HYBRID FILM: A CASE ANALYSIS OF THE SOL-GEL TECHNOLOGY FOR IMPROVED MECHANICAL PROPERTIES APPLICATION

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The paper deals with the analysis of the mechanical characteristics of hybrid coating obtained through the sol-gel synthesis starting from $CH_3Si(OCH_3)_3$ and $C_6H_5Si(OCH_3)_3$ with colloidal silica, α-Al_2O_3, and HNO_3 as catalyst. The experimental conditions refer to a not-optimized reaction parameters trying to obtain a greater sensibility on their variations. On the base of the kinetic reaction pathway the surface morphology, analysed by SEM, the hardness, the abrasion, the film porosity and the contact angles, are interpreted. Indeed the temperature appears a relevant parameter in the control of the surface aspect and the mechanical behaviour. The roles of the colloidal silica and of the nanometric α-Al_2O_3 were analysed. The results demonstrate the strong enclosing of the silica particle in the hybrid polymer network. On the contrary α-Al_2O_3 decreases the abrasion resistance due to the lack of chemical bonds with the network.

INTRODUCTION

Hybrid materials are largely present in nature in highly complex structures and devoted to satisfy many mechanical and chemical-physic functions (Latella et al., 2003, Pinali et al., 2009). Moreover they can be synthesized and processed with environmentally friend soft chemistry and technique (Sanchez et al., 2010). Alkyl alkoxy silanes [$(R_ySiO_x)_n$, $(R_yZrO_x)_n$, etc.] form hybrid materials for high compact and high density coatings under mild conditions sol-gel reactions in aqueous, low alcoholic, solutions. Colloidal solutions containing particles of few nanometer (5-30 nm diameter) and properly considered nanosystems, constitute the intermediate step of the sol-gel process. The application in a film is accomplished before the viscosity increase due to the aggregation of the organic-inorganic nanoparticles. The coatings have high hardness, high abrasion and high scratch performances. The technology is today fully developed and formulations are available to satisfy many performances and low VOC and low carbon use constraints. By this way, hybrid films can be obtained combining ceramic and organic film properties. New types of alkyl radicals bound to Si are continuously available and new binder for coatings can be designed with innovative performances.
The major interest of this paper is to study how the hybrid binder can be formulated to produce high abrasion resistant films with elevated mechanical properties.
The paper concerns a part of a more large research study centred on the fully characterisation of siloxane based hybrid materials for metal coating formulated with the addition of nanoparticles (SiO_2 and Al_2O_3). Mechanical properties like hardness, abrasion and adhesion of the films are deeply discussed. Microscopy techniques were used to assess the particle size and the surface morphology. Nevertheless obtained with non optimised formulations, all the experimental results may be interpreted using the reaction kinetic issues derived from the rate scheme generally accepted in literature for the sol gel synthesis. Useful indications could be obtained.

EXPERIMENTAL

2.1 Materials
Polymeric silane sols were prepared by hydrolysis and condensation of reagent grade methyltrimethoxysilane [$CH_3Si(OCH_3)_3$ (MTMS)] and phenyltrimethoxysilane [$C_6H_5Si(OCH_3)_3$ FTMS]; they were purchased from EVONIK Industries, and used as received. Isopropyl alcohol (*i*-PrOH), formamide (FA), colloidal silica (CS, Ludox AM-30, 30%wt suspension in water), and HNO_3 were purchased from Aldrich and used as received. The

black pigment was copper chromite spinel Cu(Cr,Fe)2O4, C.I.Pigment bleck 28 (Heubach). Deionised water was used for hydrolysis. Molar ratios used in this synthesis are reported in Table 1. Aluminum oxide, alpha phase (Al$_2$O$_3$), was purchased from Alpha Aesar and used as received.

Table 1. Reagent molar ratio.

RATIO	
WATER/organosilanes (mole/mole)	10
HNO$_3$/ organosilanes (mole/mole)	0.1
Pigment conc. in dried film (w/w)	30-40%

2.2 Sol-gel preparation
The preparation was carried out in two steps. The hydrolysis and condensation reactions occur during the both steps. In the first step MTMS and FTMS, isopropyl alcohol, formamide and colloidal silica were mixed and the solution homogenised before the addition of water and the catalyst. After one hour from the beginning of the first step, the second one begins with the addition of a solution of (MTMS + FTMS)/isopropyl alcohol, pigment and Al$_2$O$_3$. We used both a strong acid condition (pH=1) as a weak acid condition (pH=5.5), the last obtained by partially neutralizing the acid with a solution of NaOH 1M.

