

## A PRELIMINARY STUDY OF THE EFFECT OF SURFACE COATING ON THE INITIAL DEPOSITION MECHANISMS OF DAIRY FOULING

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### ABSTRACT

Modification of heat transfer surfaces to minimize the effects of fouling in the dairy industry is investigated in the current study. Special attention is given to the initial deposition mechanisms, which are believed to determine the fouling and cleaning performance of the surfaces studied. Preliminary results have been obtained for stainless steel and titanium nitride (TiN) surfaces fouled for 3 minutes with whey protein and calcium phosphate. Scanning Electron Microscopy (SEM) images of air-dried, whey protein fouled samples showed both TiN and stainless steel surfaces were covered with a thin layer of deposit, following the topography of the heating surface. X-ray Photoelectron Spectroscopy (XPS) spectra for the TiN surfaces fouled with whey protein showed carbon and oxygen as the main components present. XPS analysis of the stainless steel surfaces is currently underway. Calcium phosphate fouling on stainless steel and TiN surfaces resulted in formation of a crystal matrix on some parts of the surface, while other parts appeared to have no deposition. X-ray microanalysis of these crystals yielded a Ca/P ratio of 1.4. X-ray Diffraction (XRD) analysis is being undertaken to better identify the phases formed. Also in consideration is SEM analysis under cryogenic conditions, and XPS analysis of freeze-dried samples to eliminate changes taking place during air-drying. Future experiments will involve fouling of diamond-like carbon (DLC) surfaces. It is expected that altering the fouling behavior and therefore deposit adhesion, may influence cleaning performance, which will be tested in cleaning runs. At a later stage, similar investigations will be performed using milk solutions to study the combined effect of proteins and minerals.

### INTRODUCTION

In many processing industries, fouling of heat transfer surfaces is the major factor responsible for the reduction of process efficiencies and performance with time (Lund 1981). Fouling in food industries is more severe in comparison to other industries (Changani, et al. 1997), and

thus requires more frequent and expensive cleaning steps (Hasting 1994).

Total fouling costs equate to 0.25% of the gross national product (GNP) for developed countries such as the USA, and 0.15% of the GNP for less industrialized countries such as New Zealand (Müller-Steinhagen, et al. 2000). Costs due to over-sizing of heat exchangers, extra fuel consumption, maintenance, and loss of production all contribute to the total costs of fouling. In the USA and New Zealand, total fouling costs have been estimated as \$US7billion (Müller-Steinhagen, et al. 2000) and \$NZ97.3million respectively (Steinhagen, et al. 1990).

The principal goal of this doctoral study is to modify the heat transfer surface in such a way that the effects of dairy fouling are reduced to some degree. The effects of fouling may be defined as increased fouling resistances and therefore decreased heat transfer coefficients; decreased processing times; and increased frequency and duration of cleaning cycles. All these factors lead to an increased cost of operation. Dairy fouling will be simplified to two cases, namely, whey protein fouling and calcium phosphate fouling, which are the main deposit components at pasteurization temperatures (Burton 1968). To better understand the fouling behavior of milk, reconstituted whole milk or skim milk solutions will be used at the latter stage of the research.

Initially, surface modification will be in the form of coating the stainless steel surface. Two surfaces will be studied in the first stages of the research, namely Diamond-like Carbon (DLC) and Titanium Nitride (TiN). The results will be used to either modify these surfaces to improve their performance or use an alternative coating that is expected to provide better results.

The fundamental mechanisms by which the deposit adheres to the surfaces studied is of primary importance to this research. Thus, the focus of the study is specific, in that, the surface chemistry of the fouling process will be studied in detail using surface analysis techniques. Techniques such as X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) have not been used to a great extent in previous fouling studies, and will be used to analyze the deposit formation process closely. Scanning

Electron Microscopy (SEM) and X-ray Diffraction (XRD) will also be used to study the deposit structure and composition.

## FOULING IN THE DAIRY INDUSTRY

### Fouling Mechanisms

Heating in the dairy industry is required in processes such as pasteurization and sterilization for preservation of milk by killing micro organisms (Walstra, et al. 1984). The effect of fouling is incorporated into heat exchanger design by including a fouling resistance,  $R_F$ , in the overall heat transfer coefficient calculation. Fouling behavior is observed by plotting  $R_F$ , against time (Fig. 1).

