 4 (a) to (d). In addition to the differences in morphology and size, it can also be observed that pores exist in the ceramic grains of $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$, which is consistent with the conclusion drawn in our previous study: when the x value is less than 0.76, TiC_x exists in an unstable structure and is prone to chemical reaction with HF. The chemical equation for this reaction follows the expression below:



The above equation is the fundamental reason for the dissolution of TiC_x crystals and grain boundaries, exposing the ceramic grains. As can be seen from the gaps between grains and the integrity of the grains, the smaller the x value, the more severe the reaction of TiC_x with HF. A comparison of the morphology of the commercially purchased TiC ceramic powder before and after corrosion, as shown in Figure 3 (e) and Figure 4 (e), indicates that TiC with a full stoichiometric ratio can resist HF corrosion. The TiC_x preparation process selected in this study did not yield stoichiometric TiC.

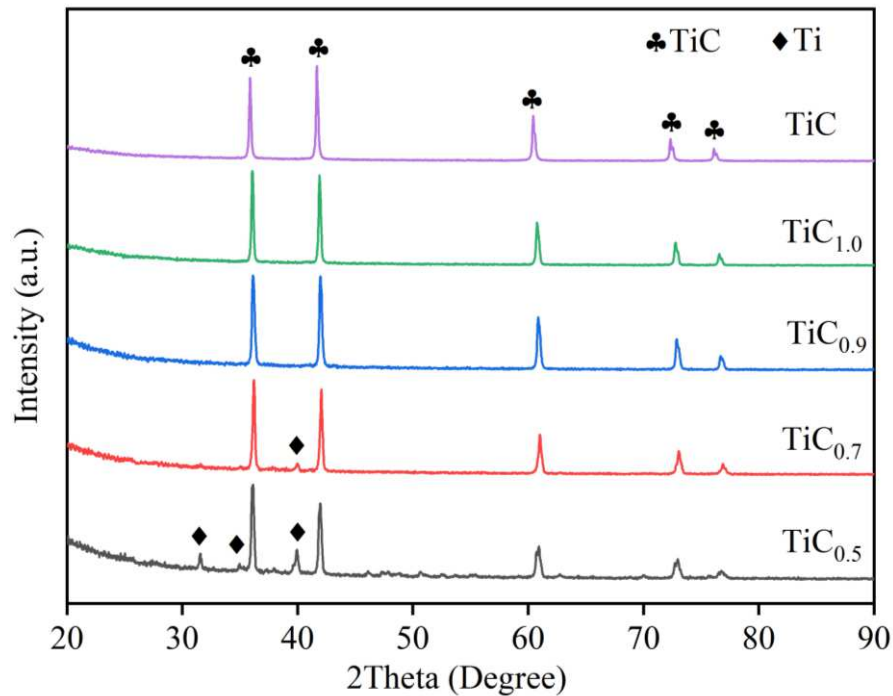
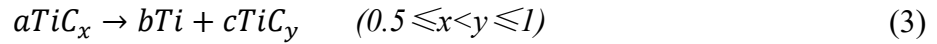


Figure 5 XRD patterns of etched TiC_x ceramic powder

Figure 5 shows the XRD patterns of TiC_x after strong acid corrosion with HF. Compared with Figure 2, the main diffraction peaks of the substances did not change, still corresponding to TiC. The diffraction peaks of Ti present in Figure 2 show a reduction in both number and intensity in Figure 5, indicating that the chemical reaction between Ti

and HF (equation 2) occurs simultaneously with Reaction (1). Both reactions involve the chemical reaction of either free Ti or Ti decomposed from TiC_x . It can be concluded that the smaller the x value of TiC_x , the more easily Ti escapes from the crystal structure to participate in other reactions, thereby increasing the x value of TiC_x and making it more stable. The main chemical expression is shown in Equation 3.



