**Ti$_3$SiC$_2$-TiC-Si Antioxidant Coating Prepared on SiC coated MG Spheres of HTR Fuel Element by Molten Salt Technique**

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**Abstract.** A Ti$_3$SiC$_2$-TiC-Si composite coating was prepared by molten salt technique on the surface of SiC coated matrix graphite (MG) spheres of HTR fuel element with different Ti content. The coating is composed of a transition layer, a SiC layer and an outer Ti-rich layer. When the content of Ti is 0.6g, the coating consists of Ti$_3$SiC$_2$, SiC, and TiC; when Ti content are 1.2g and 2.4g, the coating is composed of Ti$_3$SiC$_2$, SiC, TiC, and Si. Oxidation tests show that the kinetics of oxidation is parabolic at the beginning of oxidation; then it becomes linear after oxidation for 5h. The coating prepared with 0.6g Ti shows the best oxidation resistance, and the weight reduction of the coated MG spheres is only 0.33% after oxidation in static air at 1773K for 50h. These results show that Ti-based composites coating a kind of anti-oxidation coating system worth studying.

**1. Introduction**

Graphite exhibits several advantages, including its low neutron absorption cross-section, prominent thermal shock resistance, low thermal expansion coefficient (CTE), as well as high thermal conductivity. As impacted by the mentioned characteristics, it has extensively acted as the matrix material of thermal barrier, the absorbing elements and the fuel elements for the high-temperature gas-cooled reactor (HTR) [1-3]. However, the poor anti-oxidation performance exhibited by graphite in the oxidation environment above 773 K significantly limits its high-temperature application. If high purity helium (He) gas acts as the coolant in the HTR, the excellent properties of graphite could be maximally exploited. However, under extreme accident conditions, air or water will enter the reactor core to varying degrees. As a result, the graphite applied in the fuel element will be exposed to the oxidizing environment directly, thereby adversely affecting the safety of the HTR [4, 5]. Accordingly, enhancing the oxidation resistance of matrix graphite of nuclear fuel elements can ensure the safety and development of the HTR.

Thus far, the coating method acts as a common method to improve the anti-oxidation performance exhibited by graphite or C/C composites. As indicated from existing studies, the anti-oxidation property exhibited by single coating is limited [6-8]. Thus, multilayer coatings have been extensively studied to improve the oxidation resistance exhibited by graphite or C/C composites. SiC is widely applied as the inner transition layer of multilayer coating for its high physical and chemical compatibility with graphite [9-11]. Apart from the stability at high temperatures and low neutron absorption cross-section of SiC, it will be oxidized into the SiO$_2$ glass phase at high temperatures. SiO$_2$ has a low oxygen diffusion coefficient and high fluidity at high temperatures, so it can fill the pores, cracks and other defects in the coating. Fu et al. [12] prepared a SiO$_2$/SiC coating by employing the vapor reaction diffusion combined
with slurry techniques to improve the anti-oxidation performance exhibited by matrix graphite. After heated in high purity He for 100 h at 1273 K, the SiO$_2$/SiC could still maintain its stability and effectively prevent the oxidation of matrix graphite. In addition, the SiO$_2$/SiC-coated sample exhibited an excellent thermal shock performance. Huang et al. [13] fabricated a ZrO$_2$-SiO$_2$ layer on the surface of SiC-coated C/C composites. After the oxidation for 10 h at 1773 K in air, the composite coating could prevent the graphite from being oxidized with the weight reducing by 1.97%. The internal SiC coating could effectively release the CTE mismatch between the external coating and the graphite substate. The mentioned SiC-based multilayer coatings were found to be capable of greatly improving the anti-oxidation performance exhibited by graphite and C/C composites.

