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New type AlMo-, AlTi- or Si-based magnetron sputtered protective coatings on metallic substrates

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Three different types of refractory protective coatings deposited by means of reactive and/or non-reactive magnetron sputtering have been developed in the Technical University of Lodz in co-operation with the Academy of Mining & Metallurgy in Cracow: metallic AlMo- and AlTi- or covalent bonded Si-based coatings. The first one consist of the outer Al-Mo(Si) layer and a particular (TiC/TiN)x20 intermediate diffusion barrier multilayer coating protecting the outer layer against the mutual diffusion process at high temperature between the outer layer and the ferrous substrate. The complex nanocrystalline refractory coatings with the diffusion barrier protected the heat- and creep-resistant high chromium AISI 430 ferritic steel substrate against the oxygen *and/or* sulphur vapours up to the temperatures as high as 1023 K. Another series of amorphous coatings based on Si covalent compounds (Si_xC_y, $Si_xC_yN_z$, Si_xN_y) deposited on the same AISI 430 steel protected the substrate against the oxidation up to the temperature 1173 K. At the same time, the coatings protected the steel substrate against electrochemical corrosion as well as against the chemical corrosion even in most aggressive acidic or basic solutions up to the temperature as high as 350 K.

The heat- and creep-resistant intermetallic γ-TiAl alloys have been deposited with nanocrystalline γ-TiAl-based coatings microalloyed with Cr atoms. The deposits have imparted to the γ-TiAl substrate a very good oxidation resistance up to the temperature as high as 1173 K: the oxidation rate of the coated specimens was at least two orders of magnitude smaller than that for the uncoated ones.

The newly developed protective coatings can find a broad range of applications, as, f.ex., in power industry, ferrous- and non-ferrous metallurgy, mining, aviation, car and ship industry, chemical processing of carbon, petrochemistry, waste treatment and recycling, microelectronics, MEMS, etc.

1. INTRODUCTION

In numerous high temperature industrial environments simultaneously oxygen and sulphur vapours are present. In such environments the conventional high-temperature corrosion resistant alloys undergo a rapid gaseous corrosion [1]. The reason is that the sulfides of numerous common metals show a rather great concentration of defects which accelerate the diffusion processes of the reactive species to the substrate material of conventional alumina or chromia formers [1]. Due to that the well known refractory Me-Cr-Al-Y coatings (Me: Co, Ni, Fe), which during exploitation at high temperatures are being selectively oxidized and covered

with a thin, tight alumina (Al_2O_3) and/or chromia (Cr_2O_3) layer are corroding very quickly when used at the same temperatures in the atmospheres containing sulphur vapours or its compounds. On the other hand it has been prooved [2] that alloying the common metals by molybdenum and aluminium decreases very effectively the sulfidation rate. Recently it has been shown that the new amorphous Al-31Mo-(6-16)Si alloys (in at. %) give evidence of the best resistance against high-temperature corrosion in the atmospheres containing oxygen *and* sulphur vapours [3-6]. It is the aim of the present work to depict the applicability of the relevant alloys as the protective coatings on steels against the high-temperature corrosion in such aggresive environments.

Nevertheless, when designing the protective coatings on steels against the high-temperature corrosion one must take into account not only interaction of the coating with the surrounding atmosphere, but with the substrate itself. In order to prevent the mutual diffusion of the atoms between the coating and the substrate [7] an additional, intermediate diffusion barrier should be brought in between the external refractory coating and the steel substrate. It is the aim of the present work to proove that a 5 μm thick multilayer coating composed of alternating TiC and TiN sublayers deposited directly by reactive magnetron sputtering is an effective diffusion barrrier between the outer refractory AlMo(Si) coating and the AISI 430 stainless steel substrate at least to the temperature as high as 1023 K.

Another series of amorphous coatings based on Si covalent compounds (Si_xC_y, $Si_xC_yN_z$, Si_xN_y) have been deposited by means of reactive magnetron sputtering on the same AISI 430 steel. It was the aim of the work to verify the protective properties of these coatings against the high temperature oxidation as well as against the electrochemical and chemical corrosion even in most aggressive acidic or basic solutions as H_2SO_4, HNO_3, HF and KOH.

