Palladium interaction with silicon carbide

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\textbf{A B S T R A C T}

In this work the palladium interaction with silicon carbide is investigated by means of complementary analytical techniques such as thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Thermoscans were carried out on pellets of palladium, $\alpha$-SiC and $\beta$-SiC high purity powders in the temperature range comprised between 293 K and 1773 K, in order to study the effect of temperature on the palladium-silicon carbide reaction.

Thermoscans of $\alpha$-SiC pellets containing 5 at.\%Pd show that during differential calorimetry scans three exothermic peaks occurred at 773 K, 1144 K and 1615 K, while thermoscans of $\beta$-SiC pellets containing 3 at.\%Pd and 5 at.\%Pd do not show peaks. For the pellet $\alpha$-SiC--5 at.\%Pd XRD spectra reveal that the first peak is associated with the formation of Pd$_2$Si and SiO$_2$ phases, while the second peak and the third peak are correlated with the formation of Pd$_3$Si phase and the active oxidation of silicon carbide respectively. Thermogravimetry scans show weight gain and weight loss peaks due to the SiO$_2$ phase formation and the active oxidation. Additionally XPS fittings reveal the development of SiC$_x$O$_y$ phase during the first exothermic peak up to the temperature of 873 K. The experimental data reveals that alpha silicon carbide is attacked by palladium at lower temperatures than beta silicon carbide and the reaction mechanism between silicon carbide and palladium is strongly affected by silicon carbide oxidation.

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1. Introduction

Silicon carbide ceramic material has many applications in a wide range of industries due to its attractive combination of properties such as wide band gap [1], large electron mobility [2], high thermal conductivity, chemical inertness and low neutron absorption cross section. In the nuclear industry it is used as coating in tri-structural isotropic (TRISO) fuel [3,4] and it is seen as alternative to zirconium alloys for a new generation of nuclear fuel cladding.

Zirconium alloys have been used as fuel cladding material for water-cooled reactors for over 50 years. However, the recent Fukushima accident underlines the vulnerability of such alloys under severe accident conditions, when gross oxidation can result in the generation of large quantities of hydrogen, giving rise to the risk of an explosion. Ceramic SiC–SiC composite cladings offer significantly improved oxidation resistance and the absence of hydrogen generation at high temperatures [5].

In addition in nuclear applications silicon carbide provides an effective barrier to the diffusion of gaseous and metallic fission products [6–8]. Therefore, the integrity of silicon carbide material is crucial to the safety and the performance of nuclear power plants.

However the integrity of silicon carbide layer is compromised by palladium fission products that are formed by the fission of nuclear fuel. Palladium unlike other fission products such as rare-earth elements, causes degradation of the silicon carbide [9,10]. Therefore it is important to understand the silicon carbide interaction with palladium.

In this paper the effect of temperature on the palladium–silicon carbide reaction is analysed through thermal analysis in a temperature range comprised between 293 K and 1773 K in order to better explain the influence of the temperature on the palladium attack of silicon carbide. The studied temperature spectrum covers the operating temperature of diverse nuclear power reactors such as boiling water reactors (BWR) and very high temperature reactors (VHTR). This research work studies the palladium interaction with alpha silicon carbide and beta silicon carbide. Silicon carbide is seen as an alternative to zirconium alloys for a new generation of nuclear fuel cladding [11]. In addition chemical vapor deposited (CVD) beta silicon carbide is used as coating in tri-structural isotropic (TRISO) nuclear fuel.
Thermogravimetry and differential scanning calorimetry studies are coupled with X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS) in order to characterize the phases present in the specimens.

2. Experimental work

High purity powders of alpha silicon carbide (Goodfellow, mean particle size <1 μm, 99.9% trace metal basis), beta silicon carbide (Alpha Aesar, mean particle size 1 μm, 99.8% trace metal basis) and palladium (Sigma-Aldrich, mean particle size <1 μm, <99.9% and trace metal basis) were used to produce pellets with the procedure described in the following paragraph.

