DESIGNED COATINGS ON FOOD INDUSTRY EQUIPMENT -
A GOOD PRACTICE FOR FOOD SAFETY

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Abstract

Nowadays, one of the most important parts in food consumption is the fact to consume a safe food with a good quality. It is really important to keep these performances for the food even from early beginning - during its production and conservation. In this work few ways of treatment of materials for the equipment in food industry are presented. Particularly, Physical Vapour Deposition (PVD) and Plasma Nitriding (PN) techniques for surface engineering of materials used for equipment in the food industry are ones that are going to be described.

Namely, PVD is using for deposition of coatings such as: Ti, TiN, TiAlN, Stainless steel Nitride and other CerMet coatings on different type of materials. These coatings serve as highly protective and hygienic coatings or could be even good barrier coatings that stop reaction between food material during its processing and material from the processing tools, machine parts, etc. On the other hand, plasma nitriding is method for surface modification of materials, usually used for enhancing their properties.

In general materials like, stainless steel or the other types of steels are surface treated in order to improve wear resistant during food producing e.g. mixers, extruders, and other machine parts that are in contact with food during the production process. Case studies for bakery and milk industry production are going to be presented here as well.

Key words: Surface engineering of materials, Thin film coatings, PVD, Plasma nitriding.

1. Introduction

Nowadays, one of the most important parts in food chain is the fact to consume safe food with a good quality. It is really important to keep safe food from early beginning - during its production and all other stages in food distribution, storage, and consumption. Health, safety and hygienic design requirements should be set at high priority for all subjects involved in food processing and handling. Minimizing the food contamination, ease of cleaning and sanitizing of food processing equipment are set usually before starting with every manufacturing plant.

In the food processing industry, product contamination and infection risks coming mostly from the processing equipment by itself. Namely, contamination of the food by particles that comes from the processing machinery like, conveyors, extruders, different types of mixers, knives, dough molders, vessels, and pipes in the processing facilities is possible. Good manufacturing, proper selection and design of materials for food processing equipment are very important and become one of the critical issues in food technology.

Product contact materials must meet a number of requirements. They must be inert to the product under operating conditions, including variations in temperature and pressure, as well as to detergents and disinfectants under normal or anticipated conditions of use. They should be corrosion resistant, non-toxic, mechanically stable, smooth and cleanable, and the surface finish should not be affected by the conditions of use.

In practice, the choice of metals available for use for food processing equipment is very limited. While in certain parts of the industry alloys other than stainless steels are use; but generally the stainless steels are the materials of choice for the construction of processing plant and equipment due to their general resistance to corrosion by food products and the recommended cleaning regimes, as well as from the ease with which they can be formed, machined, welded, cleaned. However, care must be taken when polymer and elastomeric materials are used as they may contain leachable, potentially toxic components. The same applies to the use of adhesives, lubricants and other transfer liquids. In all cases, the supplier must present evidence
that the material is safe for use in contact with food. Manufacturers also need to be aware of other potential problems associated with particular processes. As an example, non-metallic surfaces used in dry materials handling can create electrostatic charges, which can cause surface adhesion by small particles of contaminating material. Electrostatic effects during dry materials handling in pneumatic conveying and other systems can be problematic.

For the case of product contact surfaces should be smooth enough to be easily cleanable. A surface finish of Ra 0.8 μm or smoother is usually recommended for product contact areas. To achieve a sufficiently smooth surface, polishing or other surface treatment may be required before surface engineering procedure. The surfaces should also be free from imperfections such as pits, folds and crevices. To retain the desired smoothness of the surface, materials must be resistant to the product under process conditions and withstand cleaning procedures during the lifetime of the material [1].

Stainless steels such as AISI 304 and AISI 316 grades and their low-carbon types are acceptable for most of these applications. The corrosion resistance of stainless steel derives from a thin film of iron/chromium oxide known as the 'passive layer', which forms naturally on a clean stainless steel surface when exposed to oxygen such as from the air or oxygenated water. If this passive layer is damaged, mechanically or chemically, it will normally repair itself very quickly if it is exposed to oxygen again. If there is a lack of oxygen, this self-repair mechanism cannot take place, and corrosion localized to the damage may happen and could ultimately cause component failure for a relatively slight metal wastage [2].

