DFT STUDIES ON THE FORMATION OF CaCO$_3$ DEPOSITIONS ONTO CRISTOBALITE, DIAMOND AND TITANIUM CARBIDE SURFACES

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ABSTRACT

Fouling caused by inversely soluble salts, like CaCO$_3$, is a general problem on heat transfer surfaces. Carbonate depositions are typically cleanable with acids, but costs of energy losses, operation and maintenance are significant. In this study, formation of CaCO$_3$ depositions was investigated on cristobalite, diamond and titanium carbide surfaces. The aim of the study was to clarify the detailed mechanisms of crystallization fouling during the initiation on crystalline phases existing in materials used as coatings (SiO$_2$, TiCN, DLC), and to compare the results to the fouling mechanism of stainless steel (Cr$_2$O$_3$).

In experimental studies of fouling, detailed mechanisms and description of sterical and electrostatic factors of surfaces are often very much simplified. In this work, molecular modelling was used to describe surface structures and to investigate the effect of process fluid (water) on the structures. The adsorption of water can be molecular or dissociative. During the dissociative adsorption, hydroxylated surface structures are formed. The existence of hydroxyl groups on the surfaces has an effect on the fouling mechanism. First, the dissociation probability of water on different surfaces was determined according to the adsorption mechanism and energies, and then the attachment of CaCO$_3$ onto optimized and hydroxylated surfaces was investigated. As a result, the formation mechanism with detailed intermediate steps of CaCO$_3$ deposition was obtained. The fouling takes place via hydrogen carbonate intermediates, but the final deposition structure was found to vary between surfaces.

INTRODUCTION

Fouling of heat transfer surfaces is a serious problem, and depositions of inversely soluble salts, like calcium carbonate (CaCO$_3$), are common in industrial processes. Carbonate depositions are typically cleanable with acids, but costs of energy losses, operation and maintenance are significant. Even if numerous cleaning and fouling inhibition chemicals are available on the market, the use of many of these is restricted in EU or will be prohibited by tightening environmental, health and safety legislation. Novel non-fouling materials and new heat exchanger geometries would give sustainable solution to industry in order to mitigate fouling.
layers (Pießlinger-Schweiger, 2005). However, the oxidization conditions affect significantly the thickness and composition of oxide layers. In addition to chromium oxides, there are manganese and iron oxides with different crystal structures on the outermost layer of stainless steel (Iordanova et al., 1998). In spite of the good corrosion properties, stainless steel is still exposed to sorption of ionic compounds. In order to mitigate the deposition formation and extend the operation period of the heat exchanger, coating materials are developed.

The possibility to use siloxane (SiO$_2$), titanium carbonitride (TiCN) and diamond like carbon (DLC) materials as coatings was investigated in this molecular modelling study. Simplified structures of the coatings were used: cristobalite structure of silicon dioxide (SiO$_2$), diamond and titanium carbide (TiC). Of SiO$_2$ structures, cristobalite is a high-temperature polymorph of quartz. Diamond was selected to describe in a simplified way the surface structure of amorphous DLC. However, the surface roughness cannot be taken into account in this type of modelling. The results obtained for these coatings were compared to those of dichromium trioxide (Cr$_2$O$_3$), which was used as a model structure for stainless steel. The investigated coatings were selected based on industrial interest in the aim of eliminating fouling caused by inversely soluble salts, like CaCO$_3$, on heat transfer surfaces. The objective of the study was to clarify the detailed mechanisms of crystallization fouling during the initiation on crystalline phases existing in materials used as coatings. The results were compared to the fouling mechanism of stainless steel.