A powder mixture containing 95 at.% alpha SiC and 5 at.%Pd, a powder mixture containing 95 at.% beta SiC and 5 at.%Pd and a powder mixture containing 97 at.% beta SiC and 3 at.%Pd were blended for 12 h in an automatic machine. Subsequently the obtained mixtures were uniaxially cold-pressed under a pressure 0.98 MPa in hard steel dies using a hydraulic press. The formed compacts had a cylindrical shape with a diameter of 5 mm.

NETZSCH STA 449 F1 thermal analyser was used to perform thermogravimetry (TG) and differential scanning calorimetry (DSC) studies. Thermoscans were conducted in 20 ml/min argon flow from 293 K to 1773 K at a temperature increment of 5 K/min. X-ray diffraction (XRD) measurements were performed using a PANalytical X’Pert MPD X-ray diffractometer in order to identify the phase composition of the specimens before and after thermoscans.

The temperature and current were 40 kV and 40 mA, respectively. The tube anode was Cu Kα1 (λ = 0.154 06 nm). The XRD data were analysed using PANalytical X’Pert HighScore Plus software.

XPS was performed in a Kratos Axis Ultra instrument (base pressure ≈ 2 × 10−9 mbar) equipped with a load lock system for sample introduction. Monochromated Al Kα X-rays (hv = 1486.6 eV, Δhv ≈ 0.6 eV) were employed as photon source. Emitted photoelectrons were collected using a 165 mm hemispherical energy analyser incorporating a delay line detection system (analysis area ≈ 0.3 mm × 0.7 mm). Data were acquired at analyser pass energy of 80 eV for wide energy scan overview spectra, and 20 eV for short higher energy resolution spectra of specific core levels. Two photoelectron emission angles (θ), namely 0° (emission along the surface normal) and 50°, were utilised during the measurements. The angle subtended by the X-ray beam and the entrance lens of the analyser was 60°, and the sample holder’s rotation axis was perpendicular to the plane containing these two elements. To prevent any vertical differential charging due to the presence of oxide surface films, samples were mounted using vacuum compatible double-sided adhesive tape. Charge accumulation during data collection was compensated by exposing samples to a flood of low energy electrons (≤ 3 eV). Curve fitting was carried out using CasaXPS software package.

3. Results

3.1. Thermogravimetry and differential scanning calorimetry (TG–DSC)

Thermoscans were carried out on pure silicon carbide powders and mixed silicon carbide–palladium powders in order to study the effect of temperature on the silicon-carbide palladium reaction. During the thermoscans simultaneous thermogravimetry (TG) and differential standard calorimetry (DSC) analysis were undertaken. All the measurements were carried out in argon gas in the temperature range comprised between 293 K and 1773 K.

Figs. 1 and 2 reveal the dynamical TG curves and DSC curves of pure α-SiC and α-SiC–5 at.%Pd pellets respectively.

In the TG curve the pure silicon carbide specimen did not change its weight up to the temperature of 1638 K. After reaching this temperature the specimen’s weight slowly decreased. The overall weight loss was of the 0.42%. The DSC curve of the pure silicon carbide specimen revealed an exothermic peak [12] in the temperature range comprised between approximately 923 K and 1263 K.

Conversely in the TG curve of the α-SiC–5 at.%Pd pellet, the specimen started to gain weight at about 723 K until the final temperature of 1408 K, after this temperature the specimen weight decreased. The overall weight loss was of 2.18%.

The DSC curve of the α-SiC–5 at.%Pd pellet showed three exothermic peaks, which indicate the presence of three reaction stages. The first peak was in the temperature range comprised between 673 K and 873 K, while the second and third peak occurred from 1063 K to 1253 K and from 1357 K to 1773 K respectively. Buoyance effect is observed at the beginning of the TG and the DSC curves in Figs. 1 and 2.

Fig. 3 shows the DSC curve and the TG curve of β-SiC–3 at.%Pd pellet. During differential scanning calorimetry analysis the behaviour of β-SiC–3 at.%Pd pellet was different from the behaviour of α-SiC–5 at.%Pd pellet.

For the β-SiC–3 at.%Pd pellet the DSC scan did not present peaks. The same behaviour was observed in DSC scans of β-SiC–5 at.%Pd pellets. This indicates the absence of palladium interaction with silicon carbide at lower temperatures.

