Comparative of micro and nano-structured coatings for high temperature oxidation in steam atmosphere

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ABSTRACT

For many high-temperature applications, coatings are applied in order to protect structural materials against a wide range of different environments: oxidation, metal dusting, sulphidation, molten salts, steam, etc. The resistance achieved by the use of different kind of coatings, such as functionally graded material coatings, has been optimized with the latest designs. In the case of supercritical steam turbines, many attempts have been made in terms of micro-structural coatings design, mainly based on aluminides, and other diffusion coating systems in order to consider alternatives, nano-structured coatings based on Cr and Al compositions and deposited by a physical vapor deposition technique, were assessed to high-temperature oxidation resistance in steam environments. The oxidation kinetics where analyzed for up to 2,000 h at 650 ^oC by means of gravimetric measurements. The evaporation behavior was also analyzed by thermogravimetric-mass spectrometry.
Excellent results where observed for some of the nano-structured coatings tested. Those results where compared to results obtained for micro-structured coatings. Based on that comparison, it was deduced that the nano-structured coatings have a potential application as protective systems in high-temperature steam environments.

I. Introduction

Future power generation steam turbines are being designed to meet the stringent environmental regulations, ensuring plant reliability, availability and maintainability without compromising cost. Large steam power plants today achieve roughly 46 % of efficiency (see Fig. 1) but higher values can be achieved by increasing temperature. Therefore, the operating temperature is expected to rise from 550 to 650 ^oC for supercritical steam turbines, and further to 700 ^oC, for ultra supercritical steam turbines. From a materials design perspective two approaches are being followed in order to achieve this goal: (1) the development of new materials with both optimum mechanical properties (creep) and oxidation resistance at higher temperatures and (2) the use of coated components.
The ferritic steels commonly used in the manufacture of steam turbine components at the present achieve adequate mechanical properties, such as good creep strength. Tests have been carried out in different temperatures and steam atmospheres in order to assess their high-temperature oxidation resistance [1]. At temperatures higher than 550 ^oC, steam oxidation causes the formation of very thick oxide scales that will eventually spall with consequent metal cross-section loss and producing erosion problems and component blockage [2]. Therefore, temperatures above 600 ^oC are not applicable with the present steels in steam power plants. At these temperatures diffusion processes control the creep and the oxidation processes beneath the oxide scale.
Some work in this field was performed in the US around 30 years ago, particularly addressing the protection of boiler tubes of 2.25 wt.% Cr steels and austenitic stainless steels. The range of coatings and surface treatments investigated included chromizing [3], chromate conversion, application of a Cr_2O_3 ceramic coating, and application of layers of aluminium, electroless nickel or silicon [4, 5]. At that time, it was concluded that the only satisfactory solution was achieved using chromizing and/or chromate conversion treatments. However, chromate conversion processes have been banned in several countries due to the health and

environmental hazards related to Cr^{+6}, and on the other hand, pack chromizing is carried out at temperatures too high (>800 ^oC) for the ferritic steels currently employed in the manufacture of steam turbine components.
After a gap of some 20 years, no other published work appeared in the literature, until 1998, when within the context of activities carried out in COST 522, a feasibility study regarding the use of coatings to prevent component oxidation in future supercritical high temperature steam plants (650 ^oC) was initiated for the first time in Europe [6]. Since then, several groups have begun exploring a number of coating process and materials including formers of all three known protective oxides, Al_2O_3, Cr_2O_3 and SiO_2. Available results have demonstrated that coatings can indeed significantly reduce steam oxidation at 600–750 ^oC. Studied coatings include aluminides deposited by slurry application [7], chemical vapour deposition CVD [8–10] and pack cementation [11, 12]. Less data is available regarding Si [13] and Cr [14] diffusion coatings, which should be more stable regarding degradation by interdiffusion but require high temperatures for their application process.

II. Experimental Procedure

A P92 steel was used as the substrate in this study. The nominal composition of this steel is presented in Table 1. The substrates were coated by chemical vapor deposition in a fluidized bed reactor (CVD-FBR) as micro-structured coating, and CrAlYN, CrN–CrAlYN, ZrN–CrZrN–CrN and multilayered CrN–ZrN nano-structured coatings by PVD. The coupons prior coating process were ground with SiC abrasive paper down to a 600 grind finish. Then, the coupons were oxidized at 650 ^oC for up to 2,000 h in 100 % H_2O gas, in order to reproduce in a first approach the operation parameters of supercritical turbine engines. After the oxidation testing, cross sections of the samples were observed by a scanning electron microscope (SEM). The oxide scales and stability of the coatings were analyzed by glow discharge optical emission spectroscopy (GDOES). The volatility of coating components in steam were analyzed by means of thermogravimetric (TG)-mass spectrometry in a close steam loop testing device.

