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A Study on Development of Advanced Environmental-Resistant Materials Using Metal Ion Processing

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The development of the oxidation, wear and corrosion resistant materials that could be used in severe environmental conditions is needed. The elementary technologies for surface modification include ion implantation and/or thin film coating. Furthermore, in order to develop ion implantation technique to the specimens with three-dimensional shapes, plasma-based ion implantation (PBII) techniques were investigated. As a result, it was found that the ion implantation and/or thin film coating used in this study were/was effective for improving the properties of materials, which include implantations of various kinds of ions into TiAl alloy, TiN films formed on surface of base material and coatings in high-temperature steam. The techniques proposed in this study provide useful information for all of the material systems required to use at elevated temperature. For the practical applications, several results will be presented along with laboratory test results.

Key Words : Oxidation, Wear, Corrosion, Metal, Ion Implantation, Surface Modification

1. Introduction

Recently, since the effective solutions relating to environmental problems such as reduction of carbon-dioxide emission and energy-saving apparatus become more important, the development of advanced environmental-resistant materials and furthermore the improvement of its reliability are more necessary. As for the conventional techniques, which usually add alloying elements to target materials, for developing the materials capable of using in high-temperature, they have often deteriorated properties of cast or led to increase of weight.

However, the techniques using ion implantation have many merits that, for example, could combine easily implantation elements with target materials, compared with those of conventional techniques. In these days, because most of elements could be ionized, there are many trials to use ion implantation for surface modification of materials. Indeed, many components have been used in industrial field by ion beam processing (Rhee et al., 2000 ; Klingenberg et al., 2002). There are several reports concerning implantation of a few metallic ions, especially niobium ions, and its influence on the oxidation behavior of TiAl alloys (Schmutzler et al., 1996 ; Kyung et al., 2004 ; Taniguchi et al., 2000 ; Perez et al., 2001 ; Haanappel et al., 1998 ; Rhee et al., 2002). More relevant knowledge, on the other hand, is needed for efficient and reasonable choices of additional elements.

In the present study, the effects on oxidation,

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Table 1 Target temperatures for practical applications

Practical application	Material (use temp.)	Target temp.	Industrial partners
Oxidation resistant material			
Rotor of turbo charger	TiAl alloy use at 700℃	850℃ in air	Ishikawajima-Harima Heavy Industries
Wear resistant material			
Dry gas seal ring	TiN-coated SUS630 stainless steel use at 300℃	450℃ in steam	Ebara
Corrosion resistant material			
Superheater tube	T22 steel use at 300℃	550℃ in steam	Sumitomo Metal Industries, Takuma

wear and corrosion resistant materials in high-temperature by thin film coatings and/or ion implantation are investigated. For these purposes, the elementary techniques for surface modification such as cathodic arc ion plating (Oh et al., 2003), dynamic ion beam mixing and unbalanced magnetron sputtering are used. Furthermore, plasma-based ion implantation (PBII) technique is investigated for developing ion implantation techniques for the specimens with three-dimensional shapes (Adler et al., 1985 ; Tuszewski et al., 1997). The techniques are applied to industrial products. Table 1 shows the target temperatures for practical applications in each case. This article reviews the main results of NEDO (New Energy and Industrial Technology Development Organization) project, the Ministry of International Trade and Industry of Japan.

2. Experimental Apparatus and Procedure

The γ-TiAl alloy, SUS630 stainless steel (SS) and T22 steel were used as base materials. The TiAl alloys (Ti-50Al, at.%) were prepared by vacuum arc-melting followed by hot forging without any further heat treatment. Thin slices were cut from the pancake, and coupon specimens were machined out of the slices and the cast alloy to have dimensions of 15×10×2 mm. The specimen edges were ground to make 45° so that the whole surface can be implanted with two steps : one for the front surface and the other for the back surface. The SUS630 stainless steel (0.05C-0.84Mn-0.012S-0.25Si-3.27Cu-4.55Ni-15.67Cr-0.028P-0.26Nb-bal. Fe (mass%)) were prepared with dimensions of inside diameter 175 mm and outside diameter 250 mm (mating ring). The T22 (2.27Cr-1.05Mo-0.43Mn-0.16Si-0.12C-0.007P-0.003S-bal. Fe (mass%)) steels with dimensions of 4×20×30 mm were cut from tubing. Cyclic oxidation tests on TiAl alloys were performed at 850℃ in air or synthetic automobile exhaust. For one cycle test, the specimens were inserted into the hot zone of the furnace at 850℃ for an initial period of 15 min, then held for 20 h in air or synthetic automobile exhaust, and finally removed out from the furnace for the final period of 15 min. The specimen mass was measured after each cycle.

