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Full Length Article

Surface analysis of 316 stainless steel treated with cold atmospheric plasma

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ABSTRACT

The surface of 316 stainless steel has been modified using cold atmospheric plasma (CAP) to increase the surface free energy (by cleaning the and chemically activating the surface)IN preparation for subsequent processes such as painting, coating or adhesive bonding. The analyses carried out, on CAP treated 316 stainless steel surfaces, includes X-ray photoelectron spectroscopy (XPS), imaging XPS (iXPS), and surface free energy (SFE) analysis using contact angle measurements.

The CAP treatment is shown to increase the SFE of as-received 316 stainless steel from $\sim$39 mJ m^{-1} to >72 mJ m^{-1} after a short exposure to the plasma torch. This was found to correlate to a reduction in adventitious carbon, as determined by XPS analysis of the surface. The reduction from $\sim$90 at% to $\sim$30% and $\sim$39 at%, after being plasma treated for 5 min and 15 s respectively, shows that the process is relatively quick at changing the surface. It is suggested that the mechanism that causes the increase in surface free energy is chain scission of the hydrocarbon contamination triggered by free electrons in the plasma plume followed by chemical functionalisation of the metal oxide surface and some of the remaining carbon contamination layer.

1. Introduction

1.1. Pre-treatment methods

The surface of a material is a critical feature to consider with regards to how it will interact with the surrounding environment. Beyond the bulk properties (*e.g.* strength, toughness), which are the usual focus during material selection, the surface properties can influence how the material can be joined, painted or functionalised, or indeed how it reacts to aggressive environments *i.e.* corrosion resistance, oxidation resistance and the like. These are important aspects to consider during material selection as it can affect structural integrity and, potentially, the durability of any adhesive joint that is fabricated or coating that is applied.

The surface properties of a material can be modified by using different processes, which can be mechanical, energetic, chemical or a combination of these approaches each of these have its own advantages and disadvantages [1].

1.1.1. Mechanical processes

Mechanical processes such as grit blasting or abrasion generally act to increase the rugosity of the surface, and they are relatively material independent processes. This increases the surface area which can be beneficial for joining and painting, if the roughness is on a micrometre scale. There is also material removal, normally some or all of the surface oxide (in the case of metals) which will reduce surface contamination but these processes also have the potential to leave contamination behind, in the form of embedded particles for example, and therefore sometimes require supplementary cleaning steps prior to further processing. Additionally, there is the danger that such adventitious material may be redeposited if abrasive media, (grit, wire brush bristles *etc*) is reused. These processing methods are simplistic they are often effective in terms of enabling high initial bond strength and the equipment can beautomated and/or mounted on robots. However, there are issues around controlling the process. While the equipment can be mounted on robots there is difficulty in quantifying the grit-blasted surface: visual inspection is a common approach, but this adds to the cost and slows down the processing of a surface [2].

1.1.2. Chemical processes

Chemical pre-treatment processes can produce many different surface topographies and chemistries. Examples include chemical etching and anodising the variety in terms of the chemistry used is

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vast and further information can be found in other published work [3–6]. These processes leave surfaces that are rough at both the micrometre and nanometre scale with excellent wetting properties and have the potential to produce a strong bond with the adhesive or paint. Chemical processes are widely used in industry because of the excellent and diverse properties of the surface finish that are possible. They are usually energy intensive as the chemicals required take a large amount of processing during manufacture and disposal [7] and are also generally used at elevated temperature (typically75–85 °C).

These processes are generally wet (aqueous-based) which means that treating complex shapes is easily possible but the parts have to be dried and have residue removed before further processing often washing and further drying [8]. Chemical treatments tend to be tailored to a specific metal which leads to a situation whereby each materials requires its own chemical treatment; in turn this makes the manufacture of multi material structures more complex.

1.1.3. Energetic processes

Energetic processes such as flame, laser and plasma treatments are dry systems that can alter, etch or chemically functionalise the surface [9]. Laser modification at sufficiently high power can melt the surface of the substrate, be it ceramic, metal or polymer, and ablate it to produce a roughening effect. This can be beneficial but requires a large amount of energy, and local melting of the surface can lead to changes in the bulk properties as a result of microstructural changes [10], it is however, known to be an efficient method of treating polymers and ceramics for adhesive bonding [11,12].