Titanium aluminide alloy γ-TiAl with about 50 at. % of Al is a promising structural material for use at elevated temperatures for automotive and airspace applications due to its low density and high strength even at elevated temperature [8-11]. However, it has rather poor oxidation resistance at high temperature over 900 K. Numerous reserchers have reported [12-14] that the oxidation resistance of the alloy can be improved by means of surface modifications or coatings deposition. It was the aim of the work to verify the protective properties of the γ-TiAl coatings microalloyed with Cr atoms deposited also by magnetron sputtering on the surface of intermetallic γ-TiAl substrate.

2. EXPERIMENTAL

High chromium AISI 430 ferritic stainless steel or Ti48Al intermetallic titanium-aluminium alloy have been used as substrates. Rectangular specimens 30x10x0.5 mm have been cut from the steel and circular ones Ø15x0.5 mm from the Ti48Al alloy. The specimens have been mechanically polished, next ultrasonically cleaned in acetone, rinsed, dried and suspended under the rotary table in the vacuum chamber of the magnetron sputtering unit equipped with four independent planar magnetrons (Figure 1). The complex AlMo(Si) coating with diffusion barrier have been deposited onto the steel substrates in two steps. In the first step all the four magnetron targets were pure titanium disks Ø108 mm and 5 μm thick multilayer coating composed of 40 alternating TiC and TiN sublayers has been deposited by means of the reactive sputtering onto the whole surface of the steel specimens in the condition of a continuous rotation of the table. The reactive atmosphere in the vacuum chamber during deposition of TiC sublayers was 48vol.% Ar and 52vol.% C_2H_2 under total pressure $2.9 \cdot 10^{-2}$Pa, whereas the one during deposition of TiN sublayers was composed of 41vol.% Ar and 59vol.% N_2 under total pressure $3.4 \cdot 10^{-2}$Pa. The power of each one of the four magnetrons was 3 kW, the

substrate bias was -50 V, the deposition time of each one of the 40 sublayers was 180 s and the angular speed of the table was 0.3 rad·s^{-1}. In the next step the Al-30.2at.% Mo-7.3at.% Si 5 μm thick refractory coating have been deposited by simple sputtering of two pure molybdenum and two Al-Si fine-grained targets on the multilayer (TiC/TiN)x20 predeposited AISI 430 steel specimens. After each step the structure, morphology and the chemical composition of the coatings have been verified by means of X-Ray, SEM and EDX techniques, respectively. Finally, the specimens have been exposed for a period of 100 hours to an aggressive gas environment inside quartz tubes filled with He-S_2 atmosphere at total pressure 100 kPa and sulphur partial pressure 1 kPa or with oxygen at the pressure 100 kPa, at a permanent flow of the gas atmosphere at the temperature 873 K, 973 K, 1023 K and 1073 K. The progress of the gas corrosion processes has been registered by means of a thermo-gravimetric equipment (C.I. Electronics) with a continuous electronic control of the specimen weight. The results of the high-temperature corrosion tests have been analysed and compared with the relevant characteristics of the well known chromia and alumina formers.

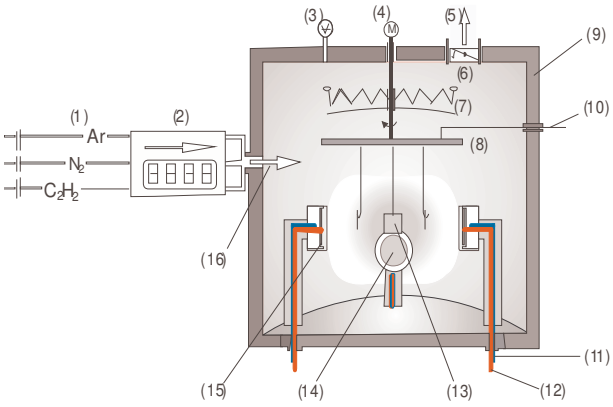

Figure 1. A scheme of the refractory coatings' deposition equipment: 1– inert and reactive gases delivery; 2–gas flow mass controller; 3–vacuum meter; 4–motor drive; 5–connection to pumping stand; 6–throttle valve; 7–IR radiator; 8–rotary table; 9– high vacuum chamber; 10–table bias; 11–magnetron cooling; 12–magnetron power feed; 13–specimen suspended under the table; 14, 15–magnetrons; 16–gas inlet (inert and reactive).

