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Effect of silane matrix composition on performances of zeolite composite coatings

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ABSTRACT

The effect of matrix compound on the behaviour of a silane-zeolite composite coatings on 6061 aluminium alloy was evaluated. It was observed that silane molecules containing long aliphatic chain or reduced hydroxyl groups influenced wettability and mechanical performances of coatings. Silane compounds with long alkyl chain or bi-hydroxyl groups allowed to obtain more adherent and hydrophobic coatings. Furthermore, composite coatings characterised by multi-component silanes mixture (short and long chain molecules) evidenced affordable impact resistance compared to coating made of silanes with aliphatic chain functional groups.

1. Introduction

The use of silanes in the formulation of protective films allows to obtain coatings characterized by a high degree of adhesion to the metal substrate and high resistance to corrosive phenomena, so representing an important alternative to chromium (VI) based coatings [1–4].

These compounds, in presence of H_2O and low pH, are able to hydrolyse with formation of silanol (Si—OH) terminations starting from Si—OR groups (where R is an organic group). Silanol terminations interact among themselves (crosslinking) but also with the hydroxyl groups present on metallic surfaces, according to the following reactions [5]:

$$\text{Metal adhesion}: \quad Si-OH + M-OH \rightarrow Si-O-M + H_2O \qquad (1)$$

$$\text{Crosslinking}: \quad Si-OH + Si-OH \rightarrow Si-O-Si + H_2O \qquad (2)$$

As a result of hydrolysis and condensation reactions of alkoxy groups linked to the silicon atoms, a sol-gel film is formed [6].

In surface engineering, the silane matrix operates as coupling agent and offers mainly a barrier protective action showing no active electrochemical behaviour [7–9].

In order to increase the protective properties of silane coatings, different attempts have been done such as the addition to the silane sol-gel film of corrosion inhibitors, salts or oxides, for example based on cerium or lanthanum compounds [10–12].

Furthermore, the enhancement of anti-corrosion performances of silane layers were evaluated by the addition of fillers [13–18], aiming at an improvement of the barrier properties of the sol-gel film itself. With this aim, in our previous works [19–21], the addition to a silane matrix of a particle component such as zeolite crystals was proposed.

Zeolites, being silica-alluminate structures, have a relatively high chemical reactivity due to their surface silanol groups. On the basis of this reactivity, various agents, as well as silanes, can react by superficial interactions [22].

The addition of a zeolite filler to the silane film influences the electrochemical and mechanical behaviour of the coating, giving promising results as anti-corrosive coating, as shown by previous studies [23–25]. Furthermore, the hydrophobicity of the zeolite surface could be enhanced by its functionalization with silanes molecules [26,27] and a hydrophobic coating can reduce the contact between water and metal surface limiting the corrosion process. The hydrophobic coating, indeed, shows an improved protection against corrosion of metal substrates because of the reduced contact between the metal surface and the electrolyte solution in which is immersed.

At the same time, the structure of a zeolite-silane composite film is strongly related to the chemistry of the silane molecules, the deposition condition and the curing process involved in the technological processes.