III. Results and Discussion

In order to analyze the effect of composition, thickness and layered structure in the nano-coatings, the following four types of coating structures were analyzed (Fig. 2). Figure 3 shows the mass gain per unit area versus oxidation time of the tested nano-structured coatings compared to that of bare P92 steel.
Taking these measurements into account, the best performance corresponds to the CrN/CrAlYN coating since almost no mass change was found, followed by the CrAlYN coating (Fig. 3b). The oxidation behavior of both coatings showed a similar tendency, with an initial increase in weight in the first about 300 h of oxidation, after which it stabilizes to values significantly lower than those measured for the steel up to 2,000 h. On the other hand, the multilayered CrN/ZrN coating evidenced a weight lost in the first stage of the oxidation, which is generally related to the formation of non-protective compounds or delamination of the coating. After that, the weight change suffers negligible variations with time of exposure up to 1,600 h. Finally the ZrN/CrZrN/CrN coating displayed an oxidation rate close to that of the bare steel.
In Fig. 4, the different morphologies observed in the cross sections of the four nano-structured coatings after selected oxidation times at 650 ^oC in 100 % steam atmosphere are shown. In the micrograph of the CrAlYN coating (Fig. 4a), which is the thinnest and single layered, it is possible to observe the remaining oxidized coating after 2,000 h of oxidation and emerging oxidation products of the underlying substrate that form nodules on the surface. However, the CrN/CrAlYN coating of approximately 17 µm of thickness and two layered, appeared almost unaffected after a similar time oxidation.
When comparing the micrographs of the ZrN/CrZrN/CrN and the multilayered CrN/ZrN coatings (Fig. 4c, d) two different behaviors can be observed. The sequential deposition of

individual CrN and ZrN layers formed a nano-structured design that is not stable under the conditions studied. After 1,000 h of oxidation the cross-section micrograph reveals partial coating delamination, in agreement with the weight-loss reported previously. Nevertheless the remaining coating, mainly the first deposited CrN layer, is sufficiently protective to avoid the oxidation of the steel substrate. On the other hand, oxidation of the ZrN/CrZrN/CrN coating leads to the destruction of the layered design by diffusion of ionic metallic species, including O from the atmosphere and Fe from the substrate.
GDOES analysis was performed, in order to analyze the nano-structured coating after oxidation. In Fig. 5 spectra of the CrN/CrAlN coating before and after oxidation to 700 h are presented as examples. The formation of a superficial oxide layer was commonly observed after oxidation. In this particular case the grain boundaries of the coating allowed the inward migration of O through it, developing an oxynitride Cr layer that prevents further oxidation of the substrate.
In order to further study the stability of the coatings and formation of volatile corrosion products, TG-mass spectrometry was performed. In Fig. 6 the mass spectrum from the ZrN/CrZrN/CrN coating obtained during oxidation at 650 ^{o}C in 60 %Ar/40 %H_2O atmosphere for 120 h is shown as an example. Here, the evaporation of Fe oxide reveals the poor protection of the coating against oxidation, which was evident from the oxidation kinetics study and cross-section micrographs.
For the purpose of comparison Fig. 7 shows a FeAl micro-structured coating obtained by CVD-FBR modified by means of a diffusion treatment for 2 h at 550 ^{o}C with different additions of Mn and Si in order to enhance the FeAl resistance against steam.
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Also in this case, and as reported previously in the literature [21], the oxidation resistance was clearly enhanced with respect to that of the bare P92 steel substrate (Fig. 8). Additionally, to the protection of the FeAl coating there is a beneficial effect of Mn, acting as a reactive element and retarding the diffusion processes during oxidation.
In order to analyze the oxidation resistance against steam, a comparative study was done at 1000 h for nano and micro-structured coatings tested in steam at 650 ^{o}C. Figure 9 shows the results of that evaluation. It is seen that, the nano and micro structured coatings show similar behavior, i.e. CrAlYN with Al–Mn micro-structured. Thus, the nano-structured coatings studied have promising behaviour to be used in steam turbine applications with many advantages, such as to prevent detrimental interdiffusion processes in the microcoating-substrate system.