Three covalent-bonded 2 μm thick SiC, SiCN and SiN coatings have been deposited in the same reactor onto the whole surface of the same type rectangular steel specimens as well as onto the surface of (100) Si(p) 0.46 mm thick monocrystalline silicon substrates suspended under the rotary table by means of the reactive magnetron sputtering in the atmospheres Ar+C_2H_2, Ar+C_2H_2+N_2 or Ar+N_2 with the compositions 59vol.%Ar+41vol.%C_2H_2, 46vol.%Ar+19vol.%C_2H_2+35vol.%N_2 or 55vol.%Ar+45vol.%N_2 and at the total pressure $2.1\cdot10^{-2}$Pa, $2.4\cdot10^{-2}$Pa or $2.85\cdot10^{-2}$Pa, respectively. During deposition all the four magnetron targets were pure Si monocrystalline disks Ø107x7 mm, the power of the magnetron discharge of each one of the four magnetrons was 0.4 kW and the angular speed of the rotary table was 0.3 rad·s^{-1}. The chemical composition of the coatings and the state of chemical bonding as well as the mechanical and protective properties of the deposits have been investigated by means of EDX, RAMAN and IR spectrometries, SEM and AFM techniques. The resistance to electrochemical corrosion has been verified by means of the potentiodynamic response in 1 N H_2SO_4 environment at ambient temperature. The resistance of the coatings to chemical corrosion has been tested in 40% HF solution in water or in the mixture of 5% HNO_3 and 5% HF water solutions at ambient temperature as well as in saturated water solution of KOH at the temperature 353 K. The resistance to high-temperature oxidation at 1073 K and 1173 K has been investigated during 86 hours in pure oxygen atmosphere at the pressure of 100 kPa with use of the thermogravimetric equipment.

In case of the intermetallic γ-Ti48Al substrate two different nanocrystalline 5 μm thick γ-TiAlXCr (X=1,27at.% or 4,45at.%) coatings have been co-deposited by magnetron

sputtering. In this case three pure metallic targets (one of Al, one of Cr and one of Ti) have been used. During deposition the pressure of pure Ar atmosphere in the deposition chamber was 0.02 Pa and the angular speed of the rotary table was 1.0 rad·s^{-1}. After deposition the isothermal oxidation tests were carried out at 1173 K in pure oxgen at 100 kPa during which the weight gain was continuously measured with use of a microthermogravimetric analyzer. Before and after oxidation the coated specimens were analysed with use of XRD, SEM and EDX techniques.

3. RESULTS AND DISCUSSION

An example of the morphology of a fracture of the complex refractory coating composed of the external protective Al31Mo7Si layer and the intermediate (TiC/TiN)x20 diffusion barrier as well as of the fracture of the $Si_{.44}C_{.31}N_{.25}$ coating on the AISI 430 steel is given in Figure 2. The examples of the fractures of the γ-Ti48Al1.27Cr coating on the intermetallic γ-Ti48Al alloy after deposition as well as after 120 hours of oxidation are given in Figure 3. An example of the X-Ray difraction profiles of the coatings from Figure 3 are given in Figure 4. The IR absorption spectra of the three Si-based refractory coatings and the corresponding potentiodynamic curves in 1 N H_2SO_4 are given in Figure 5.