2.3 Thin film preparation
To deposit the colloidal suspension we used the spray coating technique with a laboratory airless spray gun in order to obtain homogeneous and uniform thin films (30-60 μm) on sand blasted Al-Si alloy disc of 10 cm diameter about.
Alternatively, we used a spin coating technique on small disc of ZnSe.

2.4 Instruments and methods
Microscopy. A SEM Cambridge Stereo Scan 360 and an Optical SZ-BX60 Olympus instruments was used to analyse the morphology of sol-gel coating. For each sample a minimum of six areas were investigated.
Hardness. A Fisherscope H100 with WIN HCU software was used performing test following DIN 50539 /ISO 14577)
Abrasion. We performed abrasion test measuring the weight losses after 1h and 6 hours for all the samples using a self made apparatus resembling the Taber method.
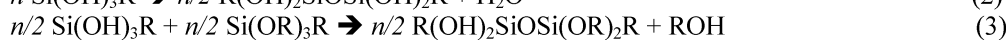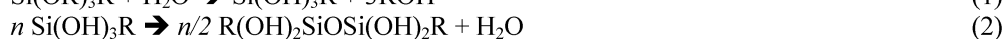*Contact angle.* The contact angles were measured with a KSV CAM 200 instrument (static and dynamic way).

3. RESULTS AND DISCUSSION

3.1 The reaction kinetic and the surface morphology
During a new investigation of the SEM microphotographies of films deposited on Mg and Al discs at 30°C and 60°C reported in a previous work (Amoriello et al., 2010) we note that many aggregates characterise the surface morphology and their size depends on the temperature as they are smaller at 60°C than at room temperature. Among the kinetic parameter, the temperature seems to control the formation of the surface morphology. Working with this hypothesis, the surface aspect can be interpreted considering the two steps of a sol-gel reaction pathway (Stöber synthesis). Firstly the alkyl alkoxy silanes hydrolyse to the corresponding silanols with a step by step reaction (see scheme, reaction 1); then silanols condense each other through an aqueous and/or alcoholic (reaction 2 and 3 respectively) with a step by step too, producing particles of colloidal dimension (sol). After the alcohol-water solvent evaporation, the particles join together to form a three-dimensional network and then a continuous material (in our case the material has a film shape)

Reaction scheme of a sol-gel synthesis*
$$Si(OR)_3R + H_2O \rightarrow Si(OH)_3R + 3ROH \qquad (1)$$
$$n\ Si(OH)_3R \rightarrow n/2\ R(OH)_2SiOSi(OH)_2R + H_2O \qquad (2)$$
$$n/2\ Si(OH)_3R + n/2\ Si(OR)_3R \rightarrow n/2\ R(OH)_2SiOSi(OR)_2R + ROH \qquad (3)$$
*Only the first step of the hydrolysis and condensation is represented

The polymer growth, whose first step is reported in the above reaction scheme (reactions 2 and 3), mainly happens with the formation of nano particles probably due to their thermodynamic stability. CS is present in our reaction mixture and the condensation may take place on the silica surface too as CS has silanols groups on the surface. By this way the particle have a SiO_2 core with hybrid organic-inorganic layer outdoor(Chevalier and Ou, 2003).

However the dimension of the particles depends on the relative rate of the condensation reaction of the silanols with CS and with the silanols itself. As showed by the SEM results cited before, a temperature of 60°C, compared with ambient temperature, probably the rate of the homogeneous condensation between silanols or the particles derived from their condensation is faster than the heterogeneous condensation between CS and silanols.

3.2 The role of CS

The CS particles are firmly enclosed in the polymer network increasing the hardness of the film as shown in the Fig. 1. The data clearly indicate an increase of the hardness measured by the Vickers method raising the CS amount in the 0-10% percent range. The values are however lower than the expected ones as a five times greater hardness would be usual with this type of hybrid coating. Some hypothesis, based on the reaction kinetic roughly introduced before, can be advanced trying to explain the hardness data. Indeed, analysing the data of Fig.2, prolonged reaction times seem to increase the hardness.

