# Evaluation of Microstructure, Phase Composition and Properties of Four Layer Zirconia Coating on API5L Steel as a Function of Different Sintering Condition

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## 1- Introduction

The protection of metals in corrosive environments by ceramic coatings is improved by increasing of refractoriness, corrosion, wear and oxidation resistance. Zirconia has the advantage of high toughness, mechanical strength, chemical inertness and high thermal stability and low thermal expansion coefficient $12–14\times10^{-6}K^{-1}$, which is very close to that of many metals and high temperature alloys. The sol–gel process is one of the most promising methods, because it offers many advantages for the fabrication of coatings, including excellent control of compositional modification and microstructural characterization, a process of low temperature, simplicity and being inexpensive. In our study, $ZrO_2$ thin films were deposited by dip coating using zirconium propoxide as $ZrO_2$ precursor on the API5L carbon steel substrate. The characterization of the coating films after sintering was done by FT-IR, TG/DTA, XRD, SEM, Vickers micro-hardness and potentiodynamic polarization tests.

## 2- Experimental

Samples of carbon steel API5L (composition in Table 1) as a substrate were used in this study. The substrate was polished using 60 and 150 grit SiC paper. In order to remove the polishing debris and degrease the surface, all substrates were ultrasonically cleaned in acetone solution.

**Table 1 Composition of carbon steel API5L grade**

| S | P | Mn | Si | C |
|---|---|---|---|---|
| 0.035 | 0.004 | 0.40 | 0.45 | 0.17 |

The propoxide solution was prepared by stirring zirconium (IV) propoxide (Sigma-Aldrich) and isopropanol at room temperature in the molar ratio 1Zr: 15 isopropanol. Catalyst solution with the molar composition of $1.0H_2O$: $0.6HNO_3$: 7.5 isopropanol was prepared using distilled water, nitric acid and isopropanol. Acetic acid was added drop-wise to the stirred propoxide solution up to the molar ratio of acetic acid to Zr equal to 2.0. The solution was stirred for 2 h to complete the reaction between propoxide and acetic acid. The catalyst solution was mixed with the above solution and stirred for 2h to produce a zirconia sol with the molar ratio of Zr:CHCOOH: $HNO_3$:$H_2O$:Isopropanol equal 1.0:2.0:1.2:2.0:30. $ZrO_2$ thin films were deposited by dipping the substrate for 40s into the solution and a withdrawal constant rate of 6cm/min. A number of samples after each layer of coating up to four layer (GA) and a number of samples after four layer of coating (GB) were sintered at different temperatures of 350 ˚C, 450 ˚C and 550 ˚C for 1h and a heating rate of 10 ˚C/min. The phase structures were identified by X-ray diffraction (XRD, X Pertpro, Holland). The microstructural characterization of the coatings was studied by a scanning electron microscope (SEM: VEGA3 TESCAN, CZECH). Hardness of coating films was measured by Vickers micro-hardness (Micro Hardness Tester KOOPA - MH3). The electrochemical behavior of the samples both before and after coating was investigated by means of open circuit potential (OCP), and potentiodynamic polarization tests (SAMA500) in a 3.5 wt% NaCl solution.

## 3- Results and Discussion

The XRD patterns indicate the amorphous phase for calcined gel at 350˚C (Fig. 1a) and monoclinic and tetragonal phases at 550˚C (Fig. 1b). The existence of the tetragonal phase below 1100˚C without a stabilizer (such as $Y_2O_3$) is due to a confinement effect (particle size of calcined sample at 450˚C smaller than the critical size). In fact, an excess of surface energy in smaller crystallites should stabilize the pure tetragonal phase. Increasing of crystallite size greater than of critical size, for the calcined sample at 550˚C, induces a decrease of surface energy permitting the transformation of tetragonal phase to the monoclinic phase.

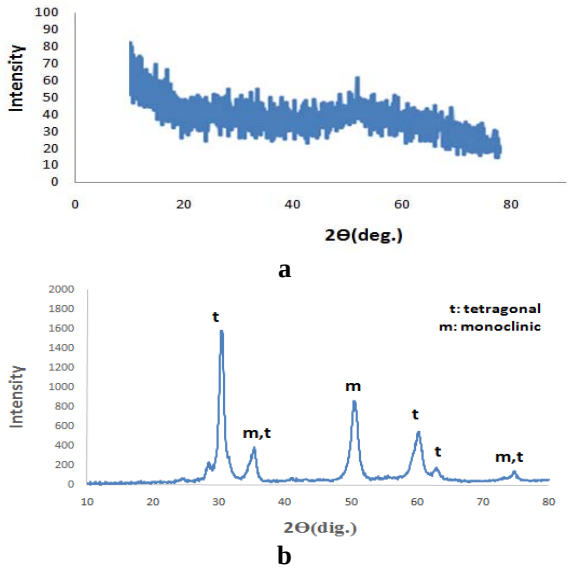


**Fig. 1 XRD pattern for calcined zirconia gel at a) 350˚C and b) 550˚C**

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Figs. 2a, b and c show microstructure of GB coated sample calcined and sintered at temperature from 350˚C to 550˚C for 1h. According to Fig. 2a, the formation of fragments on sintered sample at 350˚C can be due to presence of liquid concentration gradient in GB coated sample. To balance this gradient, liquid diffuses from inside the pores of the solid network (gel) to the outside surfaces causing tensile stresses inside the pores and compression on the solid phase following the sintering of solid network. If the stiffness of the gel is high, the generated stresses can cause the formation of islands or fragments in the structure of coating film during drying cycle. According to Fig. 2b there is less fragmentation and more homogenous structure for coating film sintered at 450˚C that can be due to the crystallization phenomenon. Fig. 2c shows the micro crack at surface of coating due to transformation of tetragonal phase to monoclinic for the coated sample sintered at 550˚C. It is necessary to mention that the GA samples show a more homogeneous and non-fragmental microstructure.