On the other hand the TG curve of the β-SiC–3 at.%Pd pellet was similar to the TG curve of α-SiC–3 at.%Pd pellet. The pellet weight starts to increase at about 760 K until the final temperature of 1418 K, after this temperature the specimen weight decreased. The TG scan registered an overall weight loss of 2.67%.

3.2. X-ray diffraction (XRD)

Given the results obtained through thermal analysis, phases developed in pure alpha silicon carbide and palladium during the heat treatment were studied through X-ray diffraction (XRD), PANalytical X’Pert HighScore Plus software was used to study the diffraction patterns.

Letters A, B, C, D, E in the DSC plot shown in Fig. 2 indicate the temperatures at which the XRD analysis were carried out. XRD spectra of specimens before heat-treatment revealed that the alpha silicon carbide powders were moissanite 6H and 4H polytypes.

The phase development due to the silicon carbide palladium reaction in the temperature range comprised between 293 K and 1773 K was checked by XRD studies. Fig. 4 displays XRD spectra before and after the first reaction stages of SiC/Pd compacts containing 5 at.%Pd.

XRD spectra were carried out at the temperatures indicated by the points A and B in Fig. 2, which are 623 K and 873 K respectively. Fig. 5 shows XRD spectra of specimens annealed at temperatures, which are before and after second reaction stage. These temperatures are 1063 K and 1253 K and are indicated in Fig. 2 with the letters C and D.

Fig. 6 shows XRD spectra of α-SiC–5 at.%Pd specimens after annealing up to 1773 K at a temperature increment of 5 K/min. The XRD spectra corresponding to the temperature of 1773 K show that at the end of the heat treatment SiO2, Pd3Si phases were present in the palladium silicon carbide pellet.

According to estimates made analysing the XRD spectra through PANalytical X’Pert HighScore Plus software, in the first reaction stage occurring from 623 K to 873 K the phase Pd3Si phase was formed.
All the Pd$_3$Si phase was converted in Pd$_2$Si phase during the second reaction stage that occurred in the temperature range comprised between 1063 K and 1253 K. XRD spectra do not detect the presence of Pd$_3$Si phase in specimens annealed to temperatures comprised between 1063 K and 1253 K.

Fig. 1. Differential scanning calorimetry (DSC) and thermogravimetry (TG) scans of $\alpha$-SiC compressed powders carried out in argon atmosphere at 5 K/min in the temperature range comprised between 293 K and 1773 K.

Fig. 2. Differential scanning calorimetry (DSC) and thermogravimetry (TG) scans of $\alpha$-SiC compressed powders carried out in argon atmosphere at 5 K/min in the temperature range comprised between 293 K at 1773 K. The letters A, B, C, D, E indicate the temperatures in which XRD spectra were carried out.

Fig. 3. Differential scanning calorimetry (DSC) and thermogravimetry (TG) scans of $\beta$-SiC compressed powders carried out in argon atmosphere at 5 K/min in the temperature range comprised between 293 K and 1773 K.
Fig. 4. XRD spectra at diverse temperatures showing the phase developed in the SiC–5 at.%Pd powders pellets after annealing up to 673 K and 873 K. The temperatures of 673 K and 873 K are indicated in Fig. 2 with the letters A and B respectively.

Fig. 5. XRD spectra at diverse temperatures showing the phase developed in the SiC–5 at.%Pd powders pellets after annealing up to 1063 K and 1253 K. The temperatures of 1063 K and 1253 K are indicated in Fig. 2 with the letters C and D respectively.

Fig. 6. XRD spectrum showing the phase developed in the SiC–5 at.%Pd powders pellets after annealing up to 1723 K. The temperature of 1723 K is indicated in Fig. 2 with the letter E.
higher than 1253 K. The XRD spectrum carried out at the final temperature show the presence of Pd$_2$Si and SiO$_2$.

### 3.3. X-ray photoelectron spectroscopy (XPS)

In order to investigate the changes in the SiC and Pd/SiC surface in detail, the chemical state of each element present in the system (i.e., C, Si, Pd) was studied. Curve fitting was carried out using the software CasaXPS. All the spectra were charge compensated to C 1s at 285 eV representing the C–C bond.

**Fig. 7** shows Si 2p XPS and Pd 3d detail spectra of SiC–5 at.%Pd specimens annealed up to the final temperatures of 623 K, 751 K, 873 K and 1253 K.