The setup of plasma-based ion implantation (PBII) device used in the experiment is shown schematically in Fig. 1. Ion implantation is effective method for surface modification because surface properties can be controlled by the implanted element. However, conventional beam-line ion implantation is limited for modification of flat substrates with small area and not suited for industrial applications. To overcome this disadvantage, an innovative ion implantation process, known as PBII, has been developed. The technique using PBII is considered as a promising method for modifying the surface properties of materials of three-dimensional topologies. As shown in Fig. 1, an electrode for plasma implantation is installed with substrate in the vacuum chamber. There are pulsed RF supply and high-voltage pulsed bias supply in order to generate plasma, and the output is transmitted through feed-through with cooling pass. The various kinds of measurement equipments, including temperature control system and vacuum system, are attached in PBII device. If negative pulsed high-voltage is impressed to feed-through that enveloped by plasma, surrounding electrons of substrate will be excluded and ion sheath with plus ion will be formed. The plus ion within ion sheath is accelerated toward substrate by high-voltage and consequently ion implantation is performed.

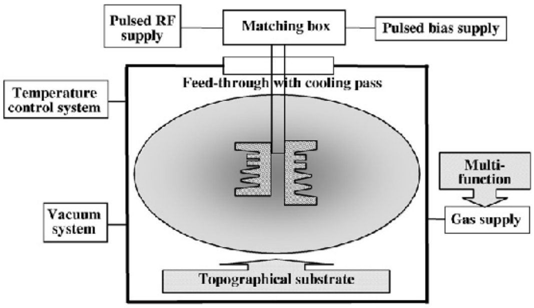

Fig. 1 The setup of PBII device

3. Results and Discussion

3.1 High-temperature oxidation resistant material (TiAl alloy)

For the purpose of improvement of oxidation resistance of γ-TiAl alloy, the effects of implantation elements were investigated. The elements and the implantation conditions are summarized in Table 2. The implantations of Nb, Mo, Ta, W, F and Cl ion show improvement for oxidation resistance. The implantations of Fe, Si and P ion show a little improvement. Furthermore, the im-

Table 2 Oxidation behavior of TiAl alloys by ion implantation of a range of elements

Elements	Acceleration voltage (keV)	Dose (ions m^{-2})	Oxidation resistance	Ref.
Nb	50	10^{19}, 10^{20}, 10^{21}	×	Taniguchi et al., 1998
Nb	50	1.2×10^{21}	◎	Taniguchi et al., 1998
Mo	40	2×10^{21}	◎	Taniguchi et al., 1998
	50, 200, 340	10^{21}	◎	
Ta	180	10^{21}	◎	
W	100	10^{19}	×	
W	100, 180	10^{21}	◎	
Mg	50	10^{20}, 10^{21}, 10^{22}	×	
V	50	10^{21}	×	
Si	80, 150, 260	2.5×10^{21}	○[a]	Taniguchi et al., 2000
B	50	10^{21}	×	
P	50	10^{21}	○[a]	
Fe	50	10^{21}	○	
Zr	50	10^{19}, 10^{20}	×	
Zr	180	10^{19}, 10^{20}, 10^{21}	×	
C	50	10^{19}, 10^{20}, 10^{21}	×	Li et al., 2001
N	50	10^{20}, 10^{20}	×	
F	50	10^{20}, 10^{21}	◎	Zhu et al., 2002
Cl	50	10^{19}	×	
Cl	50	10^{20}, 10^{21}	◎	

(◎) Improvement, (○) a little improvement, (×) no improvement.