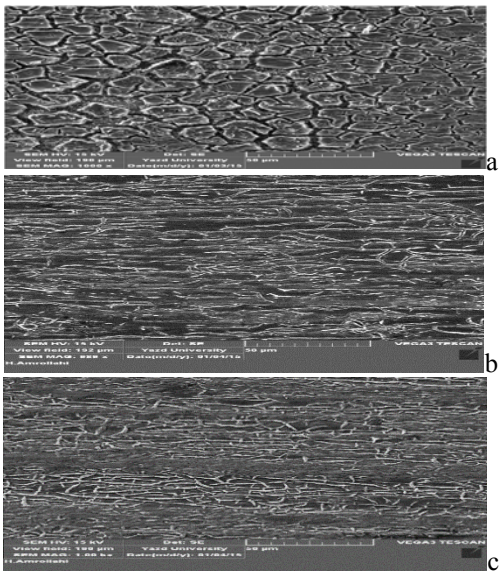

**Fig. 2 SEM micrographs of zirconia coating for the GB sample sintered at a) 350˚C b) 450˚C and c) 550˚C for 1h**

According to the result of micro-hardness measurements (Tables 2 and 3) higher sintering temperatures deliver a higher value of microhardness for coating films. Crystallization of amorphous phase to tetragonal and monoclinic zirconia by increasing of sintering temperature can be responsible for higher microhardness. For the same temperature of sintering, the GA samples show higher values of microhardness for the reason that sintering process was done on each layer. The corrosion behavior of uncoated and $ZrO_2$ coated samples which had been sintered at different temperatures 350 to 550˚C for two group of samples were studied in 3.5 wt% NaCl using potentiodynamic polarization curves and Tafel extrapolation method.
According to Tables 2 and 3 that show the effect of sintering temperature on corrosion behavior of $ZrO_2$ coating, by increasing sintering temperature from 350 to 450˚C, the corrosion potential and corrosion current density ($i_{corr}$) shift towards noble state and a lower value, respectively. The possible reason for improvement of corrosion resistance at sintering temperature of 450˚C can be due to completion of dehydration of zirconium hydroxide and higher densification of sintered coating. It seems that 350 ˚C is not enough for removing of zirconium hydroxide completely. By increasing the temperature from 450 to 550 ˚C due to the associated volume expansion in the tetragonal to monoclinic phase transformation, the corrosion resistance is reduced. Appearance of cracks in the coating film act as penetrating channels for the corrosion of substrate. For all of the sintering temperatures, the corrosion resistance of coated samples is higher than uncoated samples.

**Table 2 The electrochemical parameters derived from potentiodynamic polarization curves (GA samples)**

| samples | $I_{corr}$(A/cm$^2$) | $E_{corr}$(mv) | HV |
|---|---|---|---|
| 350 $^0$C | $6*10^{-7}$ | -0.43 | 213.3 |
| 450 ˚C | $3.5*10^{-7}$ | -0.33 | 242 |
| 550˚ C | $7.5*10^{-7}$ | -0.50 | 250 |
| Uncoated sample | $4*10^{-6}$ | -0.83 | 180 |

**Table 3 The electrochemical parameters derived from potentiodynamic polarization curves (GB samples)**

| samples | $I_{corr}$(A/cm$^2$) | $E_{corr}$(mv) | 206 |
|---|---|---|---|
| 350 $^0$C | $9*10^{-7}$ | -0.652 | 233 |
| 450 ˚C | $8.3*10^{-7}$ | -0.63 | 233 |
| 550˚ C | $7.9*10^{-7}$ | -0.52 | 247 |
| Uncoated sample | $4*10^{-6}$ | -0.83 | 180 |

## 4- Conclusions

1- Calcined gels at 350˚C have a non-crystalline state but increasing the calcination temperature to 450˚C and 550˚C, tetragonal and tetragonal/ monoclinic phases appeared, respectively.
2- A denser and more homogenous microstructure is obtained for samples sintered at 450˚C after each coating layer up to four layers (GA samples) but for sample sintered after four coating layer (GB samples), there is the formation of islands or fragments in the structure of coating film during drying and sintering processes.
3- By increasing of sintering temperature from 350 to 550 ˚C, the microhardness of coating films for both GA and GB samples is increased.
4- By increasing of sintering temperature from 350 to 450 ˚C, the corrosion resistance is improved but higher than 450˚C, there is an increasing corrosion current density of coating samples for both GA and GB samples.