IV. Conclusions

1. The nano-structured coatings tested (CrYAlN, CrN/CrYAlN and ZrN-CrZrNCrN) have shown a good oxidation resistance in steam environments in comparison with FeAl micro-structured coatings on P92 ferritic-martensitic steel.
2. Effect of layered structure on chromium composition have a beneficial effect in nano-structured coatings.
3. Oxidation resistance of some micro and nano-structured coatings shows similar results. The key factor is that the nano-structured coatings have not the interdiffusion effect as the

micro structured had.

4. Volatilization processes are in much lower scale (few magnitude orders), in comparison with oxidation processes, that form solid protective scales on the different coating systems studied. Moreover, in some cases, as the ZrN multilayer coating, it accelerates the volatilization of the oxide scale in the nano-structured coating studied, due to its spallation and detachment from the substrate surface.

Acknowledgments

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References

(1) P.J. Ennis, W.J. Qudakkers, Int. J. Press. Vessels Piping 84 (2007) 75
(2) G. Scheffknecht, Q. Chen, 5th Int. Parsons Conf., July 2000, Cambridge
(3) C. Berger, R.B. Scarlin, K.H. Mayer, D.V Thornton, S.M Beech, Materials for Advanced Power Engineering, Liege, 1994, Kluwer Academic Press, Dordrecht, Part I, 47
(4) J.C. Nava-Paz, R. Knödler, Materials for Advanced Power Engineering, Liege , Nov. 1998
(5) V. Lepingle, G. Louis, D. Petelot, B. Lefebre, J.C. Vaillant, Eurocorr Conference London, Sept. 2000
(6) J.P.T. Vossen, P. Gawenda, K. Rahts, M. Röhrig, M. Schorr, M. Schütze, Materials at High Temperatures 14 (1997) 387
(7) P.J. Ennis, A. Zielinska-Lipiec, O. Wachter, A. Czyrska-Filemonowicz, Acta mater. 45 (1997) 4901
(8) B.A. Pint and Y. Zhang, Mater. Corr. 62 (2011) 549
(9) K. Zabelt, Technische Überwachung 39 (1998) 11
(10) R. Blum, Q. Chen, C. Coussement, J. Gabrel, C. Testani, L. Verelst, VGB Kongreß Essen, Okt. 2000
(11) R. Knödler, P.J. Ennis, BALTICA V conference, Porvoo, Finland, June 2001
(12) ORDICO project in GROWTH , Ref. Nr.: G4RD-2000-00319
(13) P. Niranatlumpong, H.E. Evans, Oxidation of Metals 53 (2000) 241
(14) C.V. Cojocaru, D. Lévesque, C. Moreau and R.S. Lima, Surf. Coat. Techn. 216 (2013) 215–223
(15) J.A. Haynes, K.A. Unocic and B.A. Pint, Surf. Coat. Techn. 215 (2013) 39
(16) A. Agüero, R. Muelas and V. Gonzalez, Materials and Corrosion, 59 (2008) 393
(17) W. Gao, Z.Liu and Z. Li, Adv. Mater. 13 (2001) 1001
(18) W. Gao and Z. Li, Materials Research 7 (2004) 175
(19) P.E. Hovsepian, A.P. Ehiasarian, I. Petrov, Surface Engineering 26 (2010) 610
(20) S. Tsipas, J.M. Brossard, M.P. Hierro, J.A. Trilleros, L. Sánchez, F.J. Bolívar, F.J. Pérez, Surf. Coat. Techn. 201 (2007) 4489

Tables

	Cr	V	Ni	Mo	Mn	Si	W	C	Fe
ASTM P92	9.07	0.2	0.06	0.46	0.47	0.02	1.78	0.1	87.84

Table 1.- Composition of the ferritic steel P92 used as substrate (% in weight).