[a] Vacuum annealing at 1100 K for 3.6 ks resulted in reduced oxidation rate.

plantations of B, C, N, Mg, V and Zr ion show no improvement. It is noticeable that the improvement of oxidation resistance by Nb, W and Cl ion implantations is strongly affected by amount of ions implanted into the TiAl alloy.

The mass change for the Nb implanted TiAl alloy during cyclic oxidation in air is shown in Fig. 2. The as-received TiAl specimen shows a rapid mass gain for up to about 900 ks, and then a mass decrease owing to the partial scale spallation. After about 900 ks, a mass loss masks the mass gain resulting from the oxidation, and results in a rapid net mass loss. The mass gain in Nb implanted alloy decreases with increases of Nb ions. The specimen implanted with 1.2×10^{21} ions$\cdot$m^{-2} exhibits a very low oxidation rate. This result is shown as "improvement" in Table 2. It is obvious that the oxidation resistance of TiAl alloy is improved by the Nb implantation. Several mechanisms for the improvement of oxidation resistance by Nb implantation into TiAl alloy have been proposed (Li et al., 2001 ; Zhu et al., 2002).

From the present investigation, it can be considered as follows ; the oxide scale of binary TiAl alloy is composed of a porous oxide mixture of TiO_2 and Al_2O_3, and the scales is dominated by TiO_2. The presence of Nb in the modification layer would lower the solubility of oxygen and thus propel the primary oxidation of Al than Ti. If this beneficial effect of Nb could be maintained long enough, a dense layer Al_2O_3 scale would be formed in the oxide scale, which could act as effective barrier to further oxidation.

For application to TiAl alloys in rotors of turbo chargers for automobiles, the oxidation resistance of the Nb implanted TiAl alloy was evaluated in synthetic automobile exhaust (10% O_2-7% CO_2-6% H_2-bal. N_2) at 850℃. The mass change for implanted TiAl alloy during cyclic oxidation is shown in Fig. 3. As a base material, Mo-V-Si containing TiAl alloy (48 mol% Al-1.5 mol% Mo-0.5 mol% V-0.5 mol% Si-bal. Ti) was used. This alloy was developed for improving mechanical property and castability of TiAl alloy. In Fig. 3, 'high-temp.' means Nb ion implantation performed while heating at 900℃, and its mass gain is lower than that of ordinary Nb implanted alloy. It can be concluded that ion implantation in high-temperature is an effective measures to overcome the weakness of ordinary ion implantation, such as a shallow modification layer (Wei, 1996) and the degradation of oxidation resistance due to additions of V to the base material. Furthermore, it is interesting to note that above beneficial effect of Nb implantation is further improved by the Nb+C combined implantation, although the C implantation alone shows a bad effect. The co-existence of C and Nb could enhance their resistance to the fast oxygen diffusion during high-temperature oxidation and thus propel the primary oxidation of Al rather than Ti (Li et al., 2001). These effects could lead to the formation of much more compact Al_2O_3

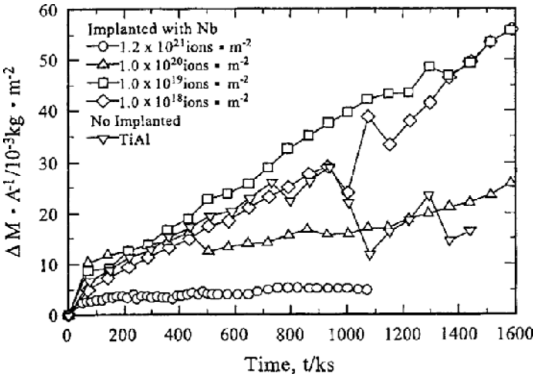

Fig. 2 Cyclic oxidation curves of the TiAl specimens implanted with Nb in air at 850℃