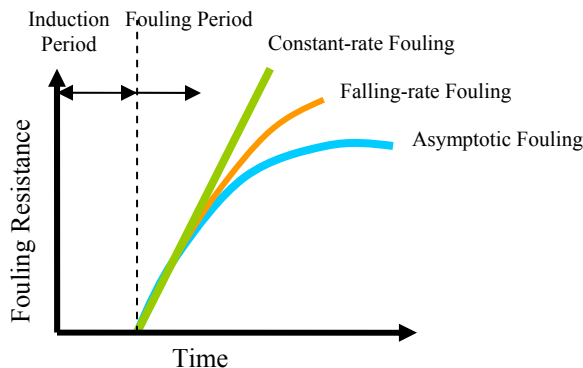


Fig. 1: Change in Fouling Resistance with Time (Fryer, et al. 1995)

Initially, there is a period where the heat transfer coefficient does not change significantly and is termed the induction period (Belmar-Beiny, et al. 1992; Belmar-Beiny, et al. 1993; Changani, et al. 1997; Visser, et al. 1997). The induction period is followed by the fouling period. Constant-rate fouling leads to rapid reduction in the heat transfer coefficient, increase in pressure drop, and finally blockage. In food processing, falling-rate and constant-rate fouling are commonly observed (Changani, et al. 1997).

Two main types of deposits have been identified (Burton 1968). Type A is formed at temperatures between 80°C and 105°C, and is a white voluminous precipitate. It contains 30-50% minerals, mainly composed of calcium and phosphate, and 50-60% whey protein, where the major whey protein present is  $\beta$ -lactoglobulin ( $\beta$ -LG). Type B is formed at temperatures above 100°C and is grey with a hard granular structure. It contains 70-80% minerals and 15-20% protein, where the main proteins present are  $\beta$ -casein and  $\alpha$ -s<sub>1</sub> casein.

The processes that take place in the bulk liquid at elevated temperatures are well understood (Hasting 1994).

Whey protein denaturation mainly refers to the unfolding of  $\beta$ -LG and subsequent exposure of reactive groups such as the free SH-group, which is buried within the structure at room temperature. Calcium phosphate precipitation is due to the inverse solubility of this salt. Depending on the pH of the solution various phases can precipitate, where hydroxyapatite (HAP) is the most thermodynamically stable phase. However, formation of HAP is preceded by precipitation of precursor phases, including, amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), tricalcium phosphate (TCP) and dicalcium phosphate dihydrate (DCPD) (van Kemenade 1988). Overall, heating of milk results in a change in pH due to processes such as water dissociation, reaction of lactose with the formation of organic acids, liberation of hydrogen ions by the insolubilization of calcium phosphate, and removal of CO<sub>2</sub> (Belmar-Beiny, et al. 1993).

### SURFACE MODIFICATION TO INFLUENCE FOULING

It is understood that several surface properties influence the adsorption and desorption behavior of fouling deposits (Britten, et al. 1988; Changani, et al. 1997; Kim, et al. 1998; Lund 1981; Muller-Steinhagen, et al. 1997; Santos, et al. 2001; Santos, et al. 2004; Visser, et al. 1997). These include, surface energy, distribution of active sites, and roughness. Maximum fouling will occur in a system which undergoes a maximum decrease in surface energy (Muller-Steinhagen, et al. 1997). As a result most recent studies have investigated fouling behavior of surfaces with a lower surface energy than stainless steel (Addesso, et al. 1997; Britten, et al. 1988; Muller-Steinhagen, et al. 1997; Rosmaninho, et al. 2003; Santos, et al. 2001; Santos, et al. 2004). Polymer coatings have been studied to some extent due to their low surface energy (Addesso, et al. 1997; Britten, et al. 1988; Santos, et al. 2001), however, the main drawback with such coatings is reduced abrasion characteristics, and heat transfer properties. Other coatings such as DLC, SiO<sub>x</sub>, Ni-P-PTFE (Rosmaninho, et al. 2003; Santos, et al. 2001), and Ti (Addesso, et al. 1997) have also been studied. To retain heat transfer properties, the thickness of such coatings is limited to approximately 5 $\mu$ m (Muller-Steinhagen, et al. 1997).