Figures

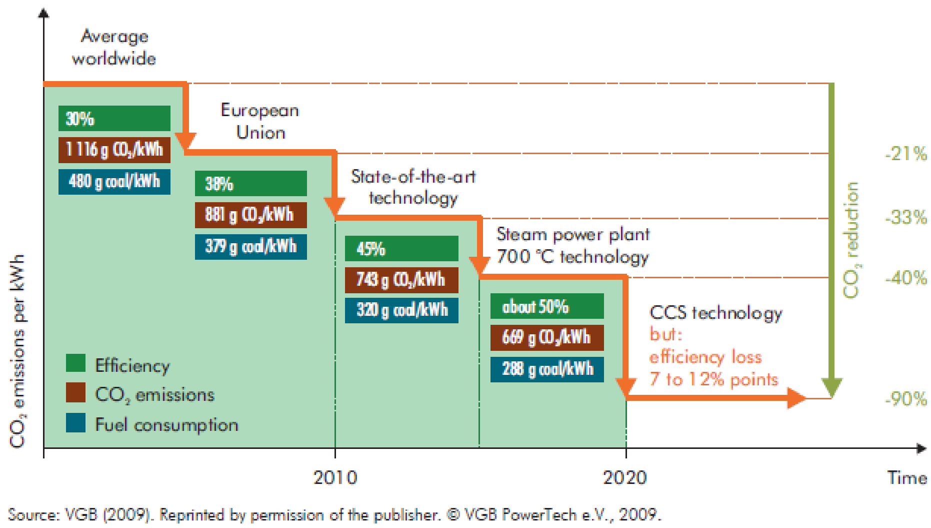


Figure-1.- Efficiency of different power technologies *(after: VGB Power Tech 1 (2009), 38).*

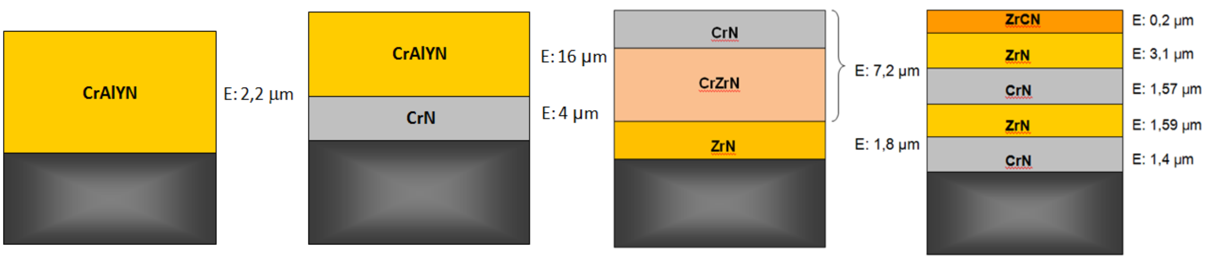


Figure-2.- Nano-coatings structured deposited by PVD and layers thicknesses (E).