3.3 Oxidation resistance

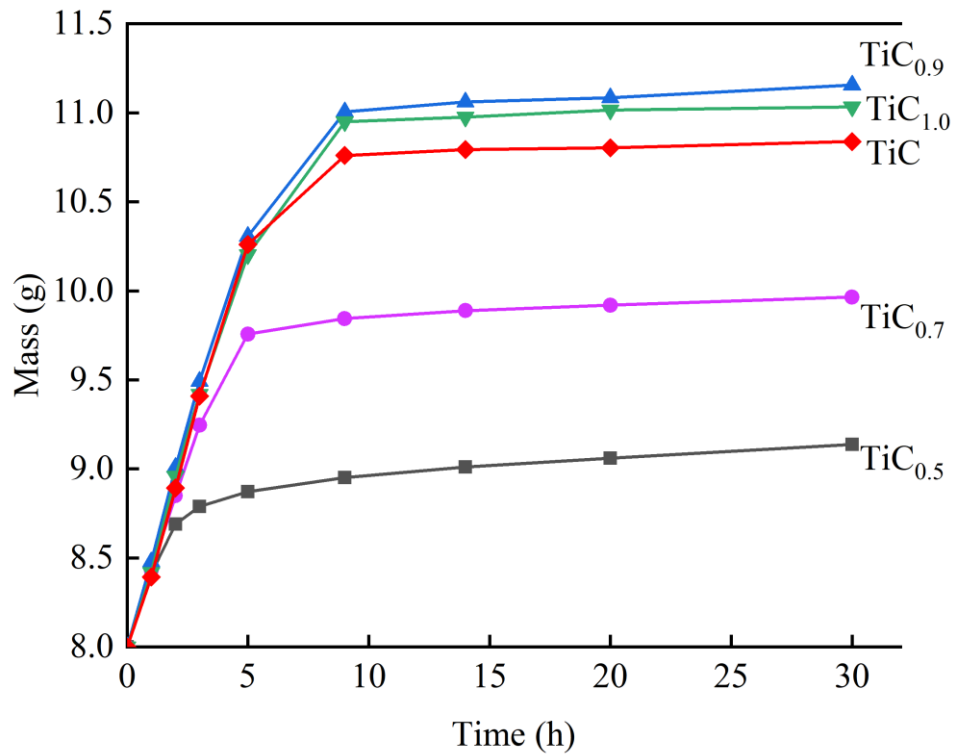


Figure 6 Mass change of TiC_x ceramic powder during oxidation

$TiC_{0.5}$, $TiC_{0.7}$, $TiC_{0.9}$, and $TiC_{1.0}$ ceramic powders, along with the commercially purchased TiC powder, were subjected to oxidation reactions in a box-type oxidation furnace at 600 °C. Figure 6 shows the mass change curves obtained by removing and weighing the samples at intervals.

From the trend of mass change in Figure 6, it can be observed that the total mass of the powders underwent two stages, a rapid increase followed by a gradual stabilization. $TiC_{0.5}$ and $TiC_{0.7}$ essentially completed their mass increase within the first 5 hours, while

TiC_{0.9}, TiC_{1.0}, and TiC powder stabilized after approximately 10 hours. Based on the mass change after 30 hours of oxidation, the weight gains of TiC_{0.5}, TiC_{0.7}, TiC_{0.9}, TiC_{1.0}, and TiC were calculated to be 14.2%, 24.6%, 39.4%, 37.9%, and 30%, respectively. Among the self-prepared powders, the degree of oxidation of TiC_x gradually increased with the increase of the x values, while the oxidation weight gain of the commercially purchased TiC was similar to that of TiC_{0.9} and TiC_{1.0}. This also indicates that the prepared TiC_{0.9} and TiC_{1.0} ceramic powders are more similar in structure to TiC and exhibit consistent stability.