Specific to multilayer coatings, numerous materials can act as the outer coatings, (e.g., MoSi$_2$ [14-16], ZrC [17, 18] and HfC [19, 20]). As impacted by the ceramic and metallic properties, the fracture energy absorption, the chemical stability, and the irradiation resistance, MAX phases are recognized as the potential materials for the nuclear application [21-23]. Wang et al. [24] investigated the oxidation behavior exhibited by Ti$_3$AlC$_2$. The bulk Ti$_3$AlC$_2$ was found to exhibit a prominent oxidation resistance in air, and the oxide scale included an Al$_2$O$_3$ inner layer and a TiO$_2$ outer layer. As reported by Ko et al. [25], the oxide scale of Ti$_3$SiC$_2$ (TSC) also covered an inner layer composed of amorphous SiO$_2$ and TiO$_2$, as well as an outer layer formed by TiO$_2$. According to Fan et al. [26], cracks could be filled by TiO$_2$ and SiO$_2$, which was suggested as the oxidation production of TSC. According to the mentioned reason, the anti-oxidation property exhibited by the material can be enhanced. Thus far, MAX phases coating has been rarely used to improve the anti-oxidation properties of graphite or C/C composites.

In this study, a Ti$_3$SiC$_2$-TiC-Si composite coating was prepared on the surface of the SiC-coated graphite spheres with the molten salt technique. The microstructure, the composition and the mechanical properties were characterized, and an investigation was conducted on the anti-oxidation property exhibited by the mentioned coatings at 1773 K in air.

2. Experiment
The substrates applied here the graphite spheres. The diameter of the sphere is 15 mm. Table 1 lists the properties of the graphite substrates. After being polished, cleaned and dried, the pack cementation was performed for the graphite spheres with mixed powers in the graphite crucibles, and then the spheres were placed in an electrical furnace. The mixed powers are composed of graphite (8-12 wt%), SiC (18-22 wt%), Al$_2$O$_3$ (2-12 wt%), and Si (58-68 wt%). The heat treatment was performed at 1973-2023 K for 2-3 h in Ar atmosphere. After the first pack cementation, the mentioned spheres were immersed in a molten salt of Al$_2$O$_3$ crucibles. The mixture for the molten salt technique was mixed with NaCl, KCl, and Ti. In addition, the mass of Ti was 0.6 g, 1.2 g, and 2.4 g. The coatings prepared with different Ti contents (i.e., 0.6 g, 1.2 g, and 2.4 g) were termed as T1, T2, and T3, respectively. The molten salt technique was used at 1373 K for 2-3 h in Ar atmosphere. For an in-depth characterization, when cooled to ambient temperatures, the mentioned coated graphite spheres were repeatedly washed with distilled water to remove residual salt. Finally, these coated samples were dried in an oven at 373 K.

![Figure 1](image1.png)

*Figure 1. The preparation process of the composite coating by pack cementation and molten salt techniques.*
Table 1. Properties of the MG spheres used in this paper [1, 27]

| Properties                        | Parameter Value                      |
|-----------------------------------|--------------------------------------|
| Density                           | 1.72–1.73 g/cm³                      |
| Ash content                       | 130-190 μg/g                         |
| Li content                        | 7-23 μg/kg                            |
| Boron equivalent                  | ≤0.15 μg/g                           |
| Thermal conductivity              | 30 W·(m·K)⁻¹, at 1273 K              |
| Anisotropy of thermal expansion   | α⊥/α∥ = 1.10                          |

The morphology and fracture cross-sections exhibited by the coatings were characterized under a Quanta 200 FEG field-emission scanning electron microscope (SEM, FEI, the Netherlands). In addition, the composition and phases of the mentioned coatings were examined with a Genesis Energy-dispersive X-ray spectroscopy (EDAX, Mahwah, NJ) and a D/Max IIIA X-ray diffractometer (XRD, Rigaku, Tokyo, Japan), respectively. To prepare the XRD samples, the graphite spheres coated were crushed, so the graphite within the spheres could be exposed. Subsequently, the crushed spheres were heated in air for 10 h at 1073 K to remove the overall graphite. The powder obtained after the coating shells were fully ground in the mortar was examined by using the XRD. The compressive strength exhibited by the coated graphite spheres was tested by employing the general electromechanical test system (CMT5105, MTS, USA). Then, the precise weighing sensor was calibrated with a force of 1/3000 kN, at and a displacement rate of 0.5 mm/min. Each experiment was repeated three times to ensure the repeatability of the experiment.