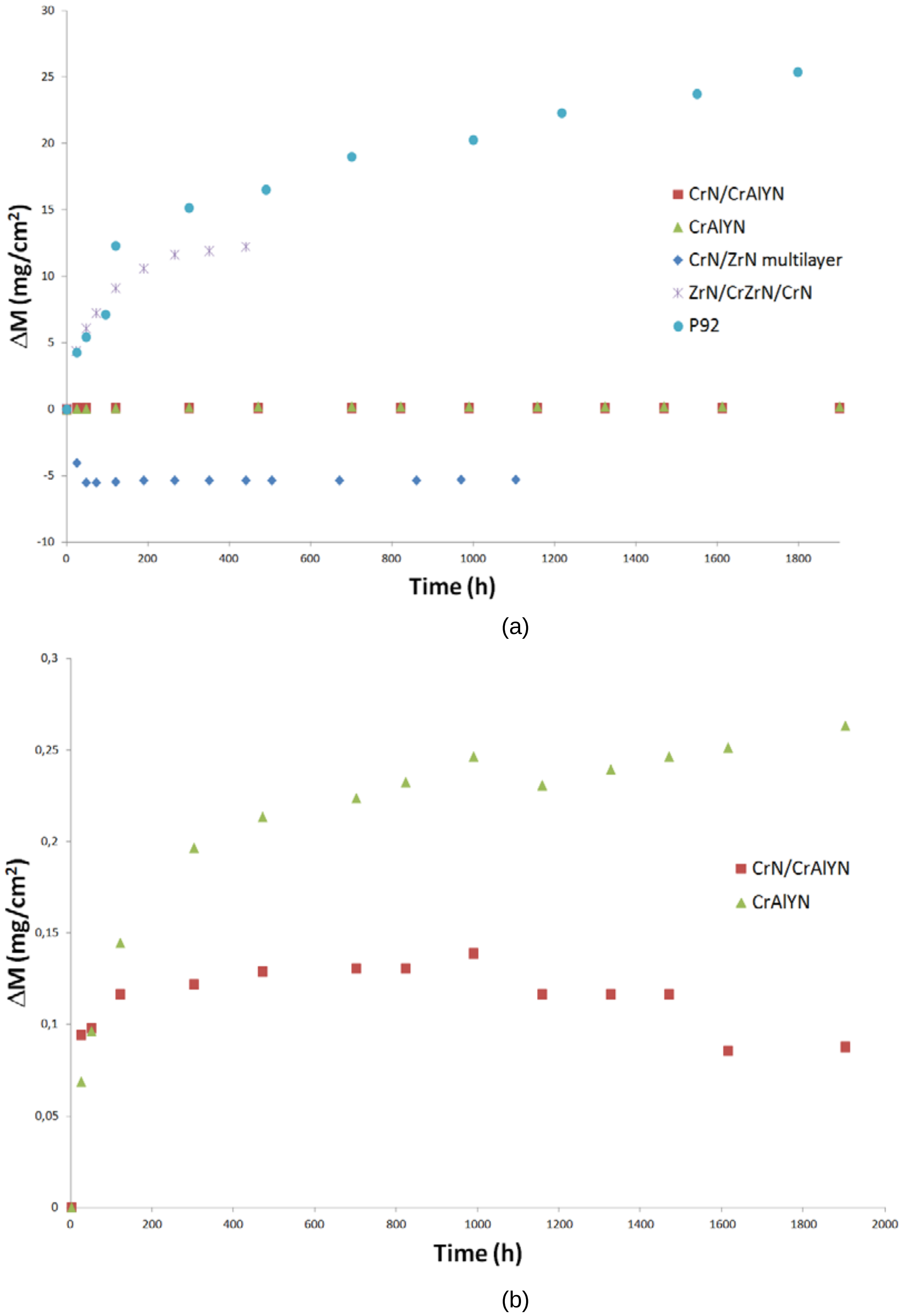


Figure 3.- Gravimetric evolution with oxidation time of the tested nano-structured coatings in steam at 650ºC.

