#### AN INVESTIGATION ON MAGNETRON SPUTTER

#### DEPOSITED ALLOY-OXIDE COATING

Ye Ruizeng, Zhou Lang, Chang Shouhua, Gao Lian and Lu Fanxiu

Division of Superalloys,
Faculty of Materials Science and Engineering,
Beijing University of Science and Technology
Beijing 100083, P. R. China

#### Abstract

Dispersive rare earth oxide in MCrAlY alloy, compared with elemental rare earth additions, can be more effective in increasing the alloy's resistance to oxidation and hot corrosion. In order to make the alloy-oxide composite coating, experiments on sputter deposition were conducted using D.C. magnetron sputtering devices with the targets specially made for cosputtering of both alloy and oxide. The deposited coatings were analyzed by TEM, XPS, XFS and EMPA methods. The TEM shows that there are very fine (5-20nm) dispersive particles in the annealed composite coating, which inhibit the grain coarsening in annealing. The XPS shows that there is measurable  $Y_2O_3$  or  $SiO_2$  in the composite coating, and the EMPA shows a homogeneous Y distribution along the cross section of the coating. The results show that a sputter deposited oxide dispersed alloy coating has been developed.

Superalloys 1988 Edited by S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich and C. Lund The Metallurgical Society, 1988

## Introduction

MCrAlY-type coatings have been extensively developed and applied since their creation in the 1970's, with chemistries being continually adjusted and improved. But, up to now, the addition of the active element yttrium, which plays a key role in resistance to oxidation and corrosion, has been restricted by its limited solubility in MCrAlY. It is prone to forming needle- or plate-like intermetallic compounds; for example, a Co<sub>3</sub>Y phase has been formed in CoCrAlY with Y additions of more than 0.1wt% (1,2). Therefore, it is difficult to obtain a homogeneously distributed high Y content in MCrAlY. Also, the plasticity of the coating is decreased if the amount and size of the yttrium compounds are increased to a certain extent. So the potential of further developing MCrAlY coatings in this respect is restricted.

From research on mechanisms of the role of Y in the oxidation resistance of alloys, a new way to develop the MCrAlY system can be expected. J. K. Tien (3) found that, in the oxidation of FeCrAly, below the inward growing oxide scale, yttrium is oxidized, forming a dispersion of Y2O3 particles. This means that all of the beneficial effects of Y on decreasing susceptibility to scale spallation and reducing the oxidation rate are exerted in the form of  $Y_2O_3$  particles. Tien proved one of the main mechanisms is "vacancy sinks": the boundaries between the oxide particles and matrix can absorb the Kirkendall vacancies produced by the external oxidation, thus reducing the scale spallation induced by voids formed by vacancy coalescence at the interface of the scale and the alloy. Ramanarayanan et al (4,5) showed that the microstructure of the oxide scale formed on FeCrAlY is the same as that on the ODS alloy MA-956 (FeCrAlTi-Y<sub>2</sub>O<sub>3</sub>) and the authors proposed that the effects of dispersive Y2O3 on oxidation behavior is similar to that of elemental Y, with the former being more effective because of its homogeneity. The experimental results support this argument

The mechanisms of rare earth elements and their oxides on hot corrosion behavior are seldom studied, but from the fact that hot corrosion resistance is mainly based on the protectivity and continuity of the surface oxide scale, it can be expected that the dispersed rare earth oxide can enhance the hot corrosion resistance of coated alloys exactly as the elemental yttrium has done. Hot corrosion tests for ODS alloys might support this (6).

Furthermore, according to the particle strengthening effect, dispersive oxide particles in the coatings increase their erosion resistance, which has become important as industrial turbines develop. The successful practice of introducing oxide particles into sprayed wear-resistant and erosion-resistant coatings is evidence of this.

So, it can be expected to obtain better protective properties than those of the currently used MCrAlY coatings by substituting rare earth oxides for the more expensive elemental rare earth additives.