The anti-oxidation properties of the mentioned coated graphite spheres were characterized in static air at 1773 K. Next, the coated spheres were placed into the muffle furnace for a certain period and then taken out. When the spheres cooled to ambient temperatures, the weight of the sample was recorded. In order to ensure sufficient air during oxidation process, a hole was drilled in the muffle furnace. The oxidation weight loss percentage of the coated graphite spheres Δm, was calculated determined by using Eq. 1.

\[
\Delta m_t = \frac{m_t - m_0}{m_0} \times 100\%
\]

where \( m_t \) and \( m_0 \) denote the weight of the coated graphite spheres after the oxidation for \( t \) h and the original weight of the coated sample, respectively.

3. Results and discussion

![Figure 2](image-url)

**Figure 2.** The fracture cross of the composite coating prepared with different Ti contents (a) 0.6 g, (b) 1.2 g, (c) 2.4 g.

Fig. 2 presents the cross-section morphologies of the mentioned composites coating. The thickness of the mentioned coatings is around 500–600 μm. Regardless of the amount of Ti was added, the coating consists of three parts, the transition layer, the SiC layer and the Ti-rich layer. When the amount of Ti
added was 0.6 g, the Ti-rich layer is significantly uniform with the thickness almost unchanged; when 1.2 g Ti was added, the thickness of the whole coating increased, the internal transition layer thickened, and the Ti-rich layer is discontinuous; the Ti-rich layer thickened, and the thickness was not uniform when 2.4 g Ti was added, and an obvious contrast was identified on this layer. The XRD patterns of different coatings are presented in Fig.3. The coating composition includes TSC, SiC and TiC when 0.6 g Ti was added. However, the coating composition included TSC, SiC, TiC, and Si when the content of Ti reached 1.2 g and 2.4 g. Thus, the Ti-rich layer in Fig. 2 is largely composed of TSC and TiC.

![XRD patterns of the Ti-based composite coating.](image)

**Figure 3.** XRD patterns of the Ti-based composite coating.

The bonding strengths of the mentioned coatings and graphite were determined by performing the crushing test. The crushing strength of each the respective sample is illustrated in Fig. 4. TT1, T2 and T3 had the crushing strength of 1100.3 N, 1305.6 N, and 1247.3 N, respectively. In significant difference was reported in the crushing strength of the mentioned graphite spheres coated with different coatings. Accordingly, the Ti content was found to insignificantly affect the bonding strength of the mentioned coatings and graphite.

![Crushing strength of these coatings prepared with different Ti content.](image)

**Figure 4.** Crushing strength of these coatings prepared with different Ti content.

Fig. 5 presents the typical crushing mode and the breaking models of the mentioned coated graphite spheres. According to Fig. 5 (a), the T1-coated graphite spheres were broken in the middle during the crushing. The crack penetrated the graphite spheres via the Ti-rich layer, the SiC layer and the inner transition layer. No obvious crack was reported between different layers. After the crushing, the coating remained tightly bonded to the graphite spheres, which demonstrated a strong binding force between the coating and the graphite sphere. The crack passed through the entire coating area to the graphite sphere.
coated with T2. Subsequently, the mentioned cracks stretched in different directions over the graphite sphere till the whole graphite spheres failed. However, when T3-coated graphite spheres were being crushed, the cracks spread along the interface between the Ti-rich layer and the SiC layer, as well as the area close to the coating in graphite sphere. It was therefore suggested that the adhesion between different layers and that between the whole coating and the graphite sphere were very weak.