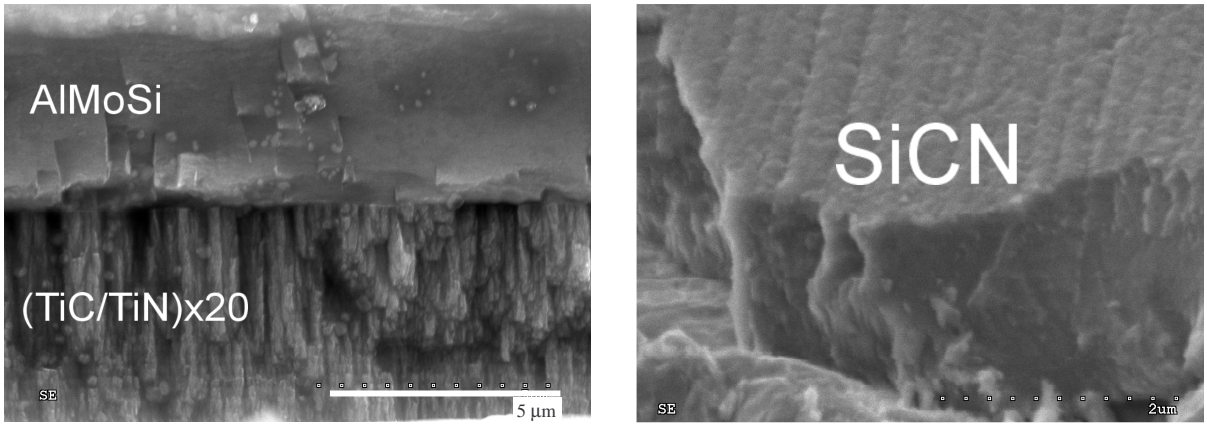

Figure 2. SEI images of the fractures of the complex Al31Mo7Si coating with diffusion barrier (TiC/TiN)x20 (left) and of the $Si_{.44}C_{.31}N_{.25}$ coating (right) magnetron sputtered onto the surface of the AISI 440 steel before oxidation.

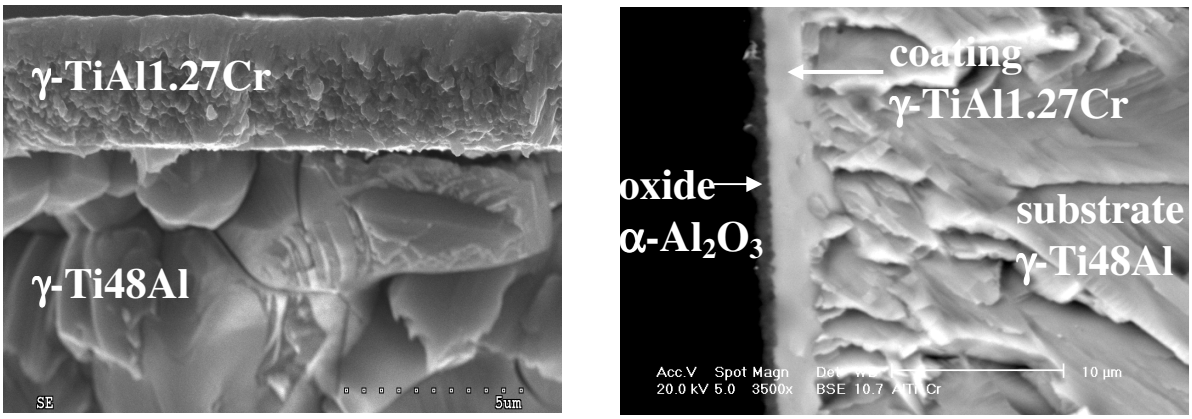

Figure 3. Fracture of the nanocrystalline γ-Ti48Al1.27Cr coating on the intermetallic γ-Ti48Al alloy after deposition (left) and after 120 hours oxidation in pure oxygen atmosphere (right).

The oxidation kinetics of different types of coatings at different temperatures in pure oxygen atmosphere under the pressure of 100 kPa are given in Figures 6 and 7. For each one of the kinetics given in the last two Figures a corresponding "parabolic" oxidation rate k_p has been calculated and all the calculated values are presented in a collective plot of the temperature dependence of the oxidation rates for AlMo-, AlTi- and Si-based coatings and compared to a number of conventional high-temperature alloys and several pure refractory metals (Figure 8). The results of the investigation of the resistance to sulfidation of the AlMoSi coating on the AISI 430 alloy are included into the last Figure as well. Besides that, several tests of the resistance of the Si-based coatings against the chemical corrosion have been performed as well: by immersion of the Si substrates with different coatings at ambient temperature in 40% HF or in the mixture of 5%HF+5%HNO_3 during 30 minutes or in saturated KOH at the temperature 353 K during 3 hours.