Although the spraying technique can be a feasible way to obtain the alloy-oxide composite coating, the serious porosity of the sprayed coating makes it less reliable for service in gas turbines. Ion sputtering can provide films of high density and good adhesion to substrates, and the development of the magnetron sputtering technique has made its deposition rate feasible for production of high temperature protective coatings. Because magnetron sputtering is a D.C. (direct current) sputtering technique, standard processing cannot be used to deposit non-conducting species like oxides; consequently, a modified method must be used to sputter deposit the composite coating. Efforts have been made on a method specially designed to obtain the composite coating with a magnetron sputtering technique. The present paper reports the work on sputtering coatings and

their metallographic and chemical analyses.

## Experimental Details

## Sputtering Devices

Two magnetron sputtering devices of different types, both made by Beijing Instrument Manufacturing Corporation, were employed. One is a prototype, with a single circular permanent-magnetron target 65mm in diameter, the working power of which is usually less than 0.2Kw. The other one is a commercial type, with double-facing rectangular electro-magnetron targets, 250x120mm, the working power of each is usually less than 5Kw, limited by the cooling capacity of its water-cooling system. The latter type has an electric-resistance furnace under the sputtering chamber to heat the substrate before deposition.

## Sputtering Targets and Deposition Process

The base targets on which the oxides were superimposed for alloy-oxide co-sputtering were made by vacuum melting and casting of alloys, namely Co-25Cr-10Ni-4Al-5Ta-0.5Y or Co-30Cr (wt%). The oxides used were  $\rm Y_2O_3$  or  $\rm SiO_2$ . The use of  $\rm SiO_2$  was expected to increase the sulfidizing resistance of the coating.

The prototype sputtering device was used to deposit thin films suitable for direct TEM studies. The deposition parameters were as follows:

Primary Vacuum: 6.7x10-3Pa
Working Ar Pressure: 1.1Pa
Working Power: 0.11Kw
Substrate Bias: Floating

Further experiments were conducted on the commercial-type sputtering device to obtain the coatings of practical, feasible thickness on superalloy substrates. After being heated to 900°C under the primary vacuum in the furnace inside the device, the substrate was raised into the sputtering chamber for sputter deposition. The deposition parameters were as follows:

Primary Vacuum: 5.3x10-³Pa
Working Ar Pressure: 1.1Pa
Working Power: 4.2-4.5x2Kw
Substrate Bias: 0-400v

Substrate Temperature: 560-600°C at the onset of sputtering,

cooled down to 440-460°C in about 4 min, and then maintaining that temperature  $\,$ 

during sputter deposition

Deposition Rate: 0.4-0.5µm/min

## Specimen and Analysis

With the prototype device, films of about 50nm thickness were deposited on carbon film pre-adhered to copper grids, while the specimens for x-ray photoelectron spectrum (XPS) analysis were prepared with glass substrates placed beside the grids. The thin foils of the coatings sputtered with the commercial-type device (45-50µm thick) were prepared as follows: sectioned with a layer of the substrate parallel to the coating's plane; electrolytically thinned the sectioned pieces only on their substrate sides; ion beam thinning done on both sides. To analyze the Y contents in the coatings, the X-ray Fluorescent Spectrum (XFS) analysis was carried out, the results being corrected by chemical analysis of the scraps of the sputtered species

spalled from the inside walls of the sputtering chamber (0 bias voltage), and an Electron Probe Microanalysis (EPMA) was used to show the distribution of Y along the cross section of the coating.

# Results and Discussion

# The Existence of the Oxides in the Coating

Both the oxide-bearing or non-oxide bearing films show a microcrystalline structure, as indicated by the TEM image, Fig. 1. As the grains of the films are very fine (<20nm), it is difficult to identify the dispersive oxides possibly distributed in the films. To determine the existence of the oxides, XPS analysis was conducted.