In order to better understand the Si 2p spectra, a curve fitting analysis was carried out. The spectra envelopes are fitted by Gaussian–Lorentzian mixture at 100.8 eV, 103.6 eV, 102 eV, 100.4 eV, 100.5 eV and 100 eV, which are assigned to the chemical states of SiC, SiO$_2$, SiO$_x$C$_y$Pd$_3$Si, Pd$_2$Si and free silicon bonds [13,14]. Respective FWHM are: 1.4, 1.1, 2, 1.15.

The results indicate that the silicon on the top surface oxidizes forming SiO$_x$. A minor formation of silicon oxycarbides (SiC$_x$O$_y$) was found on SiC surfaces and at the SiC/SiO$_2$ interfaces. The intensity of the SiC$_x$O$_y$ peak increases with temperature raise during the first exothermic peak. At the temperature of 1253 K the SiC$_x$O$_y$ peak disappear while the intensity of SiO$_2$ peak increases because at temperatures higher that 873 K the SiC$_x$O$_y$ phase dissociates forming SiO$_2$.

In the analysed temperature range a very thin layer of SiO$_x$ formed on the top of the surface and a small part of the palladium formed palladium silicides (Pd$_x$Si) at the surface [15–17]. The Pd$_3$Si phase is detected at the temperatures of 623 K, 751 K, 873 K, while Pd$_2$Si phase is detected at 1253 K.

The formation of Si–Pd bonds at the Pd/SiC interface is in good agreement with the other experimental data presented in the previous paragraphs.

The chemical state of Pd atoms on the surface of SiC–Pd pellets was determined through XPS.

The chemical states of both the surface products of the annealed samples are analysed by deconvolution of the Pd 3d3/2 and Pd 3d5/2 spectra.

In the specimen annealed up to the temperature of 623 K the palladium is present in the form of pure metal state. The metal palladium is fitted by a major Gaussian–Lorentzian combination at 335.9 eV (FWHM 1.8) and a minor Gaussian–Lorentzian combination at 341 eV (FWHM 19). Palladium oxides (PdO$_x$) bonds are detected at 623 K with a major Gaussian–Lorentzian combination at 336.6 eV (FWHM 1) and a minor Gaussian–Lorentzian combination at 342.25 eV (FWHM 1.9).

Palladium oxides (PdO$_x$) bonds are detected at 623 K with a major Gaussian–Lorentzian combination at 336.6 eV (FWHM 1) and a minor Gaussian–Lorentzian combination at 342.25 eV (FWHM 1.4).

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**Fig. 7.** Normalised the Pd 3d3/2, Pd 3d5/2 XPS and Si 2p 5/2 XPS of specimens annealed up to the following temperatures 623 K, 873 K, 1063 K and 1253 K. Solid line shows the curve. The dashed lines show the fitting component: (a) Pd 3d3/2 and Pd 3d5/2. The peaks are 335.9 eV (FWHM 1.8) and 341 eV (FWHM 1.9) for Pd, 336.6 eV (FWHM 1) and 342.25 eV (FWHM 1.4) for PdO$_x$, 336.2 eV (FWHM 1) for Pd$_3$Si, 336.7 eV (FWHM 1.8) for SiC$_x$O$_y$, 336.7 eV (FWHM 2) for Pd$_2$Si; (b) Si 2p. The peaks at 100.8 eV, 103.6 eV, 102 eV, 100.4 eV, 100.5 eV and 100 eV, represent the SiC, SiO$_2$, SiO$_x$C$_y$Pd$_3$Si, Pd$_2$Si and free silicon bonds. Respective FWHM are: 1.4, 1.1, 2, 1.15.
For specimens annealed at the temperatures of 752 K and 873 K, which are in the temperature range of the first reaction stage, the palladium spectrum can be fitted by a major Gaussian–Lorentzian combination at 336.2 eV (FWHM 1.2) and a minor Gaussian–Lorentzian combination at 341.7 eV (FWHM 1.5). The binding energy difference between 3d3/2 and 3d5/2 peaks is about 5.5 eV instead of the 5.1 eV for the pure metal state. The data confirm the presence of the Pd3Si phase [13,14].