1.1.4. Plasma treatment

Plasma treatment has been used for many years to treat polymers prior to painting, printing or bonding. The plasma treatment for polymers can be divided into corona/dielectric barrier discharge (DBD), flame treatment and low pressure plasma treatment. Probably the most widely used is either corona or DBD. These can be considered atmospheric plasmas as they operate at ambient pressure in atmosphere. Their methods of generation are discussed in detail by Conrads [13]. Most polymers react well to such treatments as they have a favourable structure to modify, and it is readily straightforward to increase the surface free energy to a level necessary for bonding and other adhesion phenomena. These plasma sources are well suited to polymer applications as they can be placed in a production line close to the polymer web being treated on a roll: this is carried out in air and known as corona treatment [14]. As the plasma is only effective over a small distance this can be easily controlled using simple geometries: using corona on a complex 3D structure however is not possible, but flame treatment used in conjunction with robotic positioning of the flame head is viable [9], as is the use of robots to position a plasma torch. Low pressure plasma treatment is essentially a batch process that is still widely used for high added-value components despite the increased cost and time for treatment.

The plasma treatment of metals is much less widespread. There are some applications which use low pressure plasma to modify the surface of components prior to painting or bonding but these are batch processes which lend themselves to low volume production and manufacturing [15–17].

Cold atmospheric plasma is a method of plasma generation which has not been as thoroughly investigated as other methods of treating surfaces. It was developed and is being used for the pretreatment of polyolefins *e.g.* [18–20], and has since been applied to the surface modification of metals, this has been investigated to a lesser extent compared to polyolefin treatment and the current analysis of the plasma treated of metals is limited to surface topography, surface free energy and single spot XPS analysis, which are invariably area integrating analyses of several to many square millimetres in area. While these do elucidate to the level of treatment at the centre of the treated area there is little work that has been done to probe the area surrounding the treated area. This is an important aspect of the treatment to consider as this will enable the use of multiple passes using one torch to treat a large area [21–23].

This work looks to complete the XPS analysis of a single plasma setup by analysing the entire treated area. This will allow for a more detailed knowledge of how the plasma interacts with the surface. Furthermore it will allow for the start of a comparison of different nozzle parameters and how changing the nozzle diameter, for example, could change the size of the treated area as there are applications where using a sub millimetre plasma torch may be advantageous such as micro-electronics [24].

This paper describes work conducted using a variant of a cold atmospheric plasma (CAP) treatment, which has been used to treat 316 stainless steel. The chemical and physical properties of surfaces obtained by the CAP treatment of the metal have been studied by calculating the surface free energy change measured using contact angle and X-ray photoelectron spectroscopy (XPS) these have been included to allow for direct comparison between this and other published work. To demonstrate how the plasma changes the area surrounding the centrepoint imaging XPS has been used which is described in Section 2.3.2.

2. Experimental

2.1. Steel

AISI 316 stainless steel (SS) purchased from Smiths Metals (Biggleswade, UK) was used for this work. This alloy differs to the more common AISI 304 by the addition of ca. 2 wt% molybdenum which provides improved crevice corrosion resistance. The main uses for the AISI 316 alloy include chemical storage, food processing, marine and surgical applications. The specification for AISI 316 is given in Table 1 along with the composition of the steel used in this project. The material was received with one side linished and covered with a 100 μm thick protective vinyl coating.

The 2 mm thick SS sheet was cut into small coupons using a guillotine. The protective coating was then peeled off the samples, which were acetone wiped with a lint-free cloth prior to CAP treatment. The vinyl coating residue provided a useful control for a steel surface with carbon contamination present (subsequently shown by XPS to be at a thickness of ca. 5 nm) and enabled ready assessment of the efficacy of the CAP treatments studied as a means to remove organic surface contaminants. Samples were treated by CAP as 40 × 40 mm coupons except for the imaging XPS (iXPS) samples which were deliberately larger, 50 × 50 mm, to avoid missing any of the treated region. Contact angle measurements were made on panels which measured 25 × 100 mm and readings were taken immediately following CAP treatment.

Table 1
Nominal composition and composition in weight% of 316 stainless steel.

	Fe	Cr	Ni	C	Mo	Mn	Si	P	S
AISI 316 spec	Bal	16–18	10–14	<0.08	2–3	<2	<1	<0.045	<0.03
Test samples	Bal	16.5	10.2	0.02	2.00	1.40	0.50	0.02	0.003