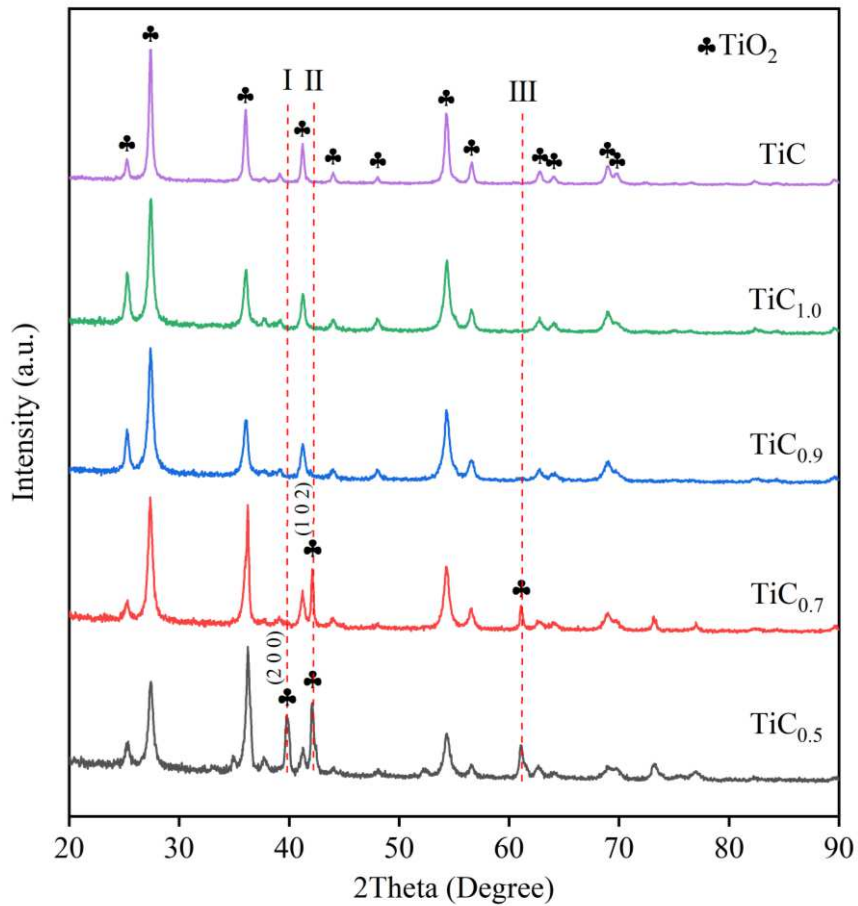


Figure 7 XRD patterns of oxidized TiC_x ceramic powder

The XRD analysis of the powders oxidized for 30 hours was performed, and the results are shown in Figure 7. It can be observed that after 30 h, only a single phase of TiO₂ remained, indicating that the powders were completely oxidized. However, differences in the diffraction peak structures were present. From the XRD results in Figure 5, it was already concluded that incompletely reacted Ti existed in the TiC_{0.5} and TiC_{0.7}

powder samples. In Figure 7, after complete oxidation of the $TiC_{0.5}$ and $TiC_{0.7}$ powders, the diffraction peaks of TiO_2 at positions I, II, and III differ from those of $TiC_{0.9}$, $TiC_{1.0}$, and TiC . Therefore, it can be concluded that the TiO_2 formed after complete oxidation of the $TiC_{0.5}$ and $TiC_{0.7}$ powders originates from two sources, and the chemical reaction equations are as follows:

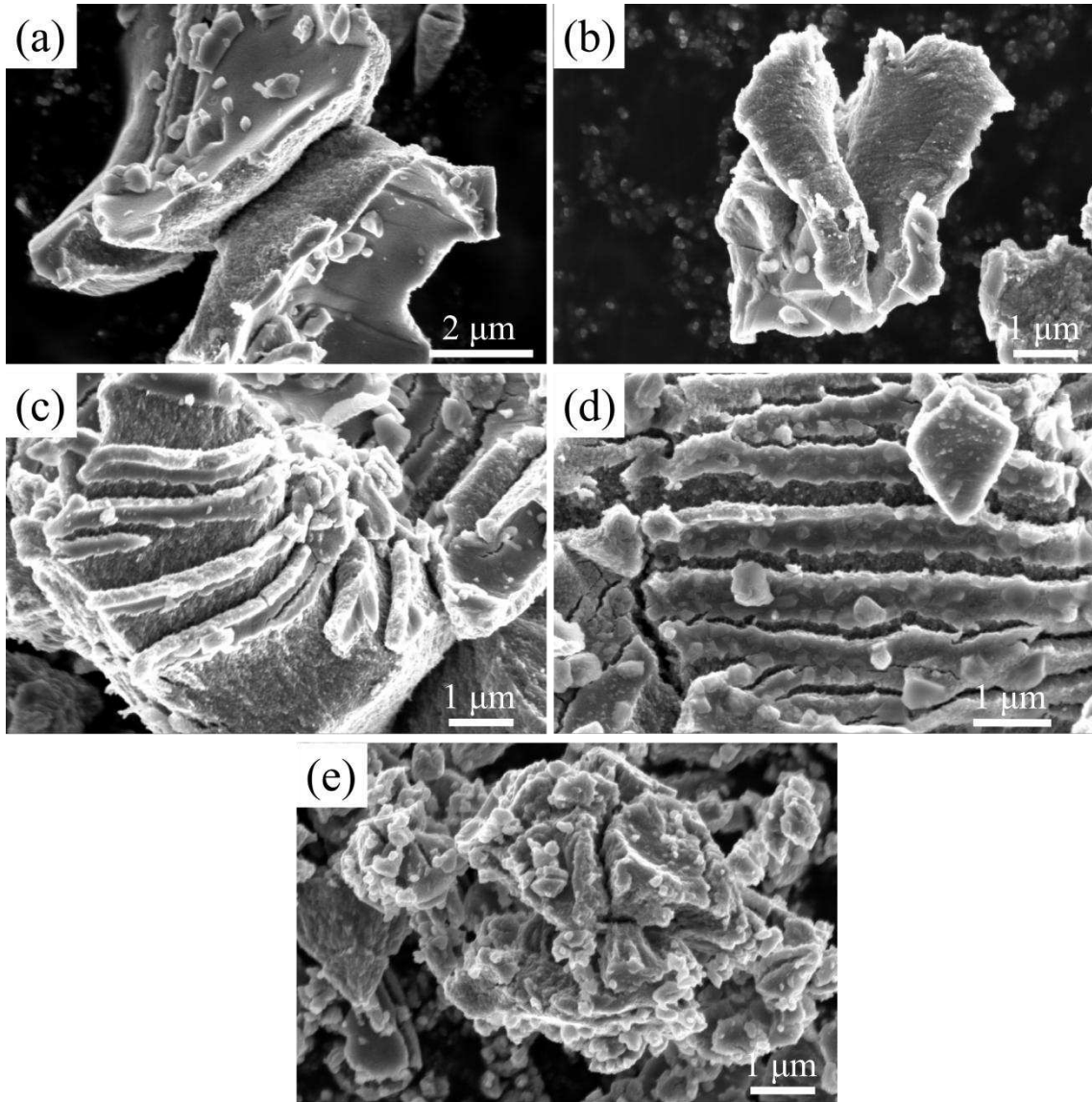


Figure 8 Micromorphology of oxidized TiC_x ceramic powder, (a) $TiC_{0.5}$, (b) $TiC_{0.7}$, (c) $TiC_{0.9}$, (d) $TiC_{1.0}$, (e) TiC

The morphologies of $TiC_{0.5}$, $TiC_{0.7}$, $TiC_{0.9}$, $TiC_{1.0}$ and TiC powders after oxidation at $600^\circ C$ for 30 hours were observed under SEM, and the results are shown in Figure 8 (a), (b), (c), (d), and (e), respectively. It can be seen from the figures that TiC_x with

different stoichiometric ratios exhibited distinct oxide morphologies. $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ mainly displayed a petal-like structure, while $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ mainly exhibited a lamellar structure. The surfaces of the oxide particles corresponding to $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ were smoother and denser compared to those of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$. Such oxidation morphologies can serve as a reference for the oxidation resistance of composites reinforced by TiC_x in an oxygen-containing environment.

4 Conclusions

This study systematically investigates the stability of non-stoichiometric TiC_x ceramic powders under strong acid (HF) corrosion and high temperature (600°C) oxidation environments. By changing the molar ratio of Ti and C, a series of $\text{TiC}_{0.5}$, $\text{TiC}_{0.7}$, $\text{TiC}_{0.9}$, and $\text{TiC}_{1.0}$ ceramic powders were prepared and compared with commercial TiC powder. The effects of carbon vacancy concentration on phase composition, microstructure evolution, and corrosion/oxidation behavior were revealed.

(1) In HF corrosion experiments, TiC_x with x values below 0.76 ($\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$) exhibited unstable crystal structures due to carbon vacancies, leading to severe dissolution and pore formation. TiC_x with x values above 0.76 ($\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$) and commercial TiC showed significantly enhanced acid resistance, indicating that sufficient carbon content is critical for maintaining structural stability against HF attack.

