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Sol-gel SiO_2 coatings doped with Nd_2O_3

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Non-doped and doped with Nd_2O_3-SiO_2 protective layers have been spin coated on low-carbon content constructions steel plates by the sol-gel method. The deposition-drying cycles have been repeated seven times and thereafter the coatings have been thermally treated at 300°C. Scanning electron microscopy (SEM) has been applied to investigate the surface morphology. The resistance of SiO_2 coated steels were examined in NaCl corrosive medium. It has been demonstrated that Nd_2O_3 dopant exerts positive effect upon the chemical resistance of the SiO_2 coatings.

Keywords: sol-gel coatings, chemical resistance, silica, Nd_2O_3.

INTRODUCTION

Unprotected metal surfaces are being exposed to the continuous or periodically unfavorable effect of severe external factors: hard abrasive particles, different aggressive chemical agents, extreme thermal variations, increased pressure and others. It is necessary to prevent the corrosion processes occurring in metals [1, 2] and this requires appropriate technology solutions, providing effective protection of load-bearing metal constructions, manufacturing equipment and factory installations in various fields of technology and industry.

Variety of technological methods to prepare coatings with diverse structures such as CVD, PVD, electrophoresis, sol-gel methods etc. have been applied so far [3–10]. The coatings possess specific thermal [11], optical [12], anti-corrosion and other properties [7, 8, 13–15], which are useful under various operating conditions. The specific features of the metals, the state of the surface, the peculiarities of working environment and the other factors determine the appropriate type of coverage and the optimal preparation method.

The coatings obtained by sol-gel process are suitable for effective protection of metallic surfaces from corrosion [16]. They significantly prolong the long-term durability of metals [17–19]. The sol-gel technology has been applied to the preparation of anticorrosive protective coatings on a steel [16], aluminium [20] and other metals.

There appear many advantages when using sol–gel coatings, several of the most important features are: (i) Sol–gel processing temperature is generally low, frequently close to room temperature. Thus thermal volatilization and degradation of entrapped species, such as organic inhibitors, is minimized. (ii) It is possible to cast coatings in complex shapes. (iii) The sol–gel method is waste-free so it does not require a stage of washing away impurities.

Several oxides possessing good chemical and thermal stability such as SiO_2, CeO_2, ZrO_2, TiO_2, Al_2O_3 are suitable for achieving corrosion protection [21].

Vasconcelos et al. [22] have been investigating the acidic corrosion resistance of sol–gel silica films deposited on AISI 304 stainless steel. In view of previous corrosion investigation experience it is well known that adding small amounts of dopants – for example rare earth elements (Ce, La etc.) greatly improves the corrosion resistance [23]. We have not found in the available literature information concerning the resistance of Nd_2O_3 doped SiO2 films in the NaCl medium.

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The aim of this work is to investigate the effect of neodymium dopant in SiO_2 sol-gel coatings on the structure and their chemical resistance in corrosive NaCl medium.

EXPERIMENTAL

The substrates for sol-gel coatings were low carbon content constructions steel USt 37-1 plates (DIN 17 100) with perlite – ferrite type of structure. They were degreased in hot acetone for 5 min in ultrasonnic bath, then they were dried at 60°C in furnace. Ethanolic solution of tetraethyl orthosilicate (TEOS, 99.5%, Merck),was hydrolyzed with water-ethanol mixture, (sol A) at a molar ratio TEOS:H_2O=4.7. Hydrochloric acid (37%) was used to catalyse the hydrolysis process. This solution was used for deposition of non-doped SiO_2 coatings. Sol B was prepared by dissolving of Nd_2O_3 in small quantity of HNO_3, followed by dissolving it into deionized water in order to obtain final concentration of neodimum salt 0.01 mol/L. The Nd_2O_3 doped SiO_2 coatings were produced using a mixtures of sol A and sol B. The concentration of the metal dopant was calculated in such a way as to give 0.14 wt% and 0.28 wt% Nd_2O_3 with respect to SiO_2 amount.

The substrates were coated by spin-on technique at a constant speed of 800 rpm for 20 s. The coating was then dried at 100°C for 20 min.These steps were repeated 7 times in order to obtain desirable films thickness. The final thermal treatment step was carried out in temperature-programmable oven at 300°C. The temperature was increased at a constant rate of 3°C/min. After 1 hour the samples were cooled naturally down to room temperature.

The surfaces of the so prepared samples were investigated by scanning electron microscope JCXA 733 JEOL (SEM).

The investigated samples were exposed to the action of salty solution of 3.5% NaCl at 35°C (EN ISO 10289/2006) in the course of 12 hours in order to study their chemical resistance.