Conversely for specimens annealed up to the temperature of 1253 K, the Pd 3d5/2 spectrum can be fitted by a major Gaussian–Lorentzian combination at 336.7 eV (FWHM 1.5) and a minor Gaussian–Lorentzian combination at 342.3 eV (FWHM 2). The binding energy difference between 3d3/2 and 3d5/2 peaks is about 5.5 eV. The data confirm the presence of the Pd2Si phase [13,14].

Fig. 8 shows C 1s XPS and O 2s detail spectra of SiC–5 at.%Pd specimens annealed up to the final temperatures of 623 K, 751 K, 873 K and 1253 K. In order to understand the chemical bonding at the Pd/SiC interface, C 1s XPS spectra of as-received and structurally disordered SiC, as well as Pd/SiC interface were studied. A quantitative analysis of the C 1s XPS spectra shows that at least three Gaussian–Lorentzian combinations at 282.9 eV, 283.7 eV and 285 eV [13,14] are necessary to describe the complete set of spectra corresponding to C–Si, SiOxCy and C–C bonds. Respective FWHM are: 1.3, 1.8, 1. It is obvious that for these spectra carbon was also present in more than one chemical environment. A main peak was observed at the binding energy of 285 eV, the peak is associated with C–C bonds present in surface contaminants. The peak increases in intensity at temperatures above 873 K due to the palladium attack of silicon carbide that causes the formation of a graphite layer on the top of the surface or free carbon. In contrast, the intensity of the component SiCyt decreases dramatically at higher temperatures.

For the O 1s XPS spectra four Gaussian–Lorentzian combinations at 532.9 eV, 532.2 eV and 533.8 eV representing SiOx/Si, SiOxCy, SiO2 are used to fit the XPS spectra at the temperatures of the 623 K, 751 K, 873 K and 1253 K [13,14]. Respective FWHM are: 1.5, 1.2, 1.2. For the specimen annealed at the temperature of 623 K the peak at 530.4 eV indicates the presence of PdO.

4. Discussion

In the initial part of this work thermo-gravimetric, differential scanning calorimetry experiments studied the palladium interaction with alpha silicon carbide and beta silicon carbide. Differential thermal analysis carried out on α-SiC–5 at.%Pd, β-SiC–5 at.%Pd and β-SiC–3 at.%Pd pellets revealed that α-SiC powders are attached by palladium at lower temperatures than β-SiC powders. Differential thermal scans of α-SiC–5 at.%Pd pellet show
that $\text{Pd}_3\text{Si}$ are formed in the temperature range comprised between 673 K and 873 K.

Conversely thermogravimetry measurements of $\alpha$-SiC–5 at.%Pd pellet were similar to the thermogravimetry measurements of $\beta$-SiC–5 at.%Pd and $\beta$-SiC–3 at.%Pd.

Thermogravimetry scans recorded a weight gain in the temperature range comprised between 723 K and 1408 K associated to the passive oxidation of silicon carbide followed by active oxidation of silicon carbide.

Beta silicon carbide and alpha silicon carbide behave in a different way in the analysed temperature range. DSC scans of palladium beta silicon carbide do not show the exothermic peaks observed in alpha silicon carbide scans. Therefore alpha silicon carbide impurities in beta silicon carbide matrix may accelerate the palladium silicon carbide reaction.

In light of these results the reaction between alpha silicon carbide and palladium was studied through X-ray photoelectron spectroscopy and X-ray diffraction.

The results showed that $\text{Pd}_3\text{Si}$ and $\text{SiO}_x$ phases were formed at different temperatures [18,19]. Differential scanning calorimetry and X-ray diffraction analysis show that in the temperature range comprised between 623 K and 1023 K $\text{Pd}_3\text{Si}$ were formed, while in the temperature range comprised between 1023 K and 1253 K $\text{Pd}_2\text{Si}$ were formed.

In order to clarify the mechanism of the palladium attack of alpha silicon carbide that can be used as nuclear fuel cladding, thermodynamic analysis on the SiC–Pd system was carried out and the thermodynamic stability of palladium silicides was compared to that of $\text{SiO}_2(s)$ and $\text{SiO}(g)$ [20].