![Figure 5](image)

**Figure 5.** Typical crushing mode and fracture models of these coatings prepared with different Ti content: (a) 0.6g, (b) 1.2g, (c) 2.4g.

Given the oxidation experimental results at different times, Fig. 6 presents the weight change curve of different coated graphite spheres over time. After the mentioned spheres were oxidized for 50 h in air at 1773 K, the weight reduction of the graphite spheres coated with T1, T2, and T3 reached 0.33%, 0.35% and 0.42%, respectively. The oxidation of the mentioned coated graphite spheres could fall to three stages in line with the different oxidation rates. At the first stage, the weight reduction of the coated graphite spheres increased in a parabolic pattern in the first 4 h. The T2-coated graphite spheres achieved the fastest oxidation rate, the T1-coated graphite spheres had the slowest rate, and the T3-coated graphite spheres achieved the medium rate. After the oxidation at 1773 K for 4 h, the weight reduction of the graphite spheres coated with T1, T2, and T3 reached 0.067%, 0.099% and 0.073%, respectively.

In the second stage of the oxidation process, the weight change trend of the coated graphite sphere changes significantly. Compared with the parabolic behavior at the early phase of the oxidation, the linear oxidation behavior was identified after 4 h, which demonstrated that the oxidation mechanism of the coated graphite spheres was transformed. The oxidation rate of the T2 coated graphite spheres continued to be the fastest, and the T3 coated graphite spheres had the slowest rate. Moreover, the oxidation rate of all coated graphite spheres at this stage is the slowest during the whole oxidation.

At the third stage, the weight of the coated graphite spheres reduced sharply, which suggested that cracks might be generated in the coating. The weight of the T3-coated spheres decreased most rapidly. The weight variation curves of the coated graphite spheres first exhibited a parabolic dependence, while the curve displayed a linear correlation over time, which is consistent with the results of other studies [28, 29].

During the oxidation, the following reactions might occur:

\[
\begin{align*}
\text{Ti}_3\text{SiC}_2+6\text{O}_2(g) & \rightarrow 3\text{TiO}_2+\text{SiO}_2+2\text{CO}_2(g) \quad (2) \\
\text{TiC}+2\text{O}_2(g) & \rightarrow \text{SiO}_2+\text{CO}_2(g) \quad (3)
\end{align*}
\]
\[ 2 \text{Ti}_3 \text{SiC}_2 + 3 \text{TiC} + 18 \text{O}_2(g) \rightarrow 9 \text{TiO}_2 + 2 \text{SiO}_2 + 7 \text{CO}_2(g) \] (4)

\[ \text{SiC} + 2 \text{O}_2(g) \rightarrow \text{SiO}_2 + \text{CO}_2(g) \] (5)

\[ \text{Si} + \text{O}_2(g) \rightarrow \text{SiO}_2 \] (6)

As indicated from the calculation results, the oxidation of graphite caused the weight to decrease, while the oxidation of TSC, TiC, Si, and SiC caused the weight of the coated spheres to increase. The oxidation rates of TSC and TiC were higher than those of SiC, thereby showing a worse oxidation resistance [26]. During the oxidation, the mentioned reactions could occur spontaneously. The content of the respective phase is different in different coatings, thereby leading to different weight variations of the coated graphite spheres.

![Figure 6](image1.png)

**Figure 6.** Weight gain curves of the isothermal oxidation tests at 1773 K in static air for Ti-based composite coated samples.