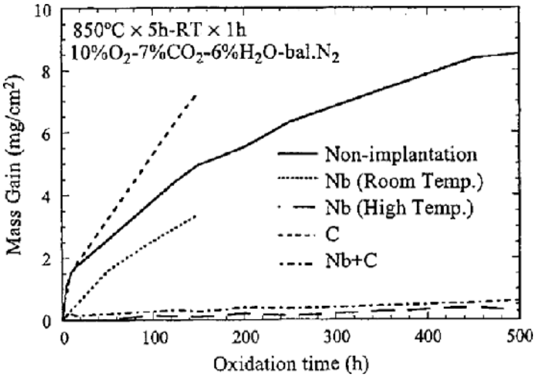

Fig. 3 Cyclic oxidation curves of the Nb, C and Nb+C combined implanted specimens in synthetic exhaust at 850℃

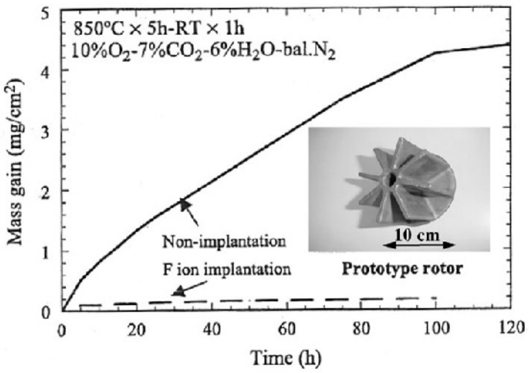

Fig. 4 Cyclic oxidation curve of the TiAl prototype rotor treated with fluorine by PBII in air at 850℃

layers in the external scale and thereby Nb+C implanted alloy shows the best long-term oxidation resistance. The implantations of Nb+Si and Nb+Al were also effective for improving the oxidation resistance of the TiAl alloy (Li et al., 2001 ; 2002).

F ions were implanted into the prototype TiAl rotor by PBII in order to apply the practical applications like an automobile. The plasma was produced from Ar-5 vol% F_2 mixed gas with a RF power supply. The substrate was pulse biased to a negative voltage of −10 kV through a feed-through with a pulsed voltage supplier. The length of the pulsed voltage was 10 μs with a repetition rate of 1000 Hz (Zhu et al., 2002). The oxidation resistance of F implanted specimen is drastically improved as shown in Fig. 4. Even though F ions were not implanted uniformly over the entire surface area of TiAl rotor, it is considered that the error could be neglected. The beneficial effect of F ion implantation on the oxidation resistance of TiAl is due to the preferentially formed volatile aluminum fluoride attributed to formation of continuous Al_2O_3 scale.

3.2 High-temperature wear resistant material (TiN/SUS630 stainless steel)

3.2.1 Improvement of wear resistance by boron ion implantation

In these days, the products like dry gas seal, which is coated with TiN films by dynamic mixing method (DM) on surface of stainless steel, have been practically used, as shown in Fig. 5. However, it is necessary to further improve the properties of material in the case of using under severe environmental conditions like high-temperature steam. TiN coating technology is used as the surface coating for improving wear resistance. Fig. 5 shows dry gas seal for steam turbine. The mating ring and seal ring are contacted under actual operation in 450℃ steam. In TiN coated mating ring, TiN reacts with oxygen, which results in a degradation of wear and corrosion resistance. For application to sliding seal materials of steam turbine, wear resistance of TiN, which is coated on steel, must be improved up to 450℃.

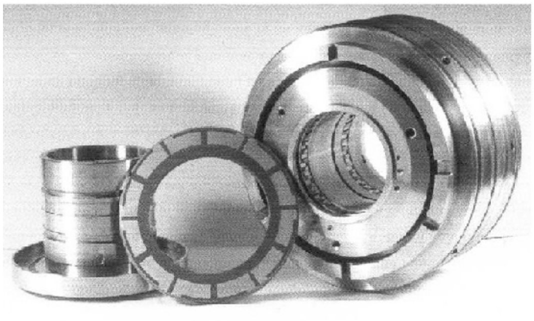

Fig. 5 Dry gas seal coated with TiN films

In the present study, the effects of boron ion implantation on wear resistance of TiN films were investigated. For these purposes, after coating with TiN (of 3 μm thickness) on surface of SUS630 base material using arc ion plating (AIP), and then boron ions were implanted into TiN films by 75 keV. As shown in Fig. 6(a) and (b), which is XPS depth profiles of boron implanted TiN, the boron ions exhibit a Gaussian distribution over a depth of about 350 nm. The maximum atomic concentration of boron ions at a depth of about 175 nm increases with increasing dose of boron ions. It is 50 at% for the dose of 8.0×10^{17} ions cm^{-2}. Conversely the concentrations of nitrogen and titanium in the same region are decreased. Furthermore, as the results of XPS measurement and X-ray diffraction in the case of specimen of Fig. 6(b), it was found that BN and TiB_2 were formed in the region of implanted boron.