(2) In isothermal oxidation tests at 600°C , all powders were completely oxidized to TiO_2 after 30 h. $\text{TiC}_{0.5}$ and $\text{TiC}_{0.7}$ exhibited lower weight gains (14.2% and 24.6%) and formed a dense, petal-like oxide layer, while $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ showed higher weight gains (39.4% and 37.9%) with a lamellar oxide structure. The oxidation behavior of $\text{TiC}_{0.9}$ and $\text{TiC}_{1.0}$ closely resembled that of commercial TiC.

(3) The carbon vacancy concentration is the key factor governing both acid corrosion and high temperature oxidation resistance. Lower x values correspond to more carbon vacancies and greater structural instability, resulting in more severe reactions. As x value approaches 1, the structure and properties of TiC_x become increasingly similar to stoichiometric TiC, exhibiting superior stability.

Acknowledgements

This work was supported by the Guizhou Provincial Basic Research Program (Natural Science) (QianKeHe Basic - [2024] Youth 28) , the High Level Innovative Talents in Guizhou Province (BiKeRenCaiHe (2025) 6) , the Joint Fund Project of Bijie City (BiKeLianHe (2025) 131) , the Bijie Key Talent Program for Science and Technology Innovation (BKRC[2026] 13), the Science and Technology Foundation of Guizhou Province (ZK[2023] General 001) and the Science and Technology Plan Project of Bijie City ([2024]25).

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Data availability

All the related data is available from the authors upon request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

Ethics, Consent to Participate, and Consent to Publish declarations

Not applicable.

References

- [1]Bin Yang,Guoxiang Chen,Jishan Zhang. Effect of Ti/C additions on the formation of Al₃Ti of in situ TiC/Al composites[J]. Materials and Design, 2001, 22(8): 645-650.
- [2]Tian,Wei-Si,Zhao, et al. Simultaneously increasing the high-temperature tensile strength and ductility of nano-sized TiCp reinforced Al-Cu matrix composites[J]. Materials Science & Engineering, A. Structural Materials: Properties, Misrostructure and Processing, 2018, 717: 105-112.
- [3]L. H.,Yu,W., et al. In-situ synthesis of TiC/Ti composite coating by high frequency induction cladding[J]. Journal of Alloys & Compounds, 2017, 701(Complete): 244-255.
- [4]Qiang Zhang,Tianbin Zhu,Bing Meng, et al. Towards high-performance TiC-based ceramics: Optimization strategies and future perspectives[J]. Journal of Materials Research and Technology, 2026, 42: 11388-11406.
- [5]Yueyang Zhao,Qian Qi,Lujie Wang, et al. Effect of Ta on the tribological behavior of in-situ TiC/Ni composites[J]. Tribology International, 2024, 199: 110034.
- [6]Samrat Kavishwar,Vinod Bhaiswar,Sonika Kochhar, et al. State-of-the-Art titanium carbide hard coatings: a comprehensive review of mechanical and tribological behaviour[J]. Engineering Research Express, 2024, 6(4): 042401.
- [7]M. Mhadhbi. Titanium Carbide: Synthesis, Properties and Applications[J]. Brilliant Engineering, 2020.
- [8]Tianbiao Tan. Microstructure and Mechanical Properties of Carbide Reinforced TiC-Based Ultra-High Temperature Ceramics: A Review[J]. Coatings, 2021, 11.
- [9]Jinyu Shi,Yiming Lei,Chenxu Wang, et al. Microstructure evolution in titanium carbide with different stoichiometry under 3 MeV Au²⁺ ion irradiation[J]. Journal of Nuclear Materials, 2025, 606: 155609.
- [10]Bo Yuan Zheng,Yi Dong Wu,De Ye Lin, et al. First-principles study on the structure, mechanical and thermodynamic properties of (Ti, Hf, Nb, Ta)C high-entropy carbide ceramics[J]. Ceramics International, 2024, 50(13): 23097-23104.