![Figure 7](image2.png)

**Figure 7.** The mass change curve and the data fitting of the T2-coated graphite spheres.

Though Eq. 2-6 could result in an increase in the mass of the coated sample, the weight of the coated graphite spheres decreased during the oxidation. Since the mass lose curve of the SiC/Si-TiC-Ti_3SiC_2 composite coating samples prepared with different Ti additions displayed the identical trend, the coating prepared with 1.2 g Ti added is 1.2 g is selected in the study. The mass change curve of the graphite sphere covered by the SiC/Si-TiC-Ti_3SiC_2 composite coating is fitted in Origin, and the mass loss rate and mass loss rate of the sample are determined. The dynamic curve is plotted in Fig.7. As more clearly indicated from the fitting curve of T2 in the oxidation in Fig.7, the coating-coated sample exhibited a parabolic oxidation model at stage I and showed a linear oxidation model at stage II and III.
At stage I, the mass loss rate $W_t$ of the graphite sphere covered with T2 is defined as:

$$W_t = -0.0048 \cdot t^2 + 0.0422 \cdot t + 0.00502 \quad (0 \leq t \leq 4 \text{ h})$$

(7)

The mass loss rate $V_I$ of the sample is expressed as:

$$V_I(\% \cdot \text{h}^{-1}) = -0.0096 \cdot t + 0.0422$$

(8)

At stage I ($0 \sim 4$ h), the mass of the sample decreased in a parabolic trend over the oxidation time, and the mass loss rate of the sample is the fastest such a period. There is a layer of white substance on the surface of the sample after the oxidation, which is attributed to the escape of residual salt in the coating during the oxidation. Though the coating quickly reacted with the oxidizing gas at the beginning of the oxidation reaction, the mass increase rate of the sample is significantly high. However, the oxidizing gas could easily diffuse via the original pores and cracks in the coating to the graphite sphere within the coating.

Due to the oxidation mass loss of graphite sphere and the escape of residual salt, the mass of the sample would decrease. Since there is insignificant cracking on the coating surface, the mass loss caused by the oxidation of the internal graphite sphere is limited. On the whole, the mass loss of the coated graphite sphere is mainly attributed to the volatilization of salt. Thus, the weight loss of the sample at this stage resulted from the oxidation, and the volatilization of residual NaCl and KCl in the coating would cause the weight of the coated sample to decrease. Over time, the weight loss rate of the sample decreased linearly, from 0.0422%·h$^{-1}$ at the beginning to 0.0038%·h$^{-1}$.

At stage II, the mass loss rate $W_t$ of the graphite sphere covered by T2 is expressed as:

$$W_t = 0.00374 \cdot t + 0.08443 \quad (4 \leq t \leq 40 \text{ h})$$

(9)

The mass loss rate $V_{II}$ of the sample is defined as:

$$V_{II}(\% \cdot \text{h}^{-1}) = 0.00374$$

(10)

At stage II ($4\sim40$ h), the oxidation weight loss rate of the sample remained unchanged at 0.00374%·h$^{-1}$, which was an order of magnitude lower than the oxidation rate at stage I. At this stage, there are two reasons for the decrease in the mass loss rate of the sample: the residual salt in the coating was basically volatilized at the first stage, and there is no sample weight loss caused by salt escape; at stage I, the oxide layer formed by the oxidation of Si, SiC, TiC and TSC aimed to isolate the oxidizing gas. The diffusion of the oxidizing gas into the coating is limited, and the oxidation loss of the internal graphite sphere is reduced, thereby reducing reduces the oxidation rate of the sample.

At stage III, the mass loss rate $W_t$ of the coated graphite sphere is defined as:

$$W_t = 0.01165 \cdot t - 0.02338 \quad (40 \leq t \leq 50 \text{ h})$$

(11)

The mass loss rate $V_{III}$ of the sample is expressed as:

$$V_{III}(\% \cdot \text{h}^{-1}) = 0.01165$$

(12)

However, at stage III ($40\sim50$ h), the oxidation mass loss rate of the sample increased again, and the mass of the sample further dropped significantly. The mass loss rate of the sample reached over 0.01%·h$^{-1}$. After 40 h of the oxidation, the residual salt in the coating is basically volatilized. Accordingly, the degradation of the T2 coated graphite spheres at stage III is largely attributed to the oxidation of the graphite spheres within the coating. It was therefore suggested that during this process, a certain number of cracks are produced in the coating and its surface oxide layer, and the graphite sphere within the coating would be rapidly oxidized. Besides the difference in CTE between the oxide layer and the coating, the escape of residual salt at stage I could be another vital factor in the formation of cracks on the coating surface. At this stage, the coating would quickly fail, and the coating would lose...
its oxidation resistance.