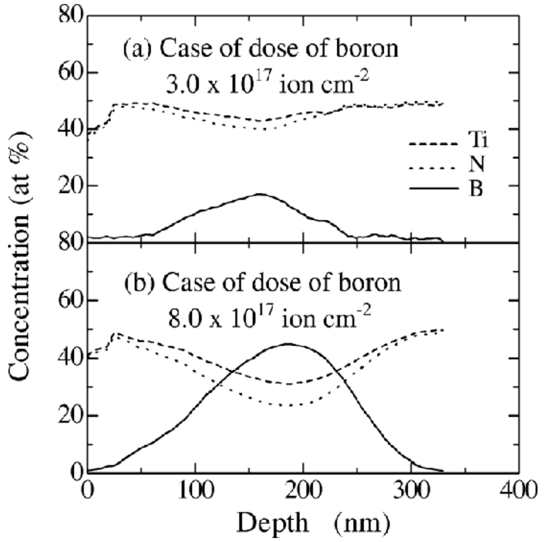

Fig. 6 XPS profiles of TiN films by B implantation

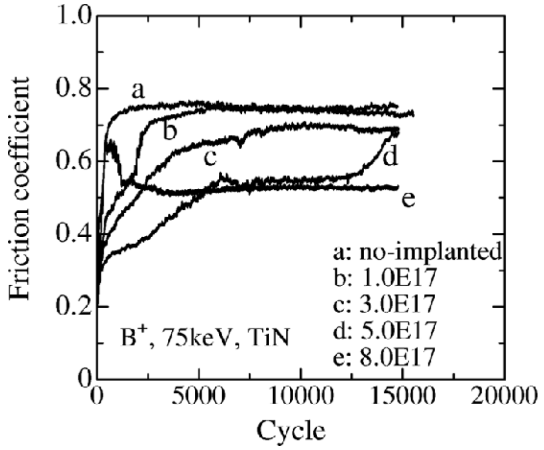

Fig. 7 The relation between cycle and friction coefficient by ball on disk machine

Figure 7 shows the friction coefficient as a function of sliding cycles. The friction and wear test was performed using ball on disk machine. An alumina ball of 5 mm in diameter was used as a counter material with an applied load of 2 N. The rotating velocity of the sample was 80 rpm with a wear track of 20 mm in diameter. The friction coefficient of TiN decreases with increasing dose of boron ions in the stable condition after the initial 5,000 cycles of sliding. As the result, boron ion implantation results in a reduction of friction coefficient.

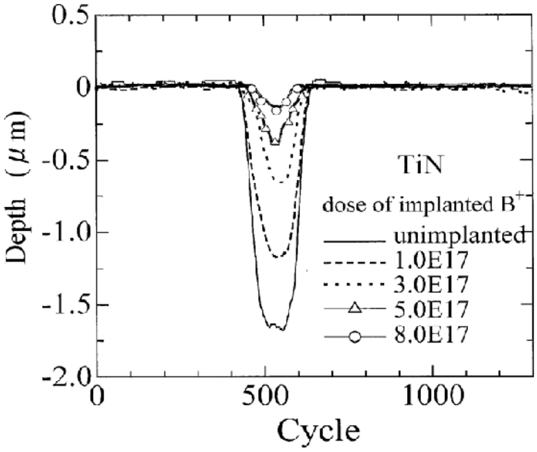

Fig. 8 The Cross-sectional profiles of wear tracks after 15000 cycles

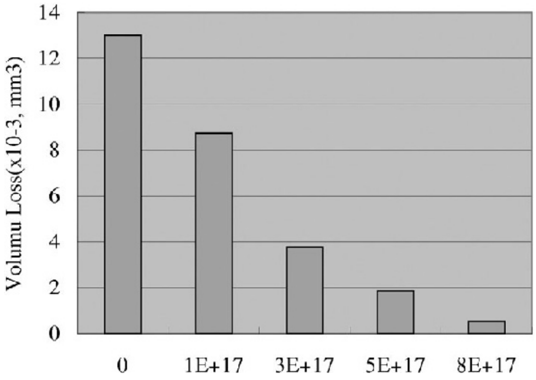

Fig. 9 The relation between volume loss of TiN films and dose of implanted boron ions