Bearing in mind that hydrolysis and condensation reactions proceed simultaneously, on the literature base (Xu et al., 2007 , Brinker and Scherer, 1990) the hydrolysis reaction is considered the rate determining step of the overall reaction due to the nucleophile S_{N2} substitution character. Care must be then applied to complete the silanols formation. Indeed if the hydrolysis reaction is not completed, some discontinuity may appear in the network of the solid material lowering the hardness (Venkateswara_Rao et al., 2006).
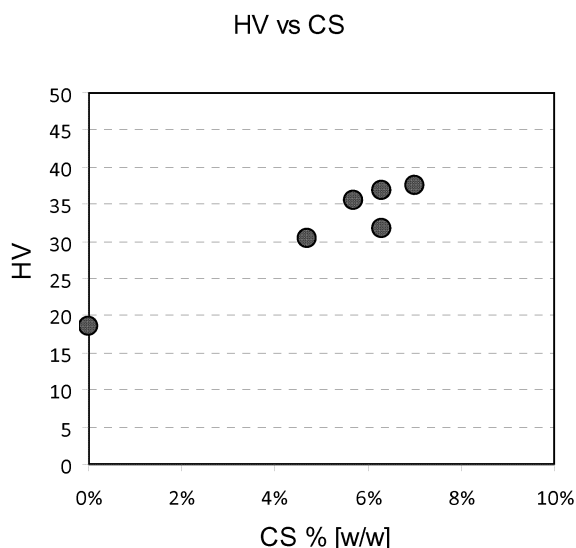

Fig. 1 Hardness relation with colloidal silica concentration in a dried film (Marchese, 2010)
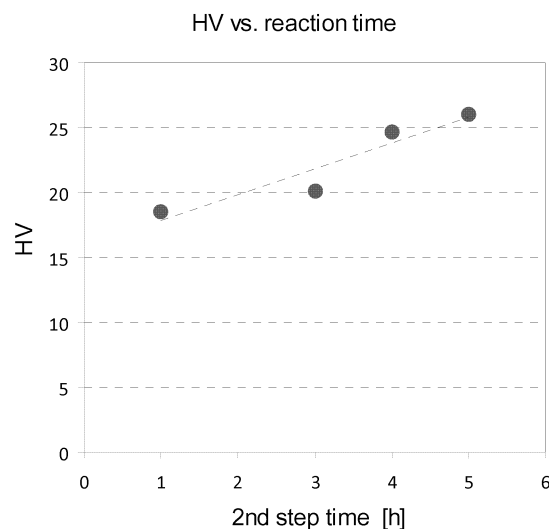
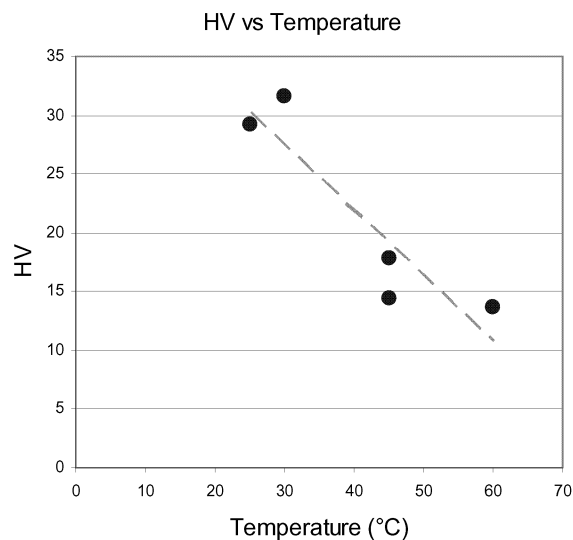Fig. 2. Hardness related to the reaction time of the second step.

Fig. 3. Hardness behaviour with temperature.

Moreover the addition of silica increases the concentration of the –OH function promoting firstly the heterogeneous condensation rate; the completeness of the hydrolysis may be reduced since the precursors are more and more separated or/and hindered in the Si-O-Si network. Similarly the hardness decrease observed with the temperature (Fig. 3), may be explained by the persistence of the –OH functions on the CS surface. Probably they are not completely reacted causing a free volume increase in the material. As a support to our hypothesis, we observed before that the temperature promotes the homogeneous condensation.