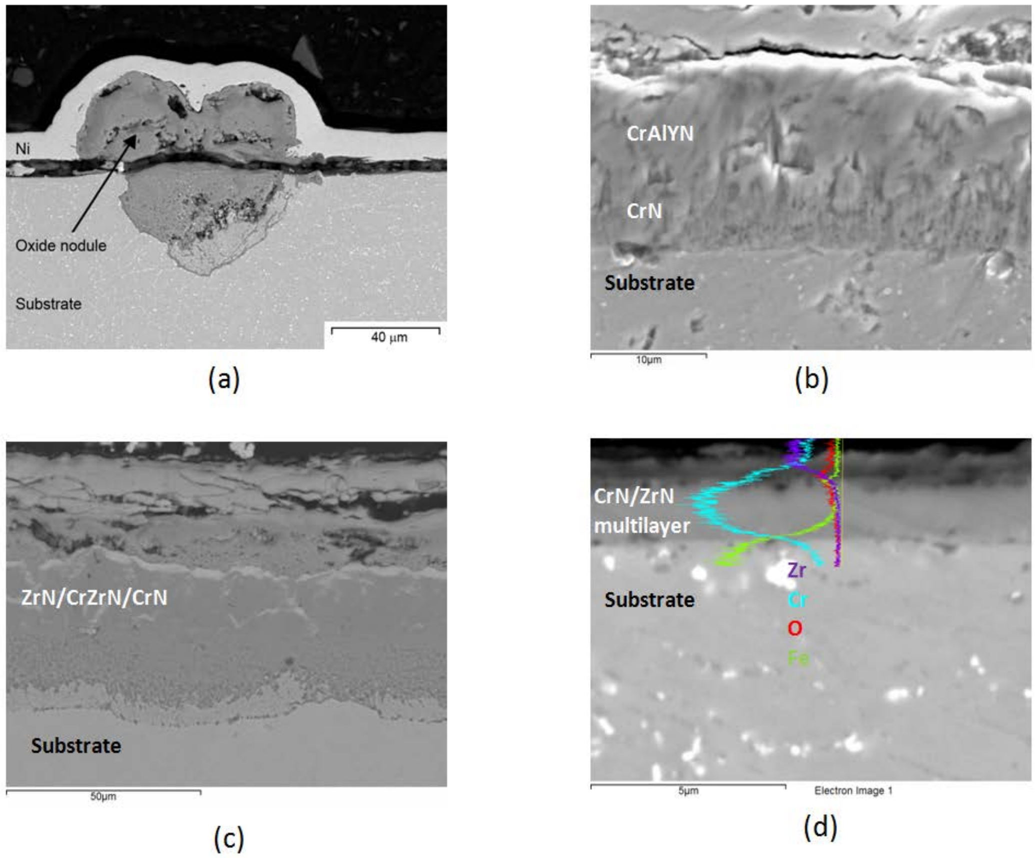
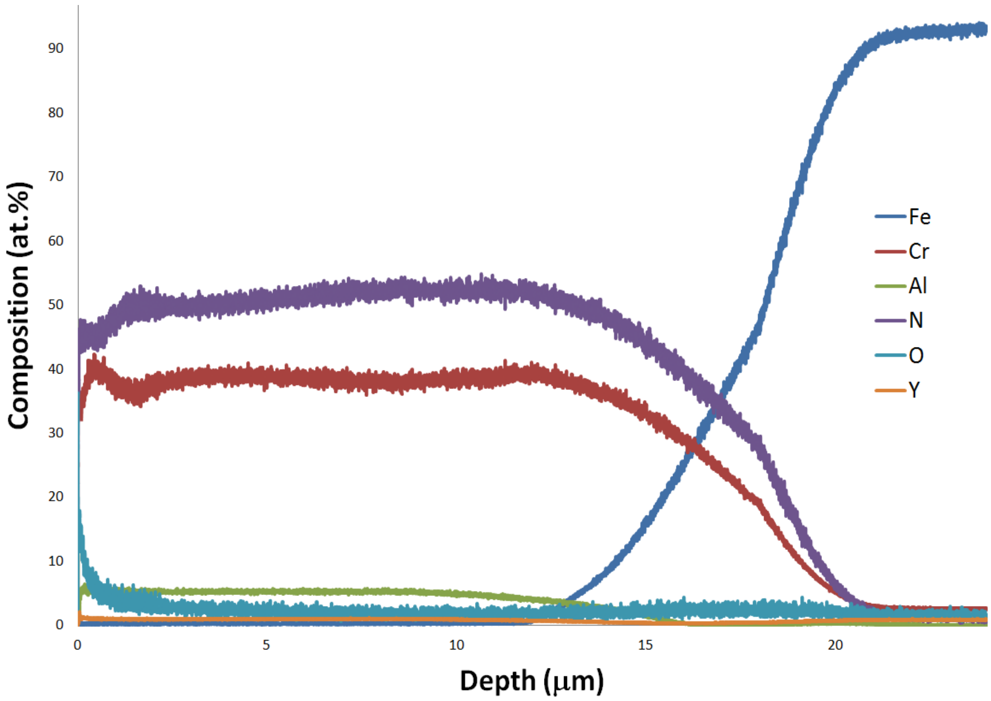
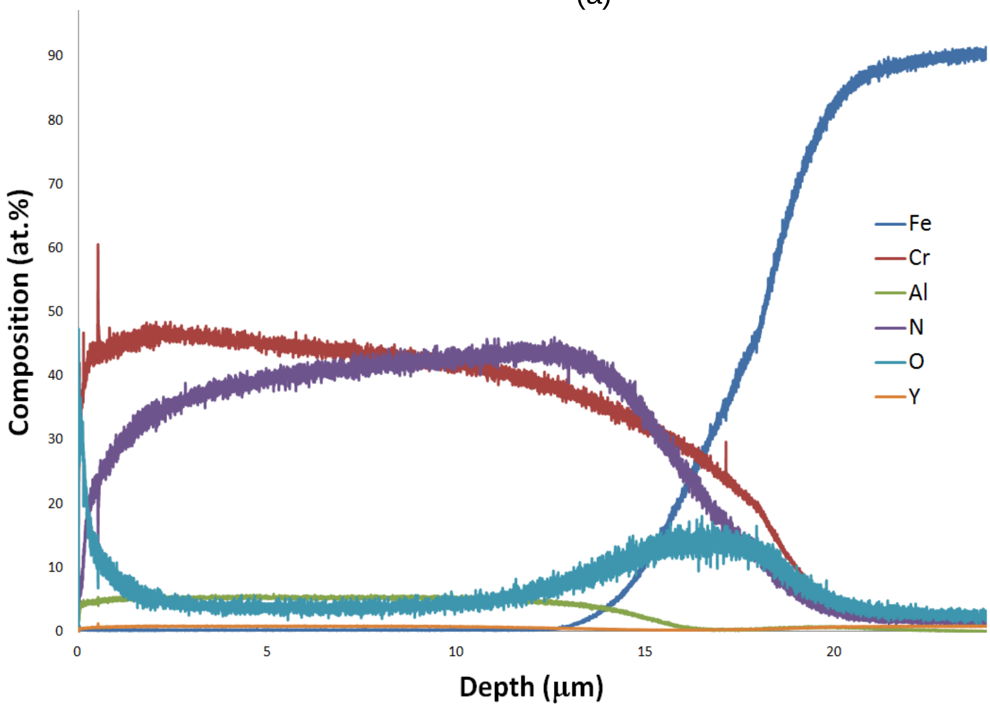


Figure 4.- Nano-structured coatings oxidized in 100% steam atmosphere at 650ºC: a) CrAlYN and b) CrN/CrAlYN oxidized to 2000 h;,c) ZrN/CrZrN/CrN oxidized to 48 h, and d) CrN/ZrN multilayer oxidized to 1000 h.