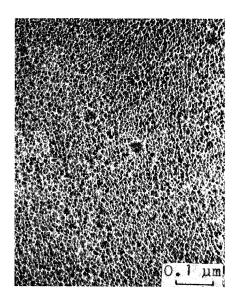


Figure 1 - The TEM image of the sputtered CoCrNiAlTaY-(Y2O3) film

Briefly, the XPS analysis directs x-rays onto the specimen so that the inner layer electrons are stimulated; the resulting photoelectronic emission is detected and characterized with respect to kinetic energy and intensity. The kinetic energy of the photoelectrons, Ek, is related to the bonding energy of the electrons, Eb, simply as:

$$Eb = hv - Ek + \phi s \tag{1}$$

where hv is the energy of the directing x-ray and  $\phi s$  is an instrument parameter. Since the bonding energy of the inner layer electrons is characteristic for every element, the chemistry information of the specimen can be obtained. Furthermore, the XPS has an important feature, the chemical displacement effect (7). In molecules, the density of valence electrons around the atoms is different from that of elemental atoms, and this induces changes in the binding energy of the inner layer electrons; thus, the characteristic energy of the elements in the molecular state will displace correspondingly. By this effect, the chemical state of the elements can be detected.

Fig. 2 is the overall spectrum of the  $CoCr-(Y_2O_3)$  film, which shows the existence of Y. Fig. 3 shows the magnified feature of the 3d electron peak of Y and the result of mathematical peak identification; Fig. 4 shows the 2s electron peak of Si in the  $CoCr-(SiO_2)$  film. Comparing them with standard spectra, it is determined that the Y and Si in the obtained films

exist as  $Y_2O_3$  and  $SiO_2$ , respectively. For the thick  $CoCr-(Y_2O_3)$  coating obtained with the commercial-type sputtering device, the XPS shows the same results.

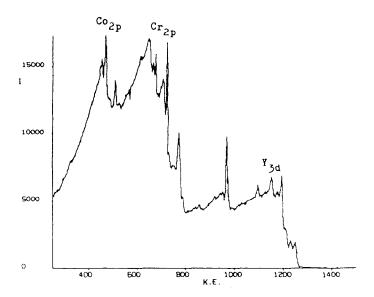


Figure 2 - The overall spectrum of the CoCr-(Y2O3) film

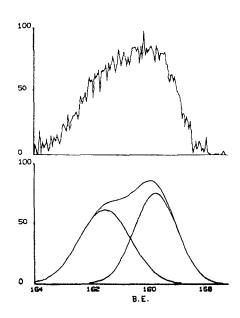


Figure 3 - The magnified Y3d electron peak and its identification

As the XPS cannot give a true quantitative analysis of contents, the XFS analyses were carried out. Table I gives the results obtained, while the characteristic x-ray image obtained by an electron probe microanalysis (Fig. 5) shows that the distribution of yttrium is homogeneous on the cross section of the coating.

# The Form of the Oxides

Fig. 6 is a TEM image of the  $CoCr-(Y_2O_3)$  coating. The very

inhomogeneous contrast inside the grain also has appeared in the coating in which no  $Y_2O_3$  has been introduced. It is, in fact, a reflection of the high density of crystal defects (mainly vacancies) in the high-rate sputter deposited coating. Such a configuration makes the identification of the

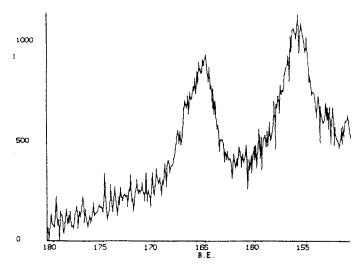


Figure 4 - The Si2s electron peak of the CoCr-(SiO<sub>2</sub>) film

Table I. The Analyzed Yttrium Content in the Coatings

 (% Area) target	Bias Voltage (V)	Y (w/o) (Chemical Analysis)	I/Im (XFS)	Corrected composition of Y (w/o)
4.7	0 -200 -400	2.07	100 83.6 30.5	2.07 1.73 0.78
2.3	0 -200	1.03	40.2 33.8	1.03 0.86

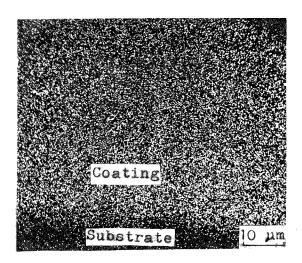


Fig. 5 - The yttrium x-ray image on cross section of the  $CoCr-(Y_2O_3)$  coating oxide particles very difficult. After annealing at 900°C for 13 hours, the grains of the coating without  $Y_2O_3$  grew one or more orders of magnitude and the inhomogeneous contrast disappeared. The grain size and defect density

inside the grains of the  $CoCr-(Y_2O_3)$  coating changed little after annealing 7 hours longer, as indicated in Fig. 7a, b.