The wear tracks after 15000 cycles of sliding were examined by using a surface profilometer with a stylus scanning surface of wear tracks. Fig. 8 shows cross-sectional profiles for wear tracks. In the case of no implanted TiN, the wear track depth is measured to be 1.67 μm. In the case of dose of 8.0×10^{17} ions cm^{-2}, wear track depth decreases to 0.14 μm. As the result, boron ion implantation results in a remarkable decrease in depth of wear tracks.

Figure 9 shows wear volume loss, which was calculated from 2D stylus profilomatries. The volume loss decreases largely with increasing dose of boron ions. For the dose of 8.0×10^{17} ions cm^{-2}, the value of volume loss is only 4% of that for no implanted TiN. This result indicates that

Table 3 The mechanical properties of TiN, TiAlN and TiCrN films

Film materials	Composition at.%				Crystal structure	Crystal orientation	Vickers hardness
	Ti	Al	Cr	N			Hv
TiN	56	–	–	44	FCC	(111)	3500
TiAlN(1)	56	9	–	35	FCC	(111)	2500
TiAlN(2)	56	12	–	32	FCC	(111)	3300
TiAlN(3)	57	19	–	24	FCC	(111)	3500
TiCrN(1)	55	–	10	35	FCC	(200)	2500
TiCrN(2)	44	–	19	36	FCC	(200)	2900
TiCrN(3)	34	–	26	40	FCC	(200)	3300

*Coatings: 4 μm thickness films by dynamic ion beam mixing
Operating Press.: 2.5×10^{-3} Pa, N_2 gas+Metal vapor

boron ion implantation induces an excellent improvement in friction coefficient and wear resistance of TiN. This is caused by the formation of hard TiB_2 and lubricating BN resulting from boron ion implantation into TiN. By the above results, it was found that the wear resistance of TiN coating layer could be improved by implantation of boron ions. Furthermore, these effects are similarly found in the case of implanting boron ions into TiAlN films (Zhu et al., 2002).

3.2.2 Improvement of wear resistance by addition of Al or Cr into TiN in high-temperature steam

In order to improve the wear resistance of TiN films in high-temperature steam, the addition of Al or Cr into TiN was investigated. The hard films of various compositions were coated on SUS630 base materials using DM, as shown in Table 3. The composition ratio of TiN (N/Ti) is about 0.8, which is the maximum value of Vickers hardness (Hv3500). Moreover, if the additions of Al and Cr exceed 30 at% and 50 at% in the case of TiAlN and TiCrN, respectively, the crystal structure becomes not FCC and therefore Vickers hardness becomes less than 2000. It was observed that the upper limits of Al and Cr additions were 25 at% and 44 at%, respectively, when Vickers hardness shows below 2000. In these ranges, as shown in Table 3, Vickers hardness is increased according to increase of Al and Cr, respectively. In TiN and TiAlN films, a preferred orientation is (111) plane. In TiCrN films, there is a tendency that orientation of crystal growth changes from (111) plane to (200) plane with increase of Cr content. Furthermore, it was obtained the films having Vickers hardness 3600 by AIP in the case of TiAlN (Ti: 31 at%, Al: 19 at%, N: 50 at%). The friction and wear tests were carried out for several films under 450℃ steam. As for dry gas seal, the influences on wear of counter material as well as wear of seal are also important. The hard films of AIP-TiAlN and DM-TiCrN(3) were little worn, and less attacks carbon (counter material), showing excellent friction wear characteristics.