(a)



(b)

Figure 5.- GDOES analysis of nano-structured CrN/CrAlYN coating before and after 700 h of oxidation at 650ºC in 100% steam atmosphere.

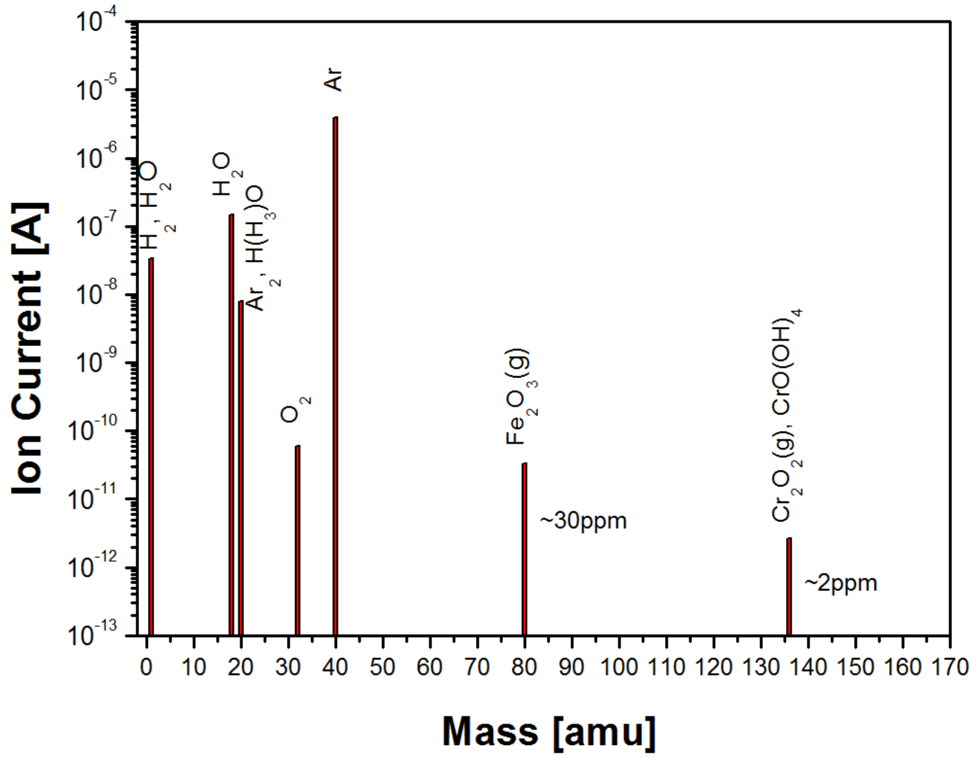


Figure-8.- Mass spectrometry of the ZrN/CrZrN/CrN coating at 650°C in 60%Ar/40%H_2O atmosphere for 120 h **(volatile species formed).**

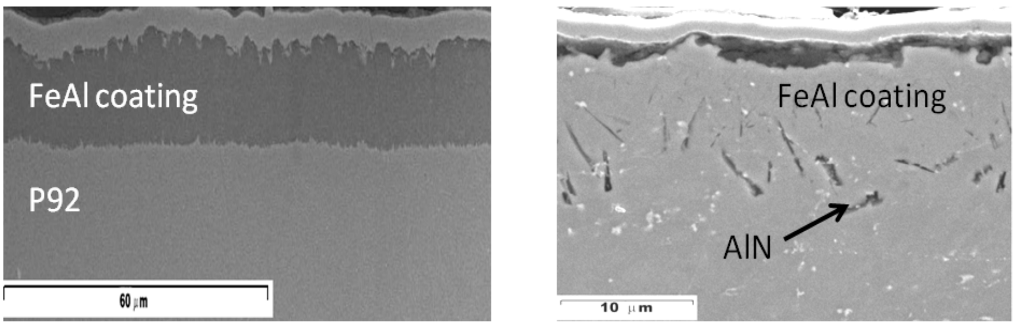


Figure 9.- FeAl micro-structured coating with Mn additions (diffusion treatment for 2 h at 550°C) by CVD-FBR before (left) and after (right) 1000 h of oxidation in steam at 650ºC.