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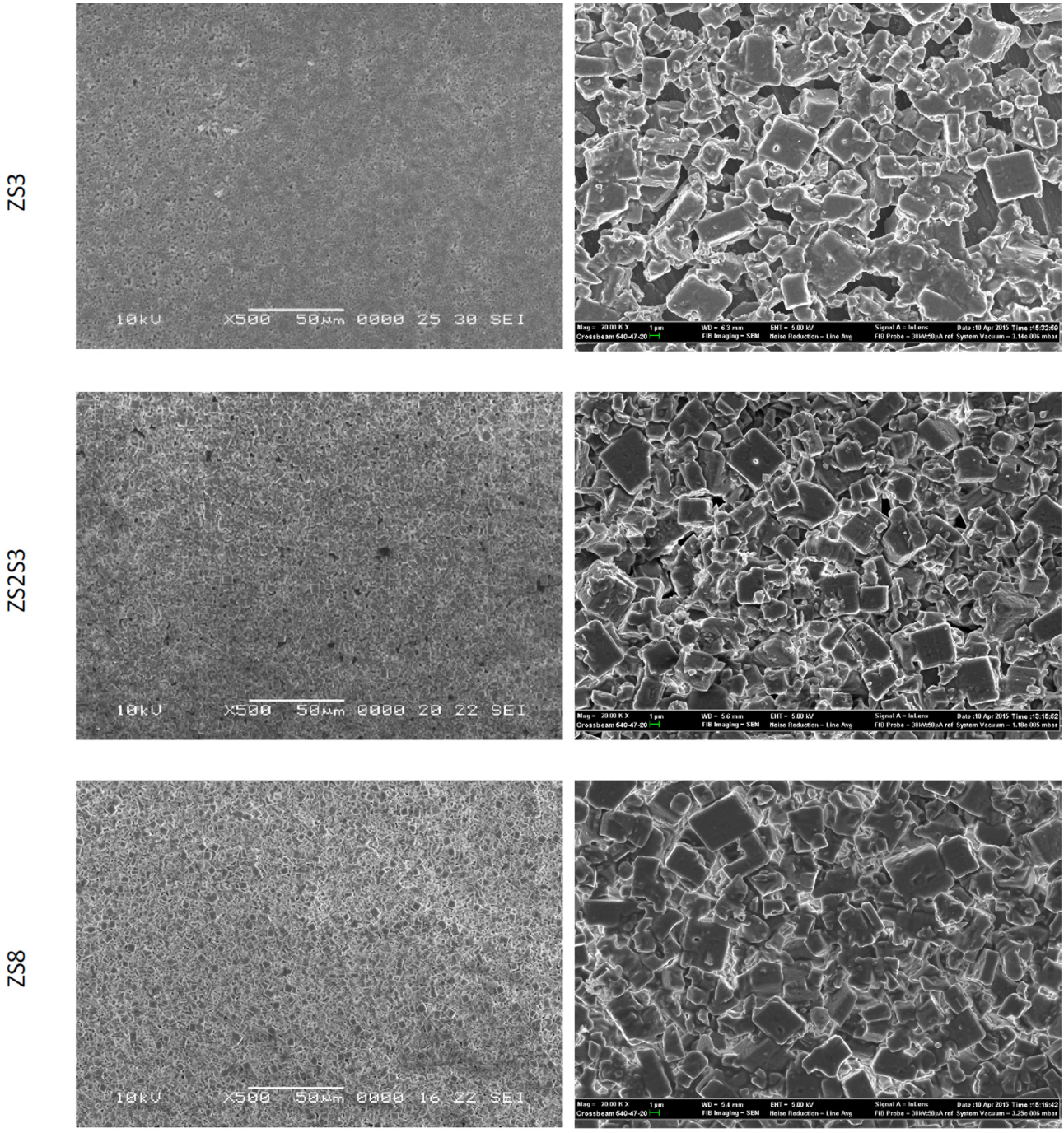

Fig. 1. SEM images at 500× and 20,000× magnifications of a) ZS3 b) ZS2S3 c) ZS8.

The properties of the silane-zeolite composite coating are a direct consequence of the interaction that can be established between their constituents. The silanol groups, generated during the acid hydrolysis, are very reactive and capable of establishing interactions (initially via hydrogen bonds) with the hydroxyl groups present on the surface of the zeolite crystals. After curing, these interactions are transformed into covalent bonds [28].

An improved comprehension of the relationship between structure and performances of composite coatings would be extremely useful in coating technology and engineering.

It has been claimed that the silane coupling agents lead to a significant improvement of the filler dispersion, reducing the formation of particle clusters and improving wettability among polymers [29].

Indeed the properties of the alkyl chain in the silane compounds play a relevant role on the performances of the composite coating. Frignani et al. [30] evidenced as the presence of long aliphatic chains in the silane molecule markedly increases the protective action of the silane layers. In particular, a more evident effect was observed for longer alkyl chains. Van der Waals interactions between aliphatic chains favour the formation of an oriented multi-layered system [31], which causes a noticeable hindrance to corrosion phenomena. Calabrese et al. [32] confirmed that good hydrophobic behaviour of composite silanes with long alkyl chains could be associated with a regular and orderly arrangement of the