**METHODS**

Methods based on the density functional theory (DFT) were used to investigate the crystal and surface structures of materials intended to be used as coatings of stainless steel heat transfer surfaces. The selected coatings were SiO$_2$ (cristobalite), diamond and TiC. Because water of the process fluids can affect the surface structures and the initiation stage of deposition formation on surfaces, the adsorption mechanism of water onto the surfaces was first investigated. The adsorption of calcium (Ca$^{2+}$) and carbonate (CO$_3^{2-}$) ions onto surfaces and the formation mechanism of CaCO$_3$ depositions were then determined. All the calculations were performed with the CASTEP (CAMbridge Serial Total Energy Package) code implemented into Materials Studio versions 4.1 (Accelrys, 2006), 4.2 (Accelrys, 2007), 4.3 (Accelrys, 2008a) and 4.3.1 (Accelrys, 2008b). The modelling is based on solving the total electronic energy and overall electronic density distribution in order to define the energetically stable structures for coatings and different adsorbates (Leach, 2001).

During the geometry optimization of the crystal and surface structures of coatings, and adsorption studies of water and Ca$^{2+}$ and CO$_3^{2-}$ ions onto the surfaces, the exchange-correlation was described with the generalized gradient approximation GGA-PBE. As a compromise between the accuracy and computational time, the ultrasoft pseudopotentials were used for each element. In the potential of titanium, the semicore states were treated as a part of the core. The used potentials were C_00PBE.usp for carbon, Ca_OOPBE.usp for calcium, H_00.usp for hydrogen, O_soft00.usp for oxygen, Si_soft00.usp for silicon, and Ti_00PBE.uspcc for titanium. The kinetic cut-off energy for a plane wave expansion of the wave function was 280 eV. The morphology of the coatings was predicted by using the BFDH (Bravais-Friedel Donnay-Harker) method.

The optimized structures were used in order to calculate energy values for the formation reaction of CaCO$_3$ depositions. The energies were calculated from the single-point energies of the ions and the surface structures with and without the adsorbed ions. The calculations were performed using the GGA-RPBE exchange-correlation, and the kinetic cut-off energy was 330 eV.

**RESULTS AND DISCUSSION**

**Crystal Structure of the Coatings**

The basic assumption of the research was that the fouling properties of different coatings depend on the atomic layered structure of the coatings. In order to investigate the surface structures, the crystal structures of the coatings have to be known. The starting point for the study has been the XRD determined crystal structures of SiO$_2$ (a = b = c = 716.0 pm) and diamond (a = b = c = 355.6 pm) with symmetry Fd-3m (Accelrys, 2006), and the crystal structure of TiC (a = b = c = 432.8 pm) with symmetry Fm-3m (Christensen, 1978).

In order to perform molecular modelling studies for the coatings, the lattice parameters of SiO$_2$, diamond and TiC were calculated. According to the density functional calculations, the lattice parameters of the energetically stable SiO$_2$, diamond and TiC are a = b = c = 692.4 pm, a = b = c = 357.4 pm and a = b = c = 437.1 pm, respectively (Fig. 1). Comparison to the experimental parameters indicates that the correspondence is good, the differences being only 0.5–3.3%.

![Fig. 1](image-url)  
Fig. 1 The optimized unit cells of a) TiC, b) diamond and c) SiO$_2$ (cristobalite).
Surface Structures

Based on the optimized structures, the morphologies of the coatings were predicted by the BFDH method (Fig. 2). The morphologies indicate which surfaces are the typical ones on the heat transfer surfaces. According to the BFDH prediction, there are two dominant surfaces for TiC. These are (111) and (200), the surface areas of which are 78% and 22%. For diamond and SiO$_2$, there is only one dominant surface, (111). The estimated data of the surface structures were compared to the results of the XRD measurements performed for the deposited TiCN (titanium carbide nitride) and the DLC coatings. The experimental analysis indicated that the TiCN is a crystalline coating. The dominating XRD peaks correspond the (111) and (200) crystal planes of TiC (Fig. 3a). In the case of diamond, the structure of stainless steel substrate dominates the XRD spectrum (Fig. 3b). This means that the DLC coating is mainly amorphous. However, there is a small peak (not detected in the stainless steel spectrum in Fig. 3c) which corresponds to the (111) plane of crystalline diamond. This is an indication that there is also a crystalline phase on the surface structure of DLC coating.