- [11]Zhichao Zhang,Changjian Geng,Yujiao Ke, et al. Processing and mechanical properties of nonstoichiometric TiC_x ($0.3 \leq x \leq 0.5$)[J]. *Ceramics International*, 2018, 44(15): 18996-19001.
- [12]Shuntaro Ida,Kotaro Hoshizaki,Takahiro Kaneko, et al. Off-stoichiometry and molybdenum substitution effects on elastic moduli of B1-type titanium carbide[J]. *Scientific Reports*, 2023, 13(1).
- [13]Qin Zou,Zhuang Li,Shuang Li, et al. Effects of $\text{TiC}_{0.4}$ and Ti addition on the microstructures and mechanical properties of TiC composites[J]. *Ceramics International*, 2024, 50(9-PartB): 9.
- [14]Haofei Sun,Luchao Sun,Xiaomin Ren, et al. Outstanding molten calcium–magnesium–aluminosilicate (CMAS) corrosion resistance of directionally solidified $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$ eutectic ceramic at 1500 °C[J]. *Corrosion Science*, 2023, 220: 111289.
- [15]Xue Tan,Haijun Su,Yuan Liu, et al. CMAS corrosion resistance and mechanism of directionally solidified $\text{Al}_2\text{O}_3/\text{YAG}$ eutectic ceramics at high temperatures of 1300–1500 °C[J]. *Corrosion Science*, 2025, 248: 112793.
- [16]Yalovega,Galina,E., et al. First principles investigations of the influence of O-adsorption on the structural and electronic properties of $\text{TiC}(111)$ surfaces with vacancies[J]. *Surface Science: a Journal Devoted to the Physics and Chemistry of Interfaces*, 2016, 649(Jul.): 20-26.
- [17]Hamed Aghamohammadi,Akbar Heidarpour,Rasoul Jamshidi, et al. Study on the chemical stability of the synthesized TiC_x in Ti-Al-C system after immersion in the $\text{HF} + \text{H}_2\text{O}_2$ solution[Z]. *Advanced Powder Technology*, 2018: 441.
- [18]Jinyu SHI,Yiming LEI,Chenxu WANG, et al. Ion Irradiation Damage Behavior in Titanium Carbide with Different Stoichiometry[J]. *Journal of Inorganic Materials*, 2026, 41: 322.
- [19]Haimin Ding,Jinfeng Wang,Chunyan Li, et al. Study of the surface segregation of carbon vacancies in[J]. *Solid State Communications*, 2012, 152: 185-188.

- [20]Lei Zhuang,Zihao Wen,Yiwen Liu, et al. Unveiling the Oxidation Mechanisms of High-entropy Carbides Through Atomic-scale Dynamic Observation[J]. Advanced Materials, 2025, 37.
- [21]Shaolou Wei,Lujun Huang,Yuntong Zhu, et al. Sub-stoichiometry-facilitated oxidation kinetics in a δ -Ti_xC-doped Ti-based alloy[J]. Npj Materials Degradation, 2019, 3.
- [22]Zhichao Zhang,Changjian Geng,Yujiao Ke, et al. Processing and mechanical properties of nonstoichiometric TiC ($0.3 \leq x \leq 0.5$)[J]. Ceramics International, 2018, 44: 18996-19001.
- [23]Jipeng Jiang,Shibo Li,Deqiang Chen, et al. Oxidation behavior of high Cr white iron composites reinforced with TiC and nonstoichiometric TiC_x in air at 600 °C[J]. Journal of Materials Research and Technology, 2023, 25: 5982-5989.
- [24]Gadifele Nicolene Mekgwe,Ojo Jeremiah Akinribide,Samuel Olukayode Akinwamide, et al. Densification and corrosion properties of graphite reinforced binderless TiC₇₀N₃₀ ceramic composites[J]. Journal of the European Ceramic Society, 2024, 44: 6223-6238.
- [25]Cong Lei,Hongxiang Zhai,Zhenying Huang, et al. Fabrication, microstructure and mechanical properties of co-continuous TiC_x/Cu-Cu₄Ti composites prepared by pressureless-infiltration method[J]. Ceramics International, 2019, 45: 2932-2939.
- [26]Cong Lei,Fangwei Jin,Shanxiang Wei, et al. Influences of solution treatments on the microstructure and mechanical properties of TiC_x-Cu ($x = 0.5, 0.6, 0.7$) cermets prepared by infiltration method[J]. Ceramics International, 2024, 50: 7211-7217.
- [27]B.M. Moshtaghioun,R. Cano Crespo,F.L. Cumbreira, et al. Mechanical performance of sub-stoichiometric titanium carbide ceramics synthesized by a hybrid SHS and SPS methodology[J]. Journal of the European Ceramic Society, 2026, 46: 117748.