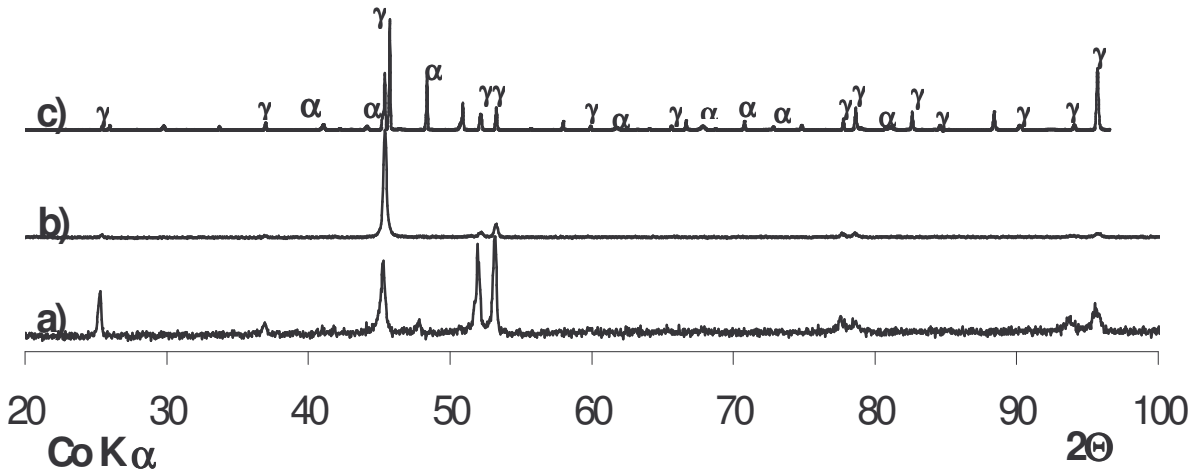

Figure 4. X-Ray diffraction profiles: a) substrate γ-TiAl without coating; b) γ-TiAl coated with γ-TiAl1.27at.%Cr before and c) after 120 hours oxidation at the temperature 1173 K. Symbol α - means the phase α-Al_2O_3 and γ means γ-TiAl one.

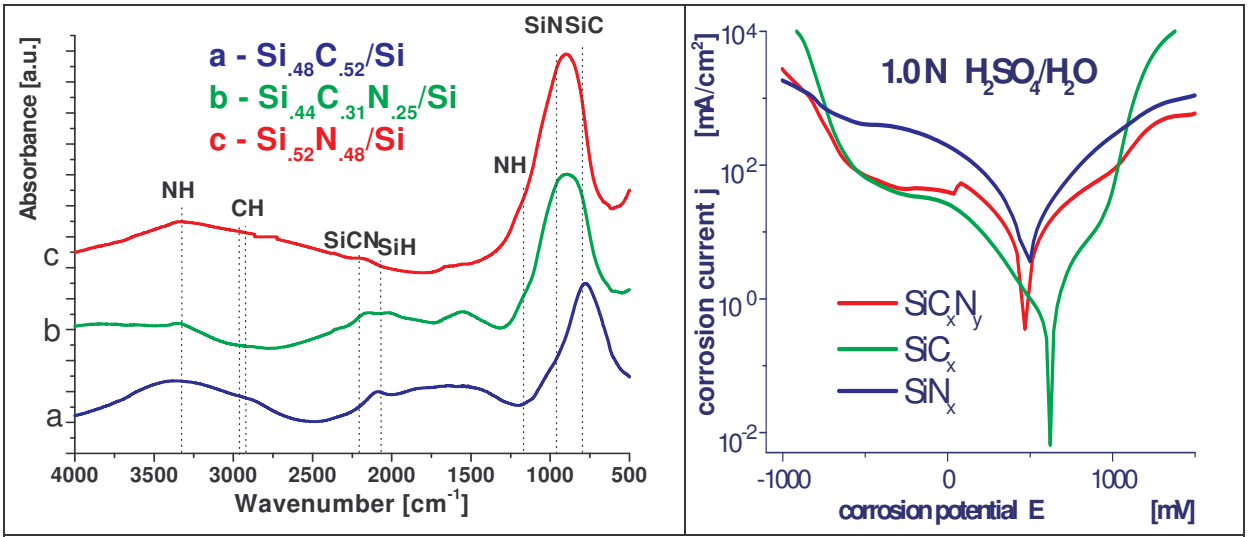

Figure 5. IR absorption spectra (left) of three magnetron sputtered covalent-bonded Si-based coatings on Si substrates and potentiodynamic curves of the AISI 430 samples deposited with the same coatings (right).