RESULTS

The surfaces of SiO_2 films were examined using a Scanning Electron Microscope. Figure 1 shows SiO_2 films doped with 0.28 wt% Nd_2O_3. The surface of the film is relatively dense without any visible cracks. The SEM micrographs of the coatings after carrying out resistance test in NaCl are shown in Fig. 2. It can be seen that on the surface of non-doped SiO_2 there appear numerous visible cracks and the film is detached in some places (Fig. 2a). The Nd_2O_3 doped silica coatings exhibit restricted

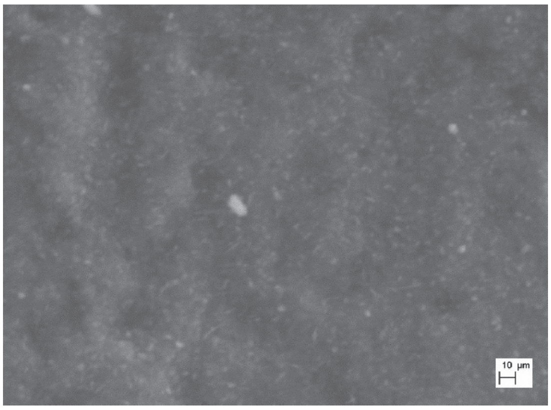

Fig. 1. SEM photograph of SiO_2 fresh films doped with 0.28% Nd_2O_3.

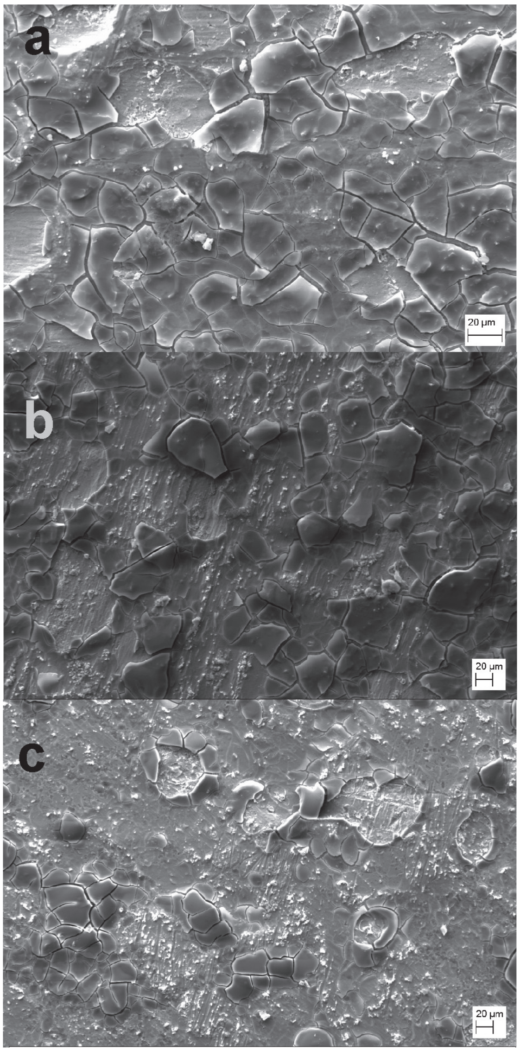

Fig. 2. SEM photograph of a) SiO_2 films after chemical resistance test, b) SEM photograph of SiO_2 films doped with 0.14% Nd_2O_3 after chemical resistance test and c) SEM photograph of SiO_2 films doped with 0.28% Nd_2O_3 after chemical resistance test.

lower number of cracks having smaller size. The films are more strongly adhered to the steel substrate surface in comparison with the non-doped SiO_2 coatings (Fig. 2b, c).

On the basis of the above mentioned results it can be concluded that the Nd_2O_3 doped silica coatings resist better to the NaCl corrosive attack than the non-doped coatings, which fact is probably due to the corrosion inhibiting effect of Nd^{3+} ions in the SiO_2 coatings similar to that of cerium ions [24] .These preliminary results about the chemical resistance of doped SiO_2 coatings are promising and they give us the reason to extend the scope of the experiments further involving electrochemical measurements for estimation of corrosion resistance.

CONCLUSIONS

The sol–gel spin-coating technique was successfully applied to obtain Nd_2O_3 doped SiO_2 coatings on steel substrates. The scanning electron photographs of the doped films reveals smoother surface in comparison with the non-doped films after chemical resistance test in corrosive NaCl medium. It has been revealed that Nd_2O_3 doped silica coatings can provide a higher chemical resistance.