Four chemical reactions occurred in the analysed temperature range:

\begin{align*}
\text{SiC} + 2\text{Pd} & \rightarrow \text{Pd}_3\text{Si} + \text{C} & (1.1) \\
\text{SiC} + 3\text{Pd} & \rightarrow \text{Pd}_4\text{Si} + \text{C} & (1.2) \\
\text{SiC} + 1.5\text{O}_2 & \rightarrow \text{SiO}_2 + \text{CO} & (1.3) \\
\text{SiC} + \text{O}_2 & \rightarrow \text{SiO} + \text{C} & (1.4)
\end{align*}

Figs. 9 and 10 present Pd–Si–C phase diagrams at the temperatures of 973 K and 1273 K, which are the final temperatures of the first reaction stage and the second reaction stage respectively [21].

An analysis of the Pd–Si–C phase diagrams reveals that the formation of $\text{Pd}_3\text{Si}$ is thermodynamically favoured at the end of each reaction stage. Thus, the XRD results, at temperatures lower than 1253 K, are in contrast with thermodynamic data.

However, previous research work revealed that $\text{Pd}_3\text{Si}$ phase is generated in specimens annealed at temperatures around 698 K, while contrasting results were observed in specimens annealed at temperature higher than 1073 K.

After annealing at temperature higher than 1073 K some specimens presented $\text{Pd}_3\text{Si}$ and $\text{Pd}_2\text{Si}$ phases while other specimens presented only $\text{Pd}_2\text{Si}$ phase [22–24].

Conversely, for $\text{SiO}_2$ and $\text{SiO}(g)$, the thermodynamic stability was analysed calculating the Gibbs free energy for the reactions 1.3 and 1.4 respectively.

The Gibbs free energy change in the reaction were calculated by the approximation:

$$
\Delta G = \Delta H - T \Delta S
$$

where $\Delta G$ is the difference between products and reactants of the Gibbs free energy at the analysed temperature, $\Delta H$ is the difference in standard enthalpies at the analysed temperature and $\Delta S$ is the difference in entropies at analysed temperature.

The thermodynamic values for $\text{SiO}_2(s)$ and $\text{SiO}(g)$ were taken from JANAF Thermochemical Tables [25]. The Gibbs free energy changes in Reaction 1.3 and 1.4 are given in Table 1.

The thermodynamic calculations suggest that during the two exothermic peaks the Pd silicides were formed together with silicon oxides. The thermodynamic data show that the chemical reactions that lead to the formation of silicon dioxide and silicon oxide have opposite trends. The formation of silicon dioxide is favoured at lower temperatures, while the formation of silicon oxide is favoured at higher temperatures [26].

| Temperature (K) | $\Delta G$ of $\text{SiO}_2$ (kJ/mole) | $\Delta G$ of $\text{SiO}$ (kJ/mole) |
|----------------|---------------------------------|---------------------------------|
| 723            | −889.1                          | −274.22                         |
| 1408           | −833.57                         | −393.15                         |

Fig. 9. Isothermal section of Pd–Si–C system at different temperature at 973 K [18].

Fig. 10. Isothermal section of Pd–Si–C system at different temperature at 1273 K [18].
The data confirm the experimental results in which weight loss due to the active oxidation of silicon carbide is observed at temperatures higher than 1408 K.

Additional results provided by the X-ray photoelectron spectroscopy analysis show the presence of SiO$_x$C$_y$ bonds. The SiO$_x$C$_y$ phase was mainly present during the first reaction stage. XPS profiles indicated a build-up of silicon oxide and unreacted carbon as the temperature increases due to the dissociation of the SiO$_x$C$_y$ phase.

The specimen annealed up to the final temperature of 1723 K showed a graphite layer at the top of its surface.

The contrasting results on the formation of the Pd$_3$Si and Pd$_2$Si phases reported in previous papers can be explained with the development of the SiC$_x$O$_y$ phase. In the first reaction stage palladium atoms might act as catalyst to break Si–C or Si–Si bonds in favour of forming other Si species such as SiO$_x$C$_y$ and Pd$_3$Si. When the temperature increases the SiC$_x$O$_y$ dissociates forming SiO$_2$ and graphite, while the Pd$_3$Si phase is converted in Pd$_2$Si phase.