2. Materials and Methods

2.1 Material: Stainless steel

Proper material selection could lead to good and sanitary equipment design. There will be maybe big initial capital investment, but it is good for long term savings during exploitation period of the particular processing equipment. Materials used for product contact must: have adequate strength over a wide temperature range; be durable and have a reasonable life; be non-toxic, non-tainting and non-absorbent; be resistant to cracking, chipping, flaking corrosion and abrasion; prevent penetration of unwanted matter under intended use; be easily cleaned and capable of being shaped.

All surfaces in contact with foodstuffs must be easily cleanable. They should be smooth, continuous and free from cracks, crevices, scratches and pits that may harbor and retain soil and/or microorganisms after cleaning. Although good cleanability is the key requirement for surfaces rather than smoothness, a maximum roughness is specified for food contact surfaces since cleaning time required increases with surface roughness [1].

In general, materials for processing equipment are stainless steel, carbon steel, aluminum, plastics and composite polymeric materials. These materials built-in the processing equipment could be attacked during their exploitation due to the variety of environmental condition or processing parameters set for the particular food processing. One of the properties that are very important for the equipment is corrosion resistance of the material. Corrosion is actually attack to the materials due to the chemical or electrochemical reaction with surrounding environment. Stainless steel is one of the most useful materials for processing in food preparation and food production. Main components in stainless steel are several metals like chromium, nickel, titanium, aluminum, molybdenum etc; they usually form oxidation layer in contact with oxygen and the oxidizing film acts as protection layer of these materials later during their exploitation/usage. Consequently, it improves corrosion resistance of these materials [2].

Very important issue for corrosion resistance of stainless steel is chemical composition of above mentioned components: Cr, Mo, Ni, etc. The best corrosion resistant material is obtained when the steel has min.18% Cr and max 10% Ni. They have satisfactory corrosion resistance, but the wear resistance is not on acceptable level. It could be very important characteristic, because it stops transfer of steel particles to migrate to food during their production process. Because of these issues, it is very important to improve wear resistant and hardness of stainless steel. In this paper, is shown attempt how a local based Macedonian company - Plasma solves these issues, increase of wear resistance and keep the acceptable level or increased corrosion resistance of stainless steel. It is the main goal of this article. Material treated in this work is stainless steel AISI304.

2.2 Methods for surface engineering

Materials science is an interdisciplinary field involving the micro and nano-structure, processing, properties of materials and its applications in different areas of engineering, technology and industry. The physical, chemical and mechanical properties of a material surface in most cases determine its applicability in various technical areas.

Surface engineering as a subset of materials science is changing the properties of the surface and sub-surface region in a desirable way. A variety of advanced properties like physical, chemical, electrical, magnetic, optical, mechanical, wear-resistant, corrosion-resistant properties at substrate-resistant, corrosion-resistant properties at substrate surfaces can be altered by surface modification of materials. The surface chemis-
try, morphology, and mechanical properties could be important to further adhesion, film formation process and the resulting film properties.

There are many surface engineering techniques for variety of materials. In general, surface treatment enhance and improve the performance of the bulk material, provides manufacturing, assembly and decorating advantages by cleaning, etching, functionalizing or depositing other material over the surfaces. A wide range of characteristics of the surface could be changed/achieved: roughness, wettability, hydrophilicity or hydrophobicity, surface charge, altering the surface energy, biocompatibility, antimicrobial activity, reactivity, etc. [3 to 9].

2.2.1 Plasma nitriding of stainless steel

Plasma nitriding (PN) is usually used for surface modification of contact areas as diffusion layer. It improves hardness and wear resistance of materials. At the same time, coatings are usually used to improve material flow, micro hardness, wear resistance, a built-in lubricity of contact surface.

Benefits of PN are many, such as: resistance to abrasive wear, low temperature nil risk process, no dimensional change, improved fatigue properties, no brittle layer, large tooling could be treated, protects both mirror and texture surfaces, ability to treat specific surfaces. In our case, authors used PN process for treatment of stainless steel type AlSi304. Initially, the process of cleaning of parts before PN is really important [10].