Britten (1988) found that the rate of fouling was not influenced by the coating since the same degree of fouling was observed for all surfaces. The results showed that the polar contribution to the solid-vapour interfacial energy was the main parameter describing the adhesion strength of the deposit. PMMA and PS had the lowest adhesion strength while nylon and agarose had values similar to bare stainless steel. It was concluded that coating the surface influenced

the deposit adhesion strength, resulting in improved desorption processes.

Santos et al (2001) found that modification of the stainless steel surface influenced the adsorption of protein. The results obtained did not provide definite conclusions regarding the possible use of such modifications in industry. Fouling behavior was characterized mainly by the decrease in the heat transfer coefficient, increase in pressure drop, and the amount of deposit in comparison to unmodified stainless steel surfaces. They found that both Ni-P-PTFE and SiO<sub>x</sub> coatings reduced the amount by which the heat transfer coefficient decreased. However, the compact deposit formed on the Ni-P-PTFE surface was harder to remove during cleaning. The SiF<sub>3</sub><sup>+</sup> ion implanted surface showed slow adsorption kinetics but rinsing did not remove as much protein as for stainless steel surfaces. MoS<sub>2</sub> ion implanted surface did not show a significant improvement from stainless steel fouling behavior.

Modification of surfaces to reduce mineral fouling has been reasonably successful. Muller-Steinhagen et al (1997) investigated the influence of the surface on scale formation during pool boiling of CaSO<sub>4</sub> solutions which represents crystallization fouling behavior. Implantation of SiF<sub>3</sub><sup>+</sup> ions onto stainless steel surfaces produced a final heat transfer coefficient 100% greater than that of the bare stainless steel surface. The deposit was loose and porous in nature and broke off more easily than the dense, packed deposit formed on the bare surface.

H, F, and Si ion implantation, and magnetron sputtering of DLC, ta-C, and ta-C with F were studied as possible modifications to influence CaSO<sub>4</sub> fouling (Bornhorst, et al. 1999). It was found that all modifications resulted in improved anti-fouling effects. The deposit formed was easy to remove suggesting a lower deposit adhesion strength. For sputtered surfaces, the fouling curve reached a constant heat transfer coefficient value, where ta-C with F showed the best fouling behavior.

Rosmaninho et al (2003) studied calcium phosphate fouling behavior on SiF<sub>3</sub><sup>+</sup> and MoS<sub>2</sub> ion implanted stainless steel surfaces as well as Ni-P-PTFE and PECVD SiO<sub>x</sub> and DLC-Si-O coated stainless steel. The coatings, in increasing order of amount of deposit formed were Ni-P-PTFE, DLC-Si-O, MoS<sub>2</sub>, SiF<sub>3</sub><sup>+</sup>, stainless steel, SiO<sub>x</sub>.

These findings show that hydrophobic surfaces such as Ni-P-PTFE resulted in the least amount of protein fouling. However, it also shows that in the deposit formed on Ni-P-PTFE was much harder to remove. This is supported by the fact that β-LG fouling increases with hydrophobicity (Santos, et al. 2004). In contrast, calcium phosphate deposits were removed more easily from Ni-P-PTFE surfaces than from stainless steel. Thus it is not yet clear what type of surface is ideal to mitigate fouling. Although low surface energy, non-polar surfaces may reduce fouling,

the deposition mechanism should be investigated alongside such that similar surfaces can be developed to improve cleaning processes as well.

In this study, initially DLC and TiN coatings will be investigated. Titanium nitride (TiN) has been selected as a model surface to simplify the understanding of the deposition process. It has been used for biological implants where adhesion and growth are crucial factors in determining its biocompatibility (Kola, et al. 1996; Park, et al. 2003). The results of this study may more clearly represent the fundamental mechanisms taking place. Diamond-like carbon (DLC) is a low surface energy material and has also been used for biological applications (Grill 2003; Hauert 2003; Sheeja, et al. 2004). However, it is expected to be even more productive for this study as it can be modified by doping with specific compounds or elements (Grill 1999; Peters, et al. 2003; Trippe, et al. 2004). As such, with careful consideration it may be tailored for a specific application.