During the oxidation, the oxidation of TSC, TiC, Si and SiC would increase the weight of the coated samples, while it failed to offset the decrease in the weight of the samples. There are two reasons for the deterioration of the sample weight, one is the volatilization of residual salt in the coating. Though the coating was repeatedly cleaned after the preparation, a certain amount of residual salt remained in the coating. Since the oxidation is performed at a high temperature of 1500°C, higher than the melting point of the salt, the salt gradually evaporated, thereby reducing the weight of the sample. The other is that the coating prepared in the study is not dense, and there are a certain number of defects in the coating, so the oxidizing gas could diffuse to the inner graphite spheres, thereby causing the weight of the sample to decrease. The reasons for the defects in the coating are presented below. First, the molten salt technique was adopted in Ar atmosphere, and the presence of the atmosphere caused the prepared coating to be relatively loose and porous. The second is the intrinsic defect of the molten salt technique. When the coating was being formed, the Ti element should diffuse into the loose SiC layer under the action of the molten salt, so the salt took up considerable space in the coating. In the cleaning process after the coating preparation, the salt in the coating was gradually dissolved in the water. After the salt is dissolved, numerous holes would be generated in the coating, and the volatilization of the residual salt at the early stage of the oxidation would produce more defects in the coating. Thus, the coating prepared by the molten salt technique is not dense. In addition, due to the difference in CTE between different phases in the coating, more cracks are generated in the coating. Accordingly, the oxidizing gas could enter the coating through the mentioned cracks and holes, and oxidize with the graphite sphere.

Thus, the mass loss of SiC/Si-TiC-Ti3SiC2 composite coating coated graphite spheres at the early stage of the oxidation is mainly caused by the volatilization of residual salts. During the oxidation, TSC, TiC, Si and SiC phases are gradually oxidized to generate TiO2 and SiO2, which remedied some defects in the coating, so the intrusion of oxidizing gas could be effectively blocked, and the weight of the coated samples could increase. Accordingly, at the second stage of the oxidation, the mass loss rate of the coating-coated graphite sphere gradually decreased. The difference in CTE between the oxide layer and the coating, as well as the volatilization of the residual salt in the early stage of the oxidation, led to the generation of increasing cracks and pores in the coating, and the oxidizing gas is more easily diffused into the coating until the coating completely failed. Thus, in the third stage of the oxidation, after 40 h of the oxidation at 1500°C, the mass loss of the coated graphite spheres increased sharply and the coating failed.

4. Conclusions
A Ti3SiC2-TiC-Si composite coating was synthesized with the molten salt technique on the surface of SiC-coated graphite spheres of the HTR fuel element with different Ti contents. The microstructure, composition, and anti-oxidation properties of the mentioned composite coatings were investigated. The composite coating consisted of an internal transition layer, an intermediate layer of SiC and a Ti-rich outermost layer. The coating composition comprised TSC, SiC, and TiC when the addition of Ti is 0.6 g during the coating preparation; while when the content of Ti are 1.2 g and 2.4 g, the coating consists of TSC, SiC, TiC, and Si. The oxidation tests revealed that the T1 coated graphite spheres showed the optimal oxidation resistance, and the weight reduction of the coated graphite spheres is only 0.33% after the oxidation in static air at 1773 K for 50 h. The T3-coated graphite spheres exhibited the worst anti-oxidation property, and the anti-oxidation property exhibited by T2 coated graphite spheres is in the middle. The weight variation curves of all the coated graphite sphere displayed a parabolic dependence initially, while the curve exhibited a linear correlation at longer times. The mentioned results suggested Ti-based composites coating as a type of anti-oxidation coating system worth studying.

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