However the role of CS is both to increase the hardness and to lower the porosity too as shown in Fig. 4 (Pecoraro, 2008).
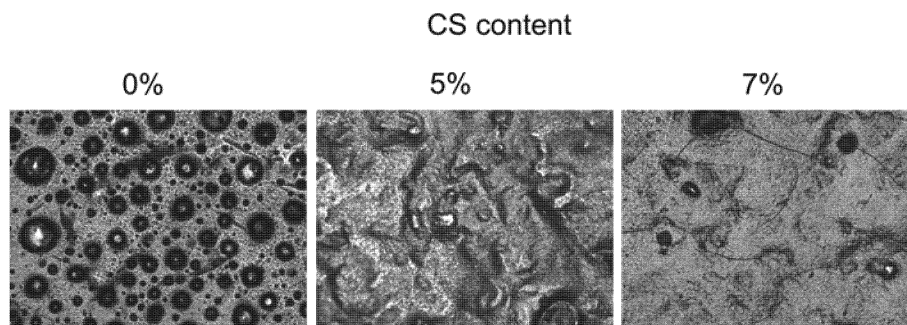

Fig. 4 .The surface morphology at different CS content
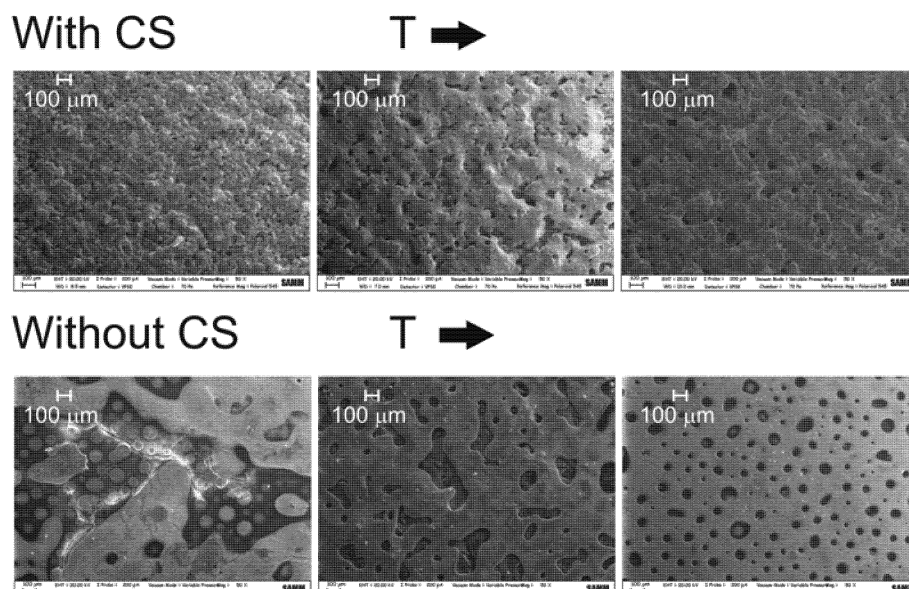(Optical microscopy; 100X) (Marchese, 2010)

Fig. 5 Effect of the CS (6 %) addition at 30-45-60°C. (SEM analysis at Mag = 50X) (Pecoraro, 2008)

The temperature effect on the porosity due to CS is shown in figure 5. Deep differences of the surface morphology are evident: a surface with a marked roughness and with a reduced porosity characterises the CS containing films. The microscopy put in evidence a low porous surface in presence of CS at the 3 temperature examined and it is remarkable that the pore volume and their sizes are reduced also at the lowest temperature among those examined.

Accordingly to what above assumed concerning the particle dimensions and the reaction rate of hydrolysis, the surface morphology can be probably related to a fast condensation promoted by the Si-OH functions that do not allow the levelling of the film.

Tab. 1. Contact angles at different temperatures.

	θ (water)	T (°C)
With SiO$_2$ (6%)	111	30
	107	45
	114	60
Without SiO$_2$	103	30
	100	45
	95	60

The contact angle analysis reported in tab. 1 confirms the greater degree of condensation obtainable in presence of CS. The greatest values have been obtained with CS at 60°C, when the particles on the surface are small.

3.3 The addition of Al$_2$O$_3$.

To increase the hardness of the film, amounts of Al$_2$O$_3$, α- form, were added to the solutions before the sol formation. The hardness values due to Al$_2$O$_3$ addition at 5.5±0.5 % CS content are reported in figure 6. Low values and a slow increase of the hardness are shown in the 0-10% alumina range.
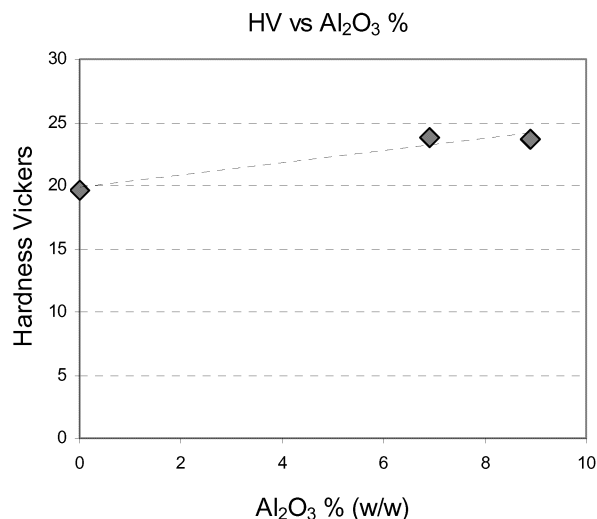
Fig. 6.Hardness vs. Al_2O_3 % at 5.5±0.5 % of CS.