## EXPERIMENTAL SET UP AND METHODOLOGY

Experiments for this study involve fouling of various surfaces by exposure to both whey protein and calcium phosphate solutions. The main techniques that will be used to analyze the fouled samples are X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Atomic Force Microscopy (AFM), and X-ray Diffraction (XRD). Most surface characterization techniques impose size restrictions on the sample to be analyzed, requiring the sample to be cut if it is too large for analysis. Cutting of a fouled sample may damage the deposit surface and therefore alter the surface structure and topography to some extent. As a result, the experimental set up and methodology have been developed such that the original sample to be fouled is of the required analysis size.

Exposure of samples to the fouling solution will take place in a non-stationary set up where either the fluid or the samples will move to mimic a flow type situation. The samples used in this study are square 304 stainless steel samples, with dimensions 15mmx15mmx5mm. The samples are sequentially polished up to a very fine grade of 0.25μm diamond before DLC or TiN deposition.

### Experimental Set Up and Equipment

The fouling module that was originally designed for the purpose of this research is currently under construction. The rig can accommodate 9 samples and the design is such that the fouling solution flows past these samples. Preliminary experiments were performed using a smaller set up. The purpose of the small rig was to provide a simple method to

foul small samples where the fouling solution could remain stationary. To maintain a flow type situation, movement of the samples is required.

Fig. 2 shows a schematic of the rig designed for this purpose. The apparatus consists of two concentric cylinders between which the fouling solution is placed. The inner cylinder is attached to an agitator shaft and a motor is used to rotate this cylinder. Samples are soldered onto the surface of the inner cylinder. Heat is provided to the fouling solution by means of a heating plate. The inner cylinder may be heated by placing it in a water bath until the required temperature is reached. To retain the thermal energy gained by heating in the water bath, the inner cylinder is filled with oil which has a high heat capacity. It should also be noted that the purpose of these experiments was to determine the methodology and identify the main obstacles present in the experimental and analysis stages of the investigation.

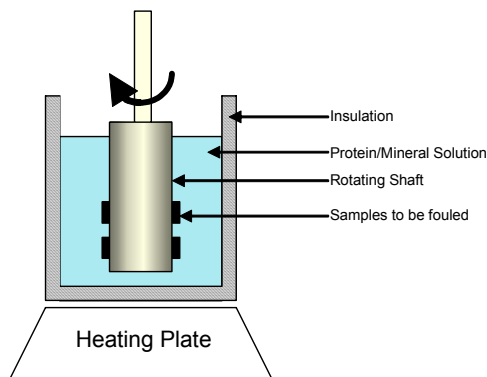


Fig. 2: Schematic of small fouling rig

### Method of Experiments

The fouling run consists of heating the fouling solution and samples to the specified temperature, exposing samples to the solution for 3 minutes, quenching the samples with water to stop the fouling reaction and to remove loosely bound material from the sample surface, and removing the samples for characterization studies.

The samples are heated to a higher temperature than the fouling solution so that fouling takes place primarily at the sample surface as opposed to the bulk.

Before experiments, samples are first cleaned with detergent, rinsed, and then cleaned with 0.2wt%NaOH before rinsing again.

The whey protein solution is formed by reconstituting whey protein concentrate (WPC) to a concentration of 6g/L. Calcium phosphate is formed by mixing solutions of 0.025mol/L  $\text{Ca}(\text{OH})_2$  and 0.025mol/L  $\text{H}_3\text{PO}_4$ .

Cleaning runs will also be performed as part of the study to further assess the fouling performance of the

surfaces. NaOH solutions prepared in the laboratory will be used as the main cleaning solution, however, industrial detergents will also be used to assess cleanability from an industrial perspective.

### PRELIMINARY RESULTS

#### Unfouled Surfaces

**Stainless Steel Surfaces.** Cleaned stainless steel surfaces were analyzed using SEM. The surface was found to be reasonably smooth due to polishing to  $0.25\mu\text{m}$ . Compositional analysis using x-ray microanalysis (Fig. 3) shows the main components of Fe, Cr, Ni, and C. Due to the high accelerating voltage and limited surface sensitivity of the technique, the oxide layer expected to form on the surface was not detected strongly. XPS analysis is currently underway to correctly identify the composition.