Based on these results, it was supposed that the dominating crystal planes of coatings have a significant role during the deposition formation. Therefore, the (111) surface of the coatings was selected for further studies.

![Fig. 2 The estimated morphology of a) TiC, and b) diamond and SiO$_2$ (cristobalite) by the BFDH method.](image)

After the basic crystal and surface structures of the coatings were determined, the surfaces predicted by BFDH were studied at atomical level. The surface structures were constructed by cleaving them from the optimized crystal structures of coatings. In order to get a more profound description of the sterical and electrostatic factors of the coating surfaces, reconstruction of the surface atom layers was taken into account. In the case of SiO$_2$ and TiC, it is possible to use the surface structures cleaved from the crystal structures, because the surface structure does not differ significantly from the crystal structures. However, in the case of diamond, the deposition conditions have to be taken into account. When the DLC coating is deposited by plasma enhanced chemical vapour deposition (PECVD) or physical vapour deposition (PVD) techniques, a hydrogen layer exists on the top-most carbon layer (Grill, 1999; Laikhtman et al., 2004). Hydrogen gives the “diamond-like” properties for materials. Therefore, the cleaved (111) surface was covered by hydrogen atoms, and the surface structure was re-optimized in order to obtain a thermodynamically stable surface, describing the real surface structure as precisely as possible (Fig. 4).

![Fig. 3 The XRD spectrum of a) TiCN, b) DLC and c) stainless steel.](image)

![Fig. 4 The (111) surface of diamond a) without and b) with the hydrogen layer on the surface.](image)
Adsorption of Water onto the Surfaces

From the point of view of potential surface reactions which take place during the deposition formation, it is important that the description of the sterical and electrostatic factors of surfaces is as realistic as possible. It has to be remembered that the coatings are exposed to the effects of the species of the process liquors. Of these species, water is the most significant adsorbate which has an effect on the properties of solid surfaces and surface. Therefore, the adsorption of water onto the coatings was investigated.

Water can adsorb onto solid surfaces as a molecule, or it can dissociate forming partially or fully hydroxylated surfaces (Cappus et al., 1993; Maurice et al., 2001; Henderson et al., 2000; Henderson, 2002; Kim et al., 2003; Asay and Kim, 2005; Ignatchenko et al., 2006; Yang and Wang, 2006; Saunders et al., 2008). Therefore, the investigated surfaces were covered by water molecules or hydroxyl groups and protons (dissociated water molecule), and the modified surface was allowed to relax a stable surface structure. The reaction energy for the dissociation of water molecules on the surfaces was then calculated.

On the (111) surface of TiC, water adsorbs onto the surface and then dissociates forming a surface hydroxyl group bonded with a titanium atom and a proton bonded with a carbon atom

\[ \text{S-H}_2\text{O} \rightarrow \text{S-OH} + \text{S-H} \] (1)

The energy released in this reaction is -2.47 eV (Fig. 5). On the (111) surface of SiO\(_2\), only one half of water molecules dissociate forming a partially hydroxylated surface

\[ 2 \text{S-H}_2\text{O} \rightarrow \text{S-H}_2\text{O} + \text{S-OH} + \text{S-H} \] (2)

The energy for this reaction is -4.78 eV, and the energy barrier for water dissociation is 0.74 eV (Fig. 6). This corresponds the values 0.3–1.1 eV reported in literature (Yang and Wang, 2006). On the (111) surface of diamond, water does not dissociate, if the adsorbed hydrogen layer exists on the surface. The adsorption energy of water is only -0.05 eV. Based on these results, it could be concluded that the adsorbed water molecules dissociate rather easily, forming the layered structure of hydroxyl groups onto the TiC and SiO\(_2\) surfaces. Therefore, the deposition formation studies were performed using the hydroxylated TiC surfaces and partially hydroxylated SiO\(_2\) surfaces. In the case of diamond, the surface structure consists of the adsorbed hydrogen layer and adsorbed water molecules. These surfaces were supposed to describe the real heat transfer surfaces as realistic as possible.