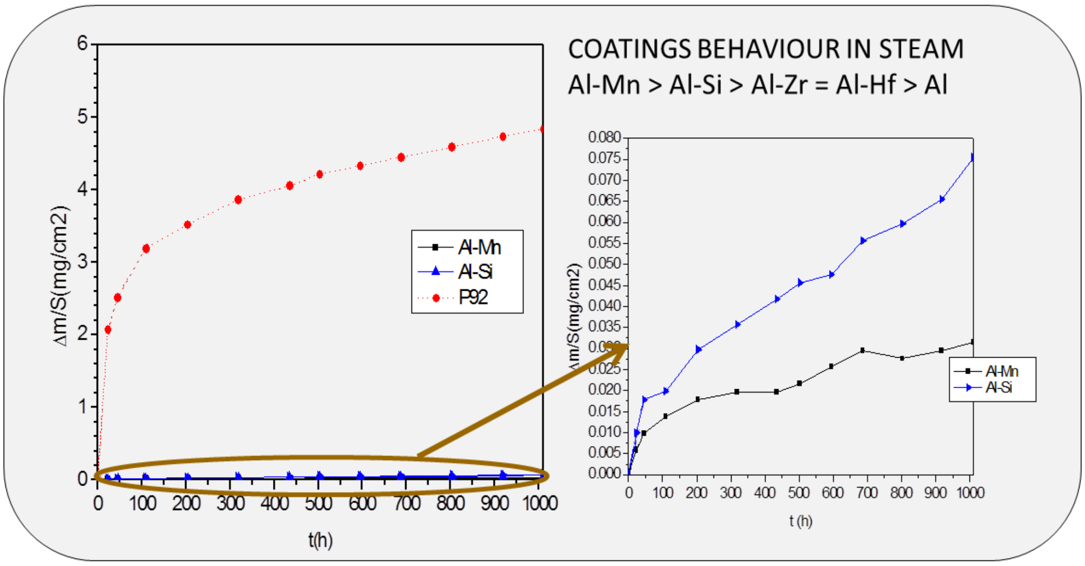


Figure 10.- FeAl micro-structured coating by CVD-FBR in steam at 650ºC for 1000 h.

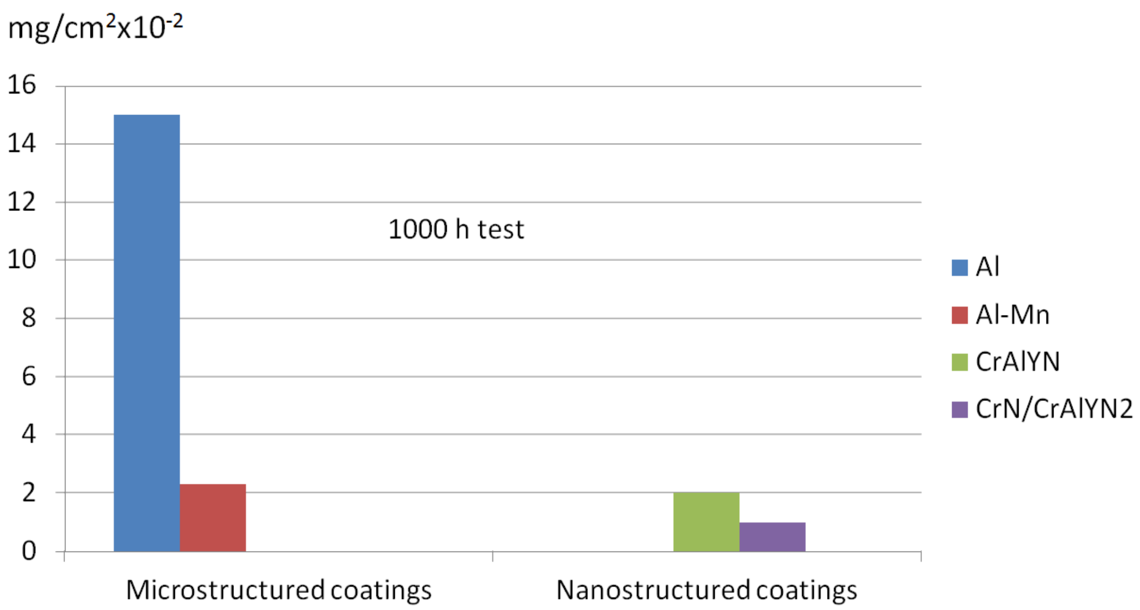


Figure 11.- Comparison of oxidation behavior against steam at 650ºC for 1000 h for micro and nano-structured coatings.