**Titanium Nitride Surfaces.** TiN surfaces, produced by magnetron sputtering of stainless steel, were analyzed and subsequently used for fouling experiments. XPS analysis showed the TiN surface is covered with an oxide layer due to air-exposure after deposition, as shown in Fig. 4. The oxide layer consisted mainly of  $\text{TiO}_2$ , and intermediate oxynitride ( $\text{TiN}_x\text{O}_y$ ) compounds which form at the beginning of the surface oxidation process. N 1s narrow scans showed the presence of interstitial N due to replacement of N with oxygen during the formation of the  $\text{TiO}_2$  oxide layer. Carbon contamination was identified by the presence of C-C/C-H, C-O, and C=O compounds.

SEM analysis was performed to study the microstructure and morphology of the TiN coating. Columnar grain formation was identified from cross sectional images of the coating (Fig. 5), with coating thicknesses ranging from 230nm to  $1.29\mu\text{m}$  depending on deposition conditions. The grain size determined from images of the coating surface (Fig. 6) ranged from 42nm to 61nm.

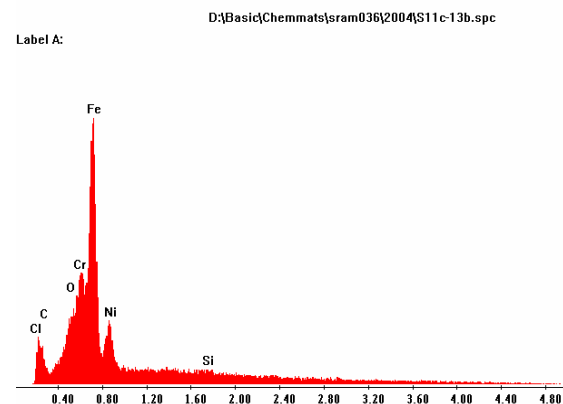


Fig. 3: EDS spectrum for cleaned stainless steel

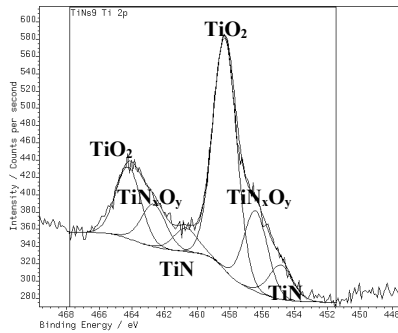


Fig. 4: Cleaned TiN - Ti 2p Narrow Scan (Wiehe 2004)

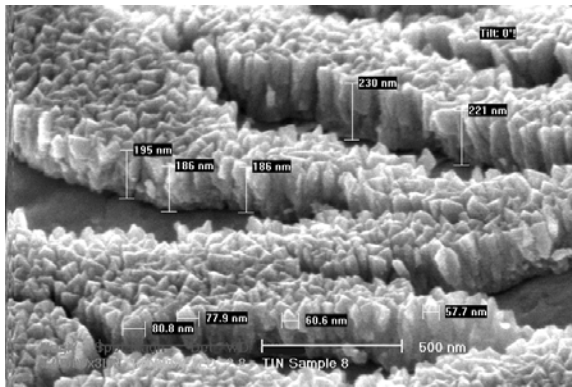


Fig. 5: Cross sectional image of TiN coating (Wiehe 2004)

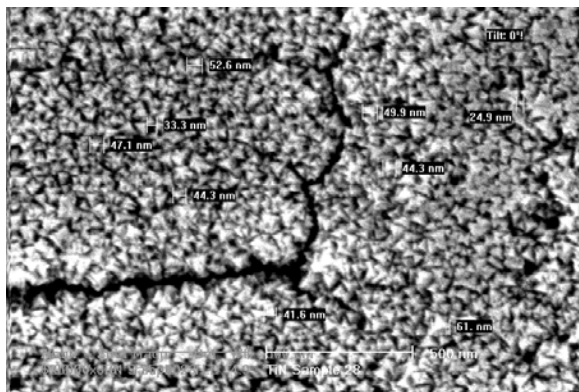


Fig. 6: Top view of TiN coating surface (Wiehe 2004)

### Whey Protein Fouling

Whey protein deposits were obtained by heating the solution to 60°C, and samples to 85°C, before exposing the

samples to the solution. Samples were dried in a desiccator before characterization.