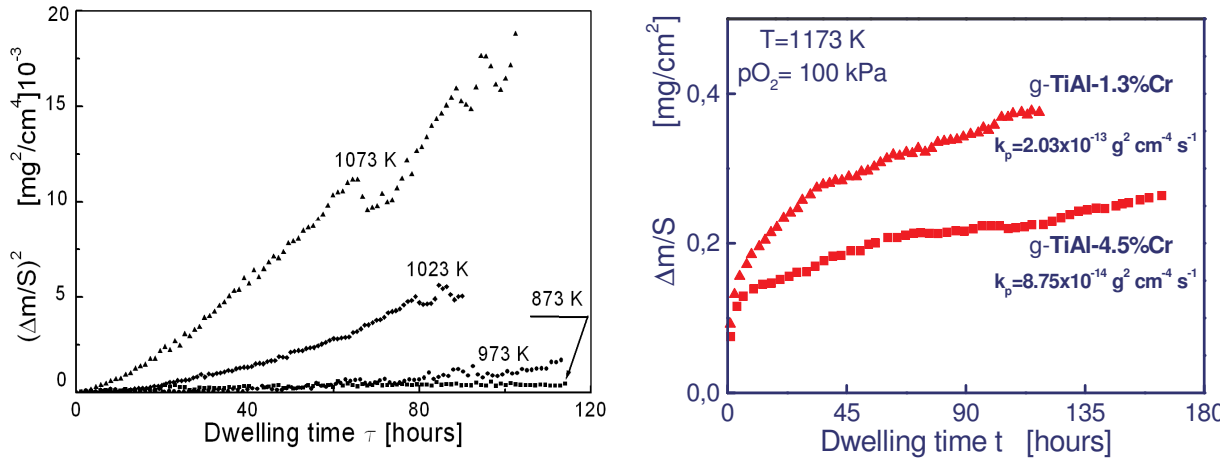

Figure 6. Oxidation kinetics in pure oxygen: AISI 430 steel samples deposited with complex nanocrystalline Al31Mo7Si coating with (TiC/TiCN)x20 diffusion barrier at four different temperatures in "parabolic" coordinates (left) and intermetallic coarse-grained γ-TiAl substrate deposited with Cr-alloyed nanocrystalline γ-TiAl(Cr) coating with two different Cr admixtures (1.3at.% and 4.5at.%) at the temperature 1137 K in linear co-ordinates (right).

In result of any of these experiments the coatings on the Si substrates were intact. In the difference, the specimens' weights after 3 hours testing in heated KOH have decreased to some extent due to some delamination of the coatings and to the etching of the Si substrate itself.

One can see from Figure 8 that the resistance to oxidation of all the three types of refractory coatings investigated in the work is fairly good: their "parabolic" oxidation rates are very small even in comparison with a number of the well known alumina and chromia formers. Incase of the AlMoSi coating this is due to a very small grain size of the magnetron sputtered deposit (see Figure 2). This statement is supported as well by the X-Ray structural investigations (not shown in this work) in which the FWHM widths of several diffraction peaks of the coating are as large as 5 deg (see, f.ex., [15]). Due to this real nanocrystallinity of the deposit very fine-grained intermetallic phases Al_8Mo_3 and Mo_5Si_3 are being formed in the coating during heating (see [1]) and, subsequently, uniform and compact oxide scale is being formed on the coating's surface [16]. For similar reasons the fairly good resistance to sulfidation of this coating is due to the formation of a very stable Mo_5Si_3 intermetallic compound which, due to its great dispersion, is forming uniform and compact MoS_2 sulfide scale [1].