Figure 1 presents PN equipment and the process in it with some of parts that are treated in this chamber.

2.2.2 Physical vapour deposited (PVD) coatings on stainless steel

In most cases final finishing of tools or mechanical parts is done by PVD coatings. Vacuum-plasma PVD technology is an environmental friendly, with no contamination of working premises, nor environmental pollution. Their various combinations of coating deposition in one chamber allow accomplishing simultaneously advantages of several methods of coating(s) in one technological run/process. The coatings can be applied on metals, ceramics, glasses, plastics, etc.

Figure 1. Plasma nitriding equipment, process and parts

Figure 2. a) PVD equipment and PVD process, b) PVD-coated samples
Depending on a coating, the process can be carried out both in vacuum, and in environment of working gasses: argon, oxygen, nitrogen, methane or in their mixture. These coatings are generally based on TiNx, TiCN, TiAlxNy, TiOx, and etc. Their hardness is not less than 2000 - 3000 HV, and it guaranties high parameters of durability of cohesion, the homogeneity and entire-ness ensure increase of the term of operation of the precision cutting and measuring tool in 5 to 10 times. Figure 2 presents PVD chamber that was used in this work for depositing the final coatings over plasma nitrided steel samples (Figure 2a) and some examples of treated parts (Figure 2b). Currently, it is proved that Ti, and particularly TiNx, is one of the best bio-inert material for the human body as well as for food processing equipment. Other metal ceramic coatings (CERMET) are in use as well.

3. Results and Discussion

In this section will be given few categories of results with discussion such as, microstructures, hardness of used materials, corrosion stability/resistance, and release of heavy metals of tested materials.

3.1 Microstructure and micro hardness

Figure 3a) presents microstructure of PN surface of samples and at the same photos are presented hardness in Vickers. Fig. 3b) is diagram of dependence of surface hardness (given in HV0,1) as a function of depth (given in microns, measured from the top coated surface towards the inner bulk material).

In Figure 3, one can see the microstructure of used Stainless steel sample. The bulk hardness is 300 HV0,1, interface microhardness is 470 HV0,1 and microhardness of the last layer is 1370 HV0,1. Increased micro hardness, and consequently increased wear resistant, is more than 5 to 10 times remaining the tool life nearly the same.

3.2 Migration of heavy metals

These experiments are conducted by Institute of Public Health, Skopje, Republic of Macedonia, under the State Regulative for materials in food contact. The test was conducted according to standard EN 13130-1 and official legislation in our country, Official Gazette of R. Macedonia No. 93/2010. It consisted of immersing of samples in 3% acetic acid solution for 24 h at 20 +/- 2°C. The samples designates as samples 1 to 3 are shown in Table 1 as well as results from the test treatment.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description of sample</th>
<th>Concentration of heavy metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AISI304/bulk</td>
<td>0,025 0,033 0,04 0,01 0</td>
</tr>
<tr>
<td>2</td>
<td>AISI304/ electropolished/ JJN 400°C; 14h;</td>
<td>0 0,016 0,032 0 0</td>
</tr>
<tr>
<td>3</td>
<td>AISI 304/ brushed / mech. polished / acetone cleaning JJN 350 °C; 4 h / Ti</td>
<td>0 0 0,014 0,01 0</td>
</tr>
<tr>
<td>Maximum allowed concentration</td>
<td>0,6 0,05 0,1 0,1 0,1</td>
<td></td>
</tr>
</tbody>
</table>

It is obvious that none of the tested samples showed leaching or releasing of heavy metals in the solution above the maximum allowed limit for heavy metals. It means that PN/PVD deposited coatings on stainless steel samples are appropriate diffusion layers that protect penetration of heavy metals out of the bulk material.