**Stainless Steel Surfaces.** Fig. 7 shows that the whey protein deposit formed on the stainless steel surface is quite thin, following the surface topography, as polishing marks identified earlier in the unfouled surfaces are still seen. A higher magnification image of the surface shows that the surface is in fact covered with a homogeneous layer of deposit which has cracked as a result of drying (Fig. 8). EDS analysis of the surface shows approximately two times the amount of carbon than for unfouled stainless steel. XPS analysis is currently in progress to further analyse the composition of the deposit.

**Titanium Nitride Surfaces.** Wide scans obtained from XPS analysis of the TiN surface fouled with whey protein showed only C and O as the detectable components. Peak deconvolution and quantification of the C 1s and O 1s spectra showed the same C components found in unfouled TiN surfaces. The major difference was the higher overall percentage of C-C bonds on the surface which increased from approximately 20% in unfouled surfaces to 74% in fouled surfaces. The overall percentage of C-O and C=O bonds did not change significantly from the values for unfouled TiN surfaces. It was expected that N would be detected in the deposit due to the fact that proteins are a sequence of amino acids. In XPS studies carried out on stainless steel surfaces fouled with whey protein, N was detected (Belmar-Beiny, et al. 1993). This result may suggest that N containing parts of the whey protein structure have oriented towards the TiN surface therefore making them difficult to be detected in the XPS. To further confirm this, a depth profile analysis will be carried out. A thinner deposit produced by fouling for shorter periods of time would also help analyse the composition of the interface between heating surface and deposit more clearly.

Fig. 9 is a SEM micrograph of the deposit structure after drying. The appearance of the deposit is similar to the deposit formed on stainless steel surfaces. The dark and light shades of the deposit correspond to thick and thin deposits respectively, according to EDS analysis which showed higher amounts of carbon in darker regions. The deposit is non homogeneous, in that, there are patches in the cracked layer where the surface appears smooth. These smooth patches also seem to be cracked in some places, suggesting it is a sub-layer of deposit rather than the TiN surface.

### Calcium Phosphate Fouling

**Stainless Steel Surfaces.** Calcium Phosphate runs were performed at room temperature conditions, where both solution and sample were maintained at room temperature. The main feature of the deposit formed is a crystal matrix

type deposit (**Fig. 10**). The stainless steel surface is covered only partially by this deposit, while the remaining parts seem to be the bare stainless steel according to EDS analysis. The crystal matrix seems to consist of small crystal flakes ranging from 200 to 300nm in size. Using EDS analysis, the Ca/P ratio is estimated as 1.4. XRD analysis would need to be performed to confirm the phases formed.

**Titanium Nitride Surfaces.** Calcium phosphate deposits formed on TiN surfaces were similar to the matrix found on stainless steel surfaces. Again, the surface was only partially covered with the deposit. The Ca/P ratio from EDS analysis was estimated at 1.4. However, the crystal flakes forming this matrix appeared smaller in size than those found in stainless steel (Fig. 12). In addition, a different type of crystal was found in some parts of the surface, and is shown in Fig. 13. This type of crystal seems to be somewhat porous in nature. EDS analysis showed these crystals had a Ca/P ratio of 1.8.