Trying to explain the influence of Al_2O_3 we examined the film abrasion measured by a Taber related test. The films were obtained at different CS/ Al_2O_3 ratio and the results are shown in figure 7 and 8. In the range of CS and Al_2O_3 analysed (0-10% by weight for both), the weight loss is more pronounced if the Al_2O_3 concentration increases while CS has an opposite impact on abrasion than Al_2O_3. An optimum CS/ Al_2O_3 ratio seems to be placed at about 6% of each oxide.

The results could be interpreted by considering that Al_2O_3 cannot participate to the reactions and does not link with covalent or ionic bonds the network. The assumption is confirmed in the figure 9, where α-alumina crystals (rods) appear free and easy detachable from the material.
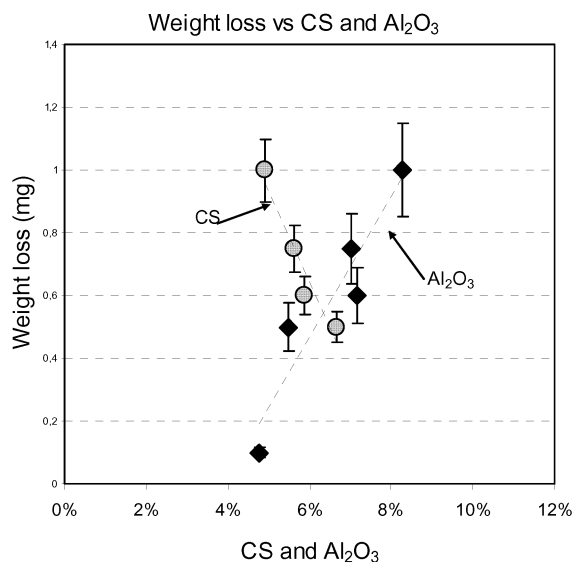

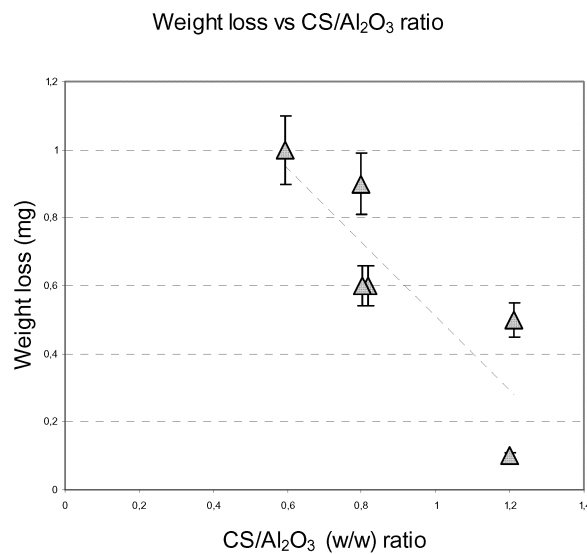*Fig. 7. Comparison of the CS and Al_2O_3 control on abrasion behaviour*