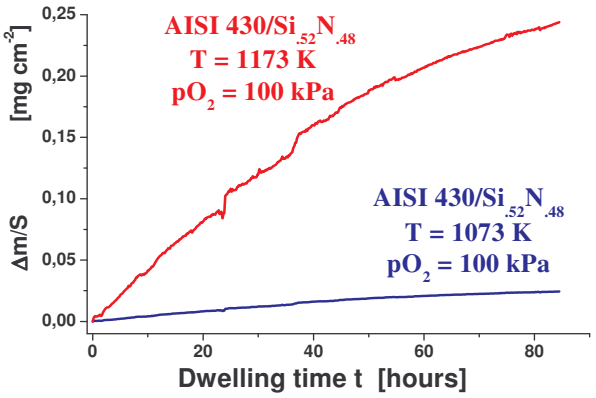

Figure 7. Oxidation kinetics at the temperature 1073 K and 1173 K of the AISI samples deposited with magnetron sputtered $Si_{.52}N_{.48}$ coating in linear co-ordinates.

In case of the Cr microalloyed γ-TiAl coating its very small oxidation rate (about two orders of magnitude smaller than for uncoated γ-TiAl alloy – see [17]) is due to formation of uniform and compact α-Al_2O_3 layer on the coating surface (see Figure 3).

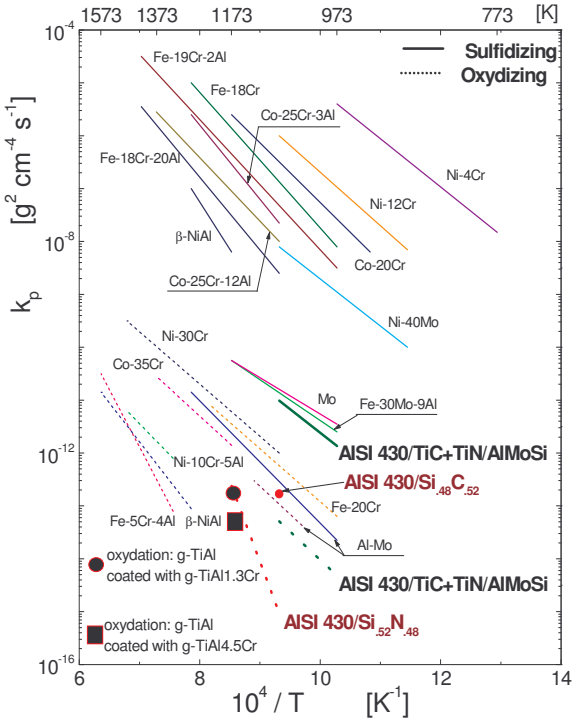

Figure 8. Collective plot of the temperature dependence of the oxidation rates for the samples deposited with AlMo-, AlTi- and Si-based coatings. The results of the sulfidation tests of the first ones are included also. With the aim of comparison the corresponding values of a number of conventional high-temperature alloys and of several pure refractory metals taken from [1] are given in the plot as well.

This compactness and uniformity is due to the nanocrystalline microstructure of the magnetron sputtered γ-TiAlCr deposit. The role of the Cr admixture in creation of the tight α-Al_2O_3 external layer (and *not rutile scale)* on the γ-TiAlCr coating during oxidation is not clear yet and will be the objective of further investigations.

In case of Si-based coatings, their excellent resistance to oxidation is due to the formation of slowly growing and dense silica scale on the coatings' surface [18] which serves an obstacle for further oxygen transport. Nevertheless, the resistance to oxidation of the $Si_{.48}C_{.52}$ coating at the temperature 1073 K is about two orders of magnitude less than that of the $Si_{.52}N_{.48}$ one (Figure 8). This is probably due to that at the temperature above about 800 K the carbon atoms react easily with oxygen ones [19].

On the other hand, the excellent resistance of the Si-based coatings to the electrochemical corrosion as well as to the chemical one in even to the most aggressive acidic and basic environments confirmed in the experiments within this work is due to well developed stable covalent bondings type Si-C and Si-N (Figure 5). This latter gives also the evidence of some hydrogen concentration in the Si-based coatings (in particular in $Si_{.48}C_{.52}$ and $Si_{.44}C_{.31}N_{.25}$ ones due to the use of the acethylene gas during the reactive magnetron deposition).