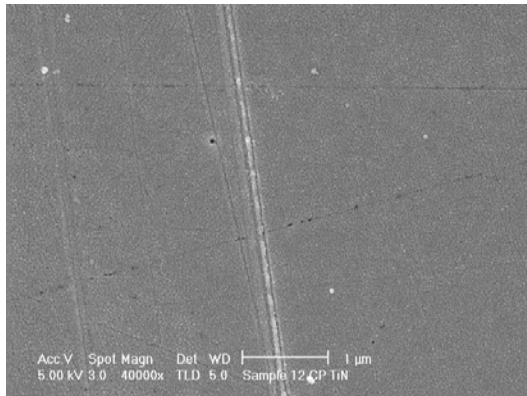


Fig. 7: Stainless steel surface fouled with whey protein

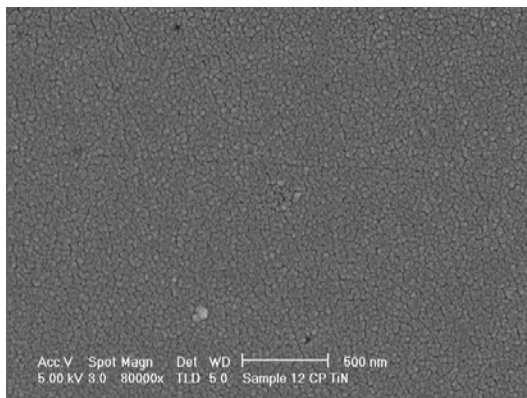


Fig. 8: High magnification image of whey protein fouled stainless steel surface

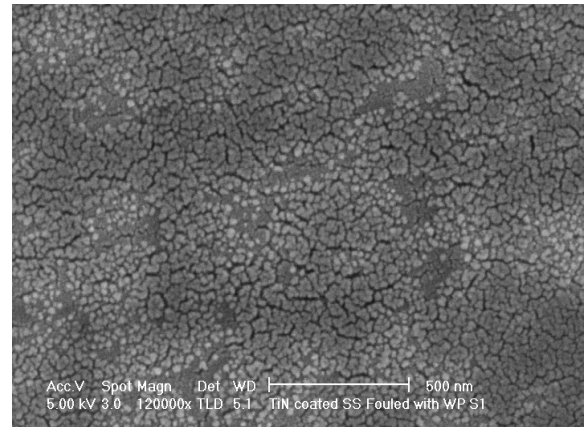


Fig. 9: Whey protein deposit structure on TiN after drying

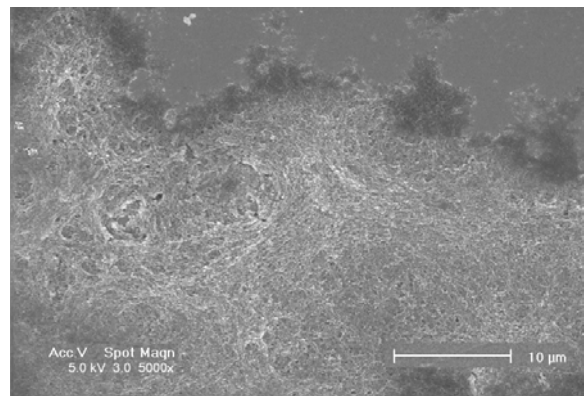


Fig. 10: Crystal matrix deposit formed on surface

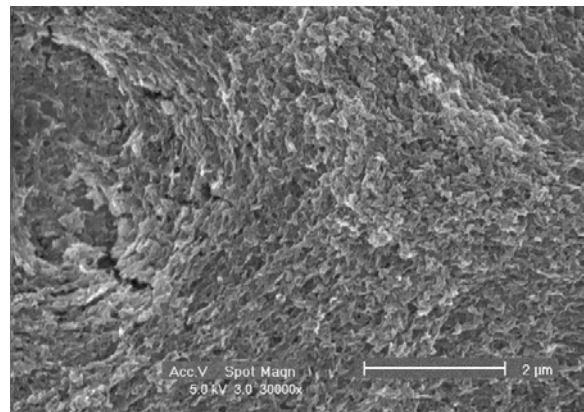


Fig. 11: High magnification image of crystal matrix

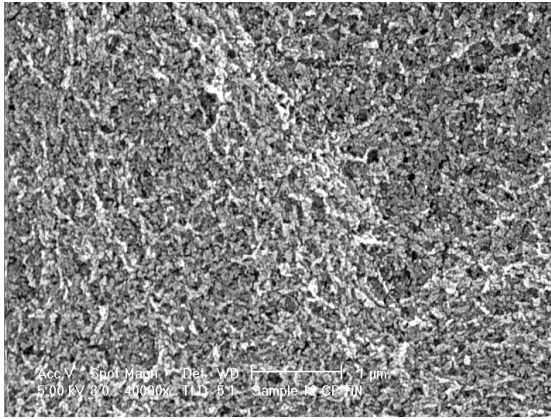


Fig. 12: Crystal matrix of calcium phosphate formed on TiN surface

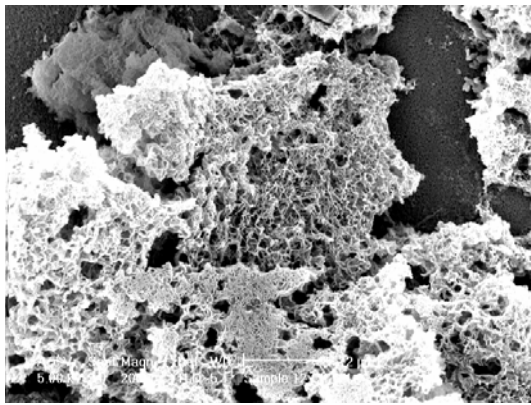


Fig. 13: Second type of calcium phosphate crystal formed on TiN surface

## DISCUSSION AND FUTURE WORK

Preliminary results have shown that whey protein deposits formed on stainless steel surfaces appear as a uniform layer of deposit. In contrast, the deposit formed on TiN surfaces was not homogeneous, and seemed to be thinner in some places than others. Further experiments will be carried out to verify these findings. XPS analysis is also underway to identify compositional differences in the deposit, and possibly lead to an understanding of the deposition mechanisms. Depth profile analysis will be particularly useful in analysing the composition at the interface between the heating surface and deposit.

Formation of the crystal matrix of calcium phosphate seems to have occurred on the surface itself, as opposed to deposition of crystals that have already formed in the bulk

solution. This is due to the fact that the flow patterns produced during the experiment can be seen in the crystal structure for both surfaces. The ratios of Ca/P for stainless steel and TiN deposits are approximately the same, therefore it can be concluded that it is the same crystal phase that has formed. However, X-ray Diffraction (XRD) will be performed to verify this. The difference in flake sizes could be due to the difference in crystallization behaviour on the two surfaces, or perhaps due to minor differences in solution and sample temperature. Such issues will be considered to further improve the experimental methodology and to identify possible challenges in obtaining repeatable results.