3.3 High-temperature corrosion resistant material (T22 steel)

In the present study, the corrosion resistance of Al2O3 films on high-Al alloy coatings on T22 steel is investigated. The unbalanced-magnetron sputtering was used to make thin films of Ni-30 at.% Cr-15 at.% Al with approximately 10 μm thickness, and then preoxidized for 12 h at 1000℃ in dry laboratory air. The corrosion resistance of the preoxidized coatings was evaluated in laboratory corrosion tests. This was performed by coating synthetic ash onto coupon specimens and then heating in 1000 ppm HCl-50 ppm SO_2-10% O_2-10% CO_2-20% H_2O-bal. N_2 for 100 h at 550℃. The synthetic ash, coated at 40 mg/cm^2, consisted of 27 mass% Al_2O_3-25% $CaSO_4$-15% $NaSO_4$-15% K_2SO_4-4% $ZnSO_4$-4% Fe_2O_3-5% NaCl-5% KCl.

Table 4 The thickness losses and surface morphologies of the specimens after reaction with synthetic ash at 550℃ for 100 h

Alloy	Average thickness loss (mm)	Corrosion morphology
Uncoated T22	0.8	General corrosion
Non-preoxidized Ni-Cr-Al coating	0.3	General corrosion
Preoxidized Ni-Cr-Al coating	0	–
Alloy 625	0	Pitting attack (20 μm)

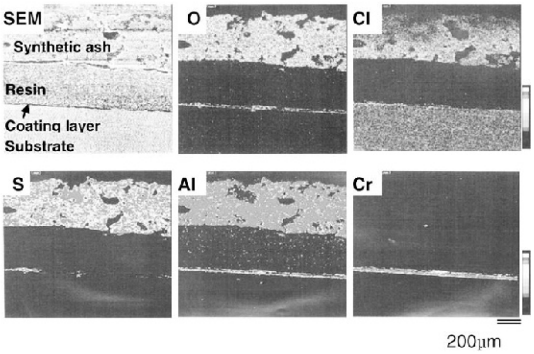

Fig. 10 SEM and EPMA images of a preoxidized Ni-Cr-Al coating after exposed by coating with synthetic ash in synthetic gas mixture at 550℃ for 100 h

Table 4 shows the thickness losses and surface morphologies of the specimens after reaction with synthetic ash. The good corrosion resistance was observed in alloy 625 (60.25Ni-21.61Cr-8.99Mo-3.68Nb-0.40Si-0.38Mn-0.04C-0.002P-0.002S (mass%)), but small pits with approximately 20 μm deep were found on the specimen surface. In this study, the preoxidized coating shows the best corrosion resistance, with essentially unmeasurable thickness loss and pitting corrosion as shown in Fig. 10. In EPMA maps of this specimen, enrichment of Al and O was observed on the surface of T22 steel. It is considered that the Al_2O_3 formed by preoxidation of NiCrAl coating acts as a protective barrier. Furthermore, the corrosion resistance of preoxidized NiCrAl-coated T22 steel was approximately similar to that of alloy 625, which shows good performance, in a field corrosion test.

4. Conclusions

The surface modification techniques by ion implantation and/or film coatings were investigated in order to develop oxidation, wear and corrosion resistant materials in high-temperature. The techniques were applied to industrial products. The obtained concluding remarks are summarized as follows.

(1) The implantations of Nb, Mo, Ta, W, F, and Cl ions, high-temperature Nb ion and Nb+C combined ion were useful for improving the oxidation resistance of TiAl alloys at 850℃. For practical application, the TiAl prototype rotor was treated with fluorine by PBII and its cyclic oxidation test showed improved oxidation resistance.

(2) The effects of boron ion implantation into TiN films were investigated using TiN-coated SUS630 SS. As the results, the wear resistance of TiN films was improved by boron ion implantation, which is due to formation of hard TiB_2 and lubricating BN.

(3) The effects on wear resistance by addition of Al or Cr into TiN were investigated using TiN-coated SUS630 SS. It was confirmed that addition of Al or Cr into TiN was effective for using in 450℃ steam.

(4) The corrosion resistance of T22 steel was improved in laboratory and field corrosion tests at 550℃ by preoxidized NiCrAl coating.

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