3.3 Corrosion resistance

The treated materials - six coated stainless steel samples, were prepared for measurement of their corrosion resistance (given in Table 2).
Table 2. Samples used for measurement of corrosion resistance

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Inherent/bulk material</th>
<th>Sample preparation (before PN)</th>
<th>PN regime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temp. [°C]</td>
</tr>
<tr>
<td>1</td>
<td>SS304</td>
<td>Oil removing with solvent/polished mechanically</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>SS304</td>
<td>Oil removing with solvent/polished mechanically</td>
<td>350</td>
</tr>
<tr>
<td>3</td>
<td>SS304</td>
<td>Oil removing with solvent/polished mechanically</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>SS304</td>
<td>Electro-polished in acid mixture</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>SS304</td>
<td>Electro-polished in acid mixture/ PVD of Ti</td>
<td>400</td>
</tr>
</tbody>
</table>

The potentiodynamic polarization measurements are conducted on AMEL instruments potentiostat/galvanostat - programmable function generator (model 568/2053) - Figure 4. All the experiments were carried out using a corrosion cell with saturated calomel as reference, and the appropriate sample as counter electrodes. The suitable solution that is usually used for these types of measurements was 3% NaCl solution. The measurements are conducted at room temperature of 20 °C [11, and 12].

![Figure 4](image-url)  
Figure 4. a) AMEL instrumentation, and galvanic set up,  
b) sample measurements (samples: #1, #5 and #6 are shown on the screen)
Table 3 gives selected measured data of potential vs. current at room temperature for 6 measured samples (sample #1 is plain/neat stainless steel sample, Table 2). The last three samples designated as samples #4 to #6 are the best according to their corrosion stability. The corrosion resistance measured from the current is improved for at least 33% (for sample #4) or even 90% (for sample #6) at 400 mV potential; or improved corrosion resistance of ~50% at 500 mV potential for most of the PN/PVD treated samples (Table 3).

Table 3. Measured potential vs. current for untreated and treated stainless steel samples

<table>
<thead>
<tr>
<th>Potential [mV]</th>
<th>Current density mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1 S2 S3 S4 S5 S6</td>
</tr>
<tr>
<td>0</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>100</td>
<td>0 0 0 0 0 0</td>
</tr>
<tr>
<td>200</td>
<td>0.29 0.48 0.24 0.24 0.24 0.2</td>
</tr>
<tr>
<td>300</td>
<td>15 7.5 7.2 10 2.1 1.4</td>
</tr>
<tr>
<td>400</td>
<td>60 50 52 33 18 30</td>
</tr>
<tr>
<td>500</td>
<td>104 110 143 87 81 78</td>
</tr>
<tr>
<td>600</td>
<td>145 133 150 120 95 92</td>
</tr>
</tbody>
</table>

From measured data, one can conclude that smaller corrosive currents are obtained for treated stainless steel samples (coated samples) compared to untreated or neat stainless steel sample (designated as sample #1). It means that PN and PVD coatings over stainless steel samples improve that corrosion resistance of the samples, and consequently smaller corrosive currents were measured. Figure 5 also compares those corrosive current densities for all treated samples.

Figure 5. Comparison of corrosion currents vs. potential for treated samples

4. Conclusions
- The surface engineering technologies like, Plasma Nitriding (PN) and Physical Vapour Deposition (PVD) techniques on different types of materials are used widely. In this paper is presented use of these technologies for surface modification of stainless steel parts and equipments that are used in food processing industry.
- Generally, stainless steel that was used for this study has very good corrosion resistance, but low hardness and wear resistance values. The authors showed that highly protective diffusion layers are achieved on the metal parts (mixers, extruders, etc.) used in food industry by PN and PVD technologies of surface modification of stainless steel. Namely, improved surface hardness on contact areas, very high wear resistant and hygienic coatings with a good barrier are achieved; the engineered and improved surface protects any reaction between food material (during its processing) and material from the processing tools, machine parts, etc... It could be used by most of food manufacturers. But, manufacturers need to be aware of other potential problems associated with particular processes, not only for releasing of heavy metals from the contact areas, but also for surface roughness important for good sanitizing and cleaning of the equipment, electrostatic charges, which can cause surface adhesion by small particles of contaminating material, etc.
- This study is continuing and authors hope that for next events, conferences, symposia, congresses, it will be extended and fully completed research.

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5. References