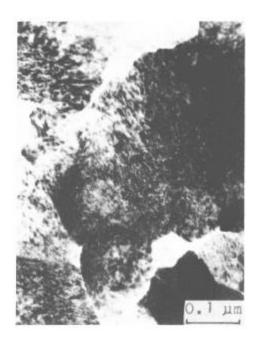


Figure 6 - A TEM image of the as-sputtered CoCr-(Y2O3) coating

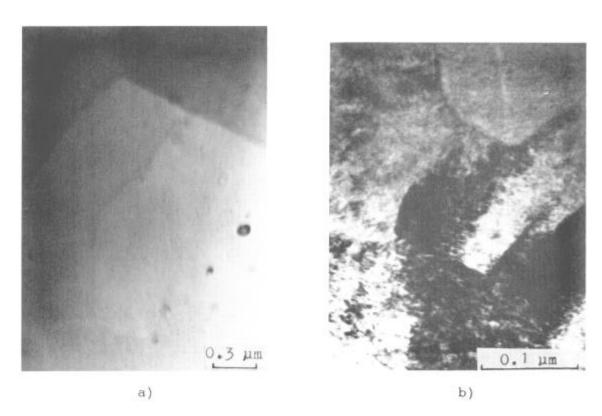


Figure 7 - The TEM image of the annealed coating a - CoCr 900°C, 13 hrs annealed b - CoCr-(Y<sub>2</sub>O<sub>3</sub>) 900°C, 20 hrs annealed

After annealing the  $CoCr-(Y_2O_3)$  coating at 1200°C for 4 hours, the contrast from the crystal defects in the TEM image was eliminated and there

emerged large amounts of particles 5-20nm in size, as indicated in Figure 8. To identify the structure and chemistry of the super fine particles directly is difficult at present, but combined with the XPS analysis and compared with the TEM analysis of the oxide-free CoCr coating, it can be deduced logically that the particles are dispersive yttrium oxide.

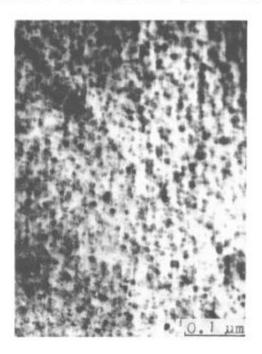


Figure 8 - TEM image of the CoCr-Y203 coating annealed at 1200°C for 4 hours

### Conclusion

- Substituting the dispersive rare earth oxides for the expensive elemental rare earth additives in coatings is a new way to improve the high temperature protective coating;
- 2) The co-sputter deposition of alloy-dispersive oxide composite coating by D.C. magnetron sputtering can be realized with the present method.

#### References

- D. R. Holmes and A. Rahmel, eds., <u>Materials and Coatings to Resist High</u> <u>Temperature Corrosion</u>, (1978), 55.
- 2. Fon Jianya, Ye Ruizeng et al, <u>Proc. of the 6th Chinese Conference on Superalloys</u>, Chinese Society for Metals, (1986), Vol. 2.
- J. K. Tien and F. S. Pettit, <u>Metallurgical Transactions</u>, 3 (1972), 1987.
- 4. T. A. Ramanarayanan et al, J. Electrochemical Society, 131 (1984).
- 5. T. A. Ramanarayanan et al, Oxidation of Metals, 22 (1984), 83.
- 6. As (1) 71.
- 7. D. Briggs et al, eds., <u>Handbook of X-Ray and Ultraviolet Photoelectron</u> Spectroscopy (Heyden and Son Ltd., 1977)