5. Conclusions

Thermal analysis studies show that alpha silicon carbide is attached by palladium at lower temperatures than beta silicon carbide.

For palladium interaction with alpha silicon carbide three exothermic reaction stages are observed in the temperature range comprised between 293 K and 1773 K. During the first reaction stage, occurring from 673 K to 873 K, palladium interacted with silicon carbide forming Pd$_3$Si phase, while in the second reaction stage from 1063 K to 1253 K Pd$_3$Si phase disappeared forming Pd$_2$Si phase. The third exothermic reaction from 1357 K to 1773 K was due to the active oxidation of silicon carbide.

XPS and XRD measurements revealed that a SiO$_x$C$_y$ phase was created together with Pd$_3$Si phase. Comparison of the present results with previous studies suggests that the oxidation of silicon carbide and the formation of SiC$_x$O$_y$ play key a role in the palladium silicon carbide interaction.

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References

[1] G.A. Slack, J. Appl. Phys. 35 (1964) 3460.
[2] D.L. Barret, R.B. Campbell, J. Appl. Phys. (1967) 38.
[3] L.H. Ford, N.S. Hibbert, D.G. Martin, J. Nucl. Mater. 45 (139) (1973) 149.
[4] L.I. Sneed, T. Nozawa, Y. Katoh, T. Byun, S. Kondo, D.A. Petti, J. Nucl. Mater. 371 (329) (2007) 377.
[5] S.J. Zookie, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Sneed, J. Nucl. Mater. 448 (2014) 374–379.
[6] K. Minato, K. Fukuda, A. Ishikawa, N. Mita, J. Nucl. Mater. 246 (215) (1997) 222.
[7] R.J. Lauf, T.B. Lindemer, R.L. Pearson, J. Nucl. Mater. 120 (1964) 30.
[8] K. Minato, T. Ogawa, K. Fukuda, H. Sekino, H. Miyanishi, S. Kado, I. Takahashi, J. Nucl. Mater. 202 (47) (1991) 53.
[9] K. Minato, T. Ogawa, S. Kashimura, K. Fukuda, M. Shimizu, Y. Tayama, I. Takahashi, J. Nucl. Mater. 172 (184) (1990) 196.
[10] M. Barrachin, R. Dubourd, S. De Groot, M.P. Kissane, K. Bakker, J. Nucl. Mater. 415 (2011) 104–116.
[11] L. Hallstadius, S. Johnson, E. Lahoda, Prog. Nucl. Energy 57 (2012) 71–76.
[12] JAERI-M-82-098 Report.
[13] NIST tables <http://srdata.nist.gov/xps/).
[14] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, 1979.
[15] S. Saliman, M. Delfino, J. Appl. Phys. 70 (1991) 3970.
[16] K. Kishi, S. Ikeda, Bull. Chem. Soc. Jpn. 46 (1973) 341.
[17] F.P.J.M. Kerkhof, J.A. Moulijn, A. Heeres, J. Electron Spectrosc. Related Phenomena 14 (1978) 453.
[18] K. Bhanumurthy, R. Schmid-Fetzer, Composites: Part A 32 (569) (2001) 574.
[19] E. Lopez-Honorato, K. Fu, P.J. Meadows, J. Tan, P. Xiao, J. Am. Ceram. Soc. 93 (4135) (2010) 4141.
[20] E. Proksch, A. Strigl, H. Nabielek, J. Nucl. Mater. 136 (129) (1985) 135.
[21] Z. D. Cao, Y. Yang, Y. Liu, Intermetallics 14 (560) (2006) 569.
[22] L. Chen, C.W. Hunter, P.G. Neudeck, C. Bansal, J.B. Peit, D. Knight, J. Vac. Sci. Technol. A 15 (1997) 1228.
[23] S. Roy, S. Basu, C. Jacob, A.K. Tyagi, Appl. Surf. Sci. 202 (73) (2002) 79.
[24] H. Suzuki, T. Iseki, T. Imanaka, J. Nucl. Sci. Technol. 14 (438) (1977) 442.
[25] M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data 14 (Suppl) (1985) 1.
[26] F. Proksch, A. Strigl, H. Nabielek, J. Nucl. Mater. 136 (129) (1985) 135.