Deposition Formation on the Surfaces

In the deposition formation reaction, the interest was on chemical reactions during the initiation stage of fouling. The focus was on inversely soluble calcium carbonate (CaCO\(_3\)) salt, and its depositions on coating surfaces. The aim was to clarify the detailed mechanisms of crystallization fouling during the initiation. The study was started by determining the adsorption positions and energies of a calcium (Ca\(^{2+}\)) ion on the coating surfaces. After that a carbonate (CO\(_3^{2-}\)) ion was adsorbed onto the Ca\(^{2+}\) covered surfaces. By optimizing the positions of Ca\(^{2+}\) and CO\(_3^{2-}\) on the surfaces at the same time, the bonding geometry of CaCO\(_3\) on different surfaces was achieved. The initial structure of the ionic compound and its stability was checked by adding a water molecule onto the surface and calculating again the structure of the CaCO\(_3\) at the presence of water. As a result, the detailed reaction mechanisms were obtained for the formation of CaCO\(_3\) deposition on the (111) surfaces of TiC (Fig. 7), SiO\(_2\) (Fig. 8) and diamond (Fig. 9).

According to the calculated results, the adsorption of Ca\(^{2+}\) onto the coating surfaces depends on the coating materials. On the TiC surface, the adsorption energy is -5.18 eV, and on the diamond surface, it is -5.00 eV. On the other hand, on the SiO\(_2\) surface, the interaction of Ca\(^{2+}\) with the surface is repulsive, and adsorption is not favourable.

Comparison of the species and the intermediate steps of the reaction during the deposition formation indicated that fouling takes place via a hydrogen carbonate (HCO\(_3^-\)) intermediate on the TiC and SiO\(_2\) surfaces. Only on the diamond surface, the reaction proceeds directly to the end product, CaCO\(_3\). On all the surfaces, the role of the hydrogen bonding of water is very significant during the deposition formation. The total energies for the investigated reactions during the CaCO\(_3\) deposition on the (111) surfaces...
of TiC, SiO$_2$ and diamond are -4.74 eV, -9.33 eV and -3.31 eV, respectively.


The surface structures of stainless steel were already investigated by Puhakka et al. (2008). The uppermost layer structure of stainless steel was described using Cr$_2$O$_3$ as a model for the surface. It was supposed that the (004) surface of Cr$_2$O$_3$ corresponds the corrosion protective chromium-rich layer. When the adsorption of water was investigated, it was concluded that the dissociative adsorption is possible, but it is more presumable that water adsorbs in a molecular form. The calculated adsorption energy was very weak, only -0.06 eV. Now the formation of CaCO$_3$ deposition was investigated on the (004) surface of Cr$_2$O$_3$ with an adsorbed water layer. The results are presented in Fig. 10. The total energy for this reaction is -3.15 eV, and it is smaller than on the other investigated coating surfaces. The corresponding energy for the non-hydroxylated (10-2) surface of Cr$_2$O$_3$ is -3.00 eV (Puhakka et al., 2008). According to the calculated results, the investigated coatings can not mitigate the formation of CaCO$_3$ depositions.


of CaCO$_3$ models have been too simplified for the structural analysis. These different morphological structures were found from the deposition on the surfaces. In particular, the initiation mechanism of crystallization fouling was determined on the SiO$_2$ surface. The authors thank the research partners and funding organizations.

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CONCLUSIONS
Molecular modelling was used in studying the formation of CaCO$_3$ depositions on different coating surfaces. In particular, the initiation mechanism of crystallization fouling was determined on the SiO$_2$, diamond and TiC surfaces at the molecular level. As a result, the formation mechanism with detailed intermediate steps for CaCO$_3$ deposition was obtained. The fouling takes place mainly via HCO$_3^-$ intermediates, and the final deposition structure was found to vary between surfaces. Based on these calculated results, it was possible to rank these coatings against CaCO$_3$ deposition formation. The results will be verified by fouling experiments for coatings and stainless steel in a laboratory scale apparatus.

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