4. CONCLUSIONS

1. The external metallic AlMoSi or intermetallic γ-TiAlCr coatings deposited by magnetron sputtering have a nanocrystalline quasi-amorphous structure which is conductive to formation of uniform, compact oxide or (sulfide) scales on the coatings surface.
2. The resistance of these coatings to oxidation is due to the formation of thin, tight α-Al_2O_3 layer on the surface of the primary deposit which lowers the oxidation rate of the latter several orders of magnitude.
3. The resistance to sulfidation of the combined Al-Mo-Si coating with an intermediate modulated (TiC/TiN)x20 is due to formation of the MoS_2 sulfide with low density of internal defects and small diffusion coefficient of sulphur and metallic atoms.
4. The resistance to oxidation of the three Si-based coatings invstigated in the work is due to formation of slowly growing and dense silica scale on the coatings' surface.

5. The excellent resistance of the Si-based coatings to the electrochemical corrosion as well as to the chemical one in even to the most aggressive acidic and basic environments confirmed in the experiments within this work is due to well developed stable covalent bondings type Si-C and Si-N in the magnetron sputtered.
6. The resistance to oxidation of all the three types of refractory coatings investigated in the work is fairly good: their "parabolic" oxidation rates are very small even in comparison with a number of the well known alumina and chromia formers
7. Magnetron sputtering deposition is a promising method for producing nanocrystalline or amorphous refractory coatings on ferrous and non-ferrous alloys.

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REFERENCES

1. S. Mrowec, Oxidation of Metals 44 Nos. 1 & 2 (1995) 177 – 209.
2. Ge Wang, D.L. Douglass, F. Gesmundo, Oxid. Metals 35 (1991) 349.
3. H. Habazaki, J. Dąbek, K. Hashimoto, S. Mrowec, M. Danielewski, Corrosion Science 34 (1993) 183.
4. H. Habazaki, K. Takahiro, S. Yamagutchi, K. Hashimoto, J. Dąbek, S. Mrowec, M. Danielewski, Materials Science A181/A182 (1994) 1099.
5. H. Habazaki, K. Hashimoto, S. Mrowec, M. Danielewski, Corrosion Science 36 (1994) 199.
6. H. Habazaki, K. Hashimoto, S. Mrowec, M. Danielewski, Corrosion Engineering 44 (1995) 174.
7. K.N. Strafford, P.K. Datta in „Surface Engineering Processes And Aplications" (K.N. Strafford, R.St.C. Smart, I. Sare, C. Subramanian, Eds.), TECHNOMIC Publ. Comp., Lancaster-Basel (1995) 253-258.
8. T. Noda, Intermetallics 6 (1998) 709-713.
9. M. Gell, Materials Science and Engineering A 204 (1995) 246-251.
10. T. Tetsui, Materials Science and Engineering A 329-331 (2002) 582-588.
11. T. Tetsui, Intermetallics 7 (1999) 689-697.
12. L. Xin,; G. Shao, F. Wang, P. Tsakiropoulos, T. Li, Intermetallics 11 (2003) 651-660.
13. C. Zhou, H. Xu, S. Gong, K. Young, Materials Science and Engineering A 341 (2003) 169-173.
14. J. Hampshire, P.J. Kelly, D.G. Teer, Thin Solid Films 420-421 (2002) 386-391.
15. B. Wendler, M. Danielewski, J. Dąbek, A. Rylski, R. Kamiński, P. Dobrosz, Proc. 13th Int. Summer School Mielno'2002, Mielno, Poland 02-05.09.2002, Ed. W. Precht, Koszalin 2002, pp. 123-132. ISBN 83-7365-004-0.
16. H. Habazaki, K. Hon-yashiki, K. Ito, H. Mitsui, A. Kawashima, K. Asami, K. Hashimoto, S. Mrowec, Materials Science A 267 (1999) 267-276.
17. Z. Li, W. Gao, M. Yoshibara, Y. He, Materials Science and Engineering A 347 (2003) 243-249.
18. K. Lee, R.A. Miller, Surface and Coatings Technology 86-87 (1996) 142-148.
19. Y.C. Zhu, S. Ohtani, Y. Sato, N. Iwamoto, Carbon 37 (1999) 1417-1423.