Fig. 8. Weight loss vs CS/Al_2O_3 ratio

Crystal 2

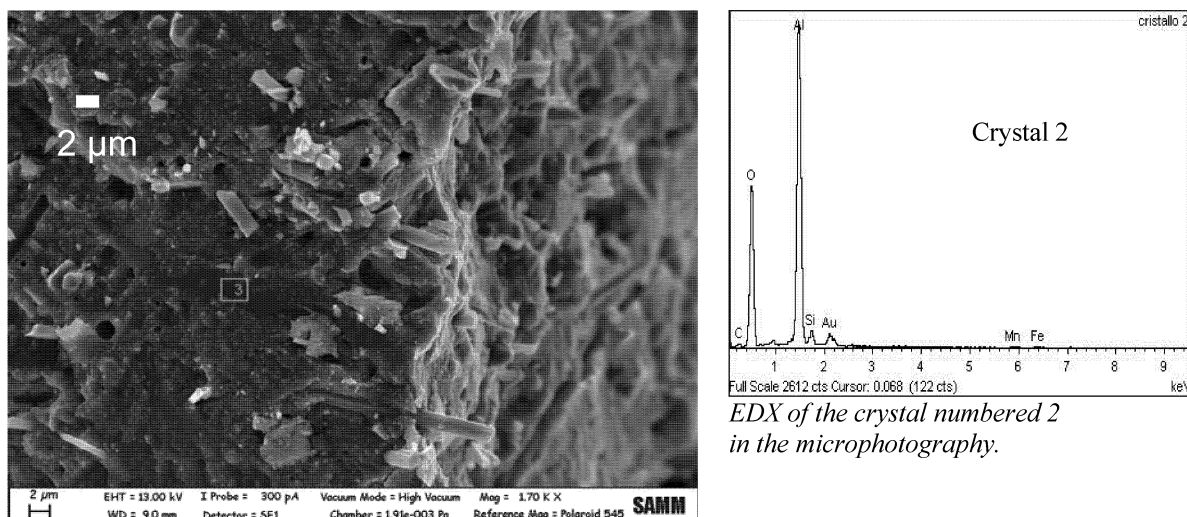*EDX of the crystal numbered 2
in the microphotography.*

*Fig. 9. SEM microphotography of the section of a film in which α- Al_2O_3 crystals (rods) of the oxide (see EDX)
are in evidence.*

3.2 Adhesion

The adhesion analyses reported in figure 10 may provide more indications useful to the characterisation of the film material. The adhesion falls down increasing the thickness in the range of 10-100 μm. The data at first confirm the efficiency of this type of coating where very small thicknesses are necessary for anti-corrosion purposes. The results seem to confirm the previous assumption that identified the hydrolysis reaction as the rate determining step since the adhesion may be promoted by –OH group. Indeed it is right to consider that amounts of silanols may be yet presents in the material due to the slow hydrolysis reaction and/or because they has been formed during the final heat treatment.
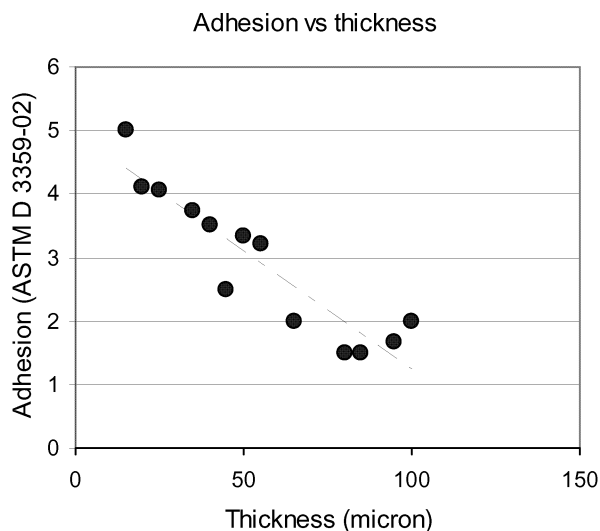

Fig. 10. Film adhesion at increasing thickness.

Their presence create many polar groups that may bind to the Al (or aluminium oxide) surface with many weak second type bonds (mainly H bonds) creating a strong adhesion force. The material more distant from the metal surface has less strong interaction bonds.

CONCLUSION

We reported the characterisation of hybrid coatings obtained through the sol-gel synthesis starting from MTMS and FTMS CS, α-Al$_2$O$_3$, and HNO$_3$ as catalyst. The data have been interpreted using the kinetic information both reported in the literature and explored in a previous research works (Amoriello, Bianco, Eusebio and Gronchi, 2010, Amoriello, 2009). Indeed, considering that the RDS of the sol-gel synthesis is the hydrolysis step of the alkyl alkoxy precursors, unreacted alkoxy groups may remain in the -(Si-O-Si)$_n$- network formed by the fast condensation reaction. Similarly the –OH functions on the CS surface may remain not condensed and the free volume increase. The occurrence of these two facts, which are related to the kinetic behaviour of the reactants, may explain the hardness loss with temperature. A further aspect that was ascertain is the firmly enclosing of the colloidal particles of silica by the heterogeneous condensation while, on the contrary, α-Al$_2$O$_3$ that was unable to participate to the network growth, clearly has a detrimental effect on the hardness.

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