REFERENCES

1. R. G. Buchheit, R.P. Grant, P. F. Hlava, B. Mcjebzue, G.L. Zender, *J. Electrochem. Soc.*, **144**, 2621 (1997).
2. T. L. Metroke, R.L. Parkhill, E. T. Knobbe, *Prog. Org. Coat.*, **41**, 233 (2001).
3. T. Kubota, N. Akao, N. Har, K. Sugimoto, *J. Jpn. Instrum. Methods*, **60**, 980 (1996).
4. K. Ohashi, K. Miyake, *Mater. Chem. Phys.*, **54**, 365 (1998).
5. F. Perdomo, P. De Lima-Neto, M.A. Aegerter, L.A. Avaca, *J. Sol-Gel Sci. Technol.*, **15** , 87 (1999).
6. B. Ferrari, R. Moreno, *J. Electrochem. Soc.*, **147**, 2987 (2000).
7. L. Fedrizzi, F. J. Rodriguez, S. Rossi, F. Deflorian, R. Di Maggio, *Electrochim. Acta*, **46**, 3715 (2001).
8. J. P. Holgado, M. Perez-Sánchez, F. Yubero, J. P. Espinós, A. R. González-Elipe, *Surf. Coat. Technol.*, **151–152**, 449 (2002).
9. R. López Ibáñez, J. R. Ramos Barrado, F. Martín, F. Brucker, D. Leinen, *Surf. Coat. Technol.*, **188 – 189**, 675 (2004).
10. R. Romero Pareja, R. López Ibáñez, F. Martín, J.R. Ramos-Barrado, D. Leinen, *Surface & Coatings Technology*, **200**, 6606 (2006).
11. P. K. Wright, A. G. Evans, *Curr. Opin. Solid State Mater. Sci.*, **4**, 255 (1999).
12. Q. Zhang, J. Shen, J. Wang, G. Wu, L. Chen, *Int. J. Inorg. Mater.*, **2**, 319 (2000).
13. H. Hasuyama, Y. Shima, K. Baba, G.K. Wolf, H. Martín, F. Stippich, *Nucl. Instrum. Methods Phys. Res.*, **B 127–128**, 827 (1997).
14. A. R. Di Giampaolo, Y. González, D. Gutiérrez-Campos, *Adv. Perfom. Mater.*, **6**, 39 (1999).
15. F. Martín, M.C. López, P. Carrera, J.R. Ramos-Barrado, D. Leinen, *Surf. Interface Anal.*, **36**, 8 (2004).
16. Duhua W., Gordon P., Bierwagen, *Sol-gel coatings for corrosion protection, Progress in Organic Cotings*, **64**, 327 (2009).
17. G.P. Bierwagen, L. He, J. Li, L. Ellingson, D.E. Tallman, *Progress in Organic Coatings*, **39**, 67 (2000).
18. C. J. Brinker, A.J. Hurd, P.R. Shunrk, *J. Non-Cryst. Solids*, **147**, 424 (1992).
19. J. D. Wright, N. A. J. Sommerdijk, *Sol–Gel Materials Chemistry and Applications*,CRC Press, OPA Overseas Publishers Association (2001).
20. M. Guglielmi, *J. Sol–Gel Sci. Technol.*, **8**, 443 (1997).
21. D. Wang, G. P. Bierwagen, *Progress in Organic Coatings*, **64**, 327 (2009).
22. D. C .L. Vasconcelos, J. A. N. Carvalho, M. Mantel, W. L. Vasconcelos, *J. Non-Cryst. Sol.*, **273**, 135 (2000).
23. M. Garcia-Heras, A. Jimenez-Morales, B. Casal, J.C. Galvan, S. Radzki, M.A. Villegas, *J. Alloys Comp.*, **380**, 219 (2004).
24. A. Pepe, M. Aparicio , A. Dur´an, S. Cer´e, *J. Sol-Gel Sci Technol.,* **39,** 131 (2006).

ЗОЛ-ГЕЛНИ ПОКРИТИЯ ОТ SiO_2, ДОТИРАНИ С Nd_2O_3

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(Резюме)

Недотирани и дотирани с Nd_2O_3 – SiO_2 защитни покрития са отложени върху нисковъглеродни стоманени подложки чрез зол-гел метод. Циклите на отлагане/сушене бяха повторени седем пъти, след което покритията са термично третирани при 300°C. Сканираща електронна микроскопия е приложена за изследване на морфологията на повърхността. Устойчивостта на покритията върху стомана е изучена в корозионна среда от NaCl. Демонстрирано е, че въвеждането на допант Nd_2O_3 в покритията от SiO_2 има положителен ефект върху химическата им устойчивост.