Diamond-like carbon samples are currently being obtained, and experiments similar to those performed on stainless steel and TiN surfaces will be carried out. To assess the change in fouling behaviour, dried samples will be weighed before and after fouling. Cleaning runs will be performed once the large rig is set up; the results of which will be used to analyse ease of removal of the deposit. At the latter part of the study, experiments using reconstituted milk solutions will be performed to study the combined effects of protein and mineral fouling.

## CONCLUSIONS

1. The initial deposition mechanisms during whey protein and calcium phosphate fouling have been the main focus of this study. The effect of nature of the heating surface has been investigated by using stainless steel, and titanium nitride coated stainless surfaces.
2. Deposit composition and structure were characterized using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy techniques, respectively.
3. Some differences in deposit appearance were found between whey protein deposits on stainless steel and titanium nitride surfaces. It is possible that the deposit on stainless steel forms more uniformly than for titanium nitride, where a more patchy deposit was found. Experiments at different temperatures and fouling times would allow further investigation of this.
4. Calcium phosphate deposits appeared as a crystal matrix for both stainless steel and TiN surfaces. Compositional information obtained from x-ray microanalysis showed it was possibly the same crystal phase that formed on each surface.
5. As a preliminary investigation on the deposition behaviour, the results provided some useful information on what areas to focus on for future work. The bonding mechanisms on the two surfaces may in fact be different, as suggested by the changes in deposit

structure. This would be investigated further through the use of XPS and XRD.

6. Future experiments will be performed on the small rig using DLC coated stainless steel samples. Compositional variation in the deposit as a function of deposit thickness will also be analysed using depth-profiling techniques in XPS. Analysis without air-drying will also be considered by freeze-drying samples before XPS and SEM analysis. Measuring the dry weight of samples before and after fouling, along with cleaning runs of fouled samples will be used to assess the fouling and cleaning performance of each surface.

## NOMENCLATURE

$R_F$  fouling resistance to heat transfer,  $m^2K/W$

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