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Layer coatings of Re and Re-NiCr obtained by thermoionic vacuum arc technique

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In this paper we report Re and Re-NiCr layers obtained by Thermoionic Vacuum Arc (TVA) technique. The films deposited onto copper, glass and ceramic substrates were characterized by XRD and AFM methods. We have found that Re film crystallinity is not dependent on substrate composition while Re-NiCr layer structure strongly depends on the substrate composition. The prepared films were found to be very adherent, pure and smooth providing that TVA is a good method to produce high quality coatings of refractory metals.

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1. Introduction

Coatings of Rhenium are desirable to protect surfaces from corrosion caused by hot air due to its high chemical corrosion resistance. Re layers can also be used as thermal barrier coatings in applications like turbine components against high temperatures and in semiconductor devices [1].

In high technology applications, the coatings must fulfill several requirements simultaneously. Therefore, they are usually made of multiple-layers having different properties like: a stress-relaxation layer to attain high adhesion with the substrate, a barrier against coming and outgoing elements, a reservoir supplying lost elements and a heat resistant layer. For example, Re was found to be a good thermal barrier layer within a Ni-Cr coating on Nb super-alloy [2]. However, it is very difficult to deposit Re due to its high melting and boiling points, low vapor pressure and high work function.

Thermoionic Vacuum Arc (TVA) method was proved to be one of the few methods currently available to produce high quality coatings of refractory metals. The TVA deposition method offers a high degree of flexibility due to its unique combination of properties [3-6].

In this paper, we used XRD and AFM methods for characterization the thin films of Re and Re-NiCr obtained by TVA. The films were deposited on Cu, glass and ceramic substrates.

2. Experimental

The experimental set-up of TVA discharge, shown in figure 1, was presented in detail elsewhere [3] and briefly consists of a tungsten filament cathode externally heated by a low voltage. In our experiment, a Rhenium rod and also a pool of 50% Ni metals and 50% Cr powder were used as anodes. The thermal electrons emitted by cathode are focused on the top of the anodes surfaces by a Whenelt cylinder. Due to electron bombardment, the anode material evaporates and at a certain vapour pressure the electron-atom ionizing collisions generate plasma in pure anode material.

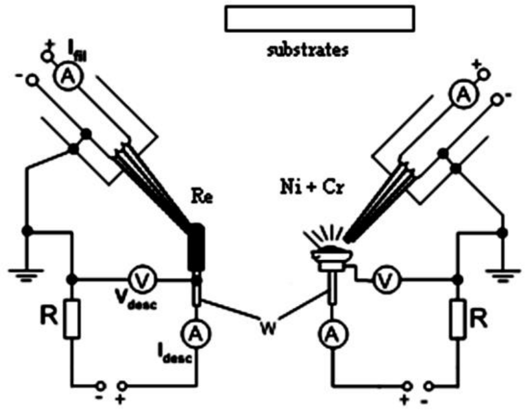


Fig. 1. The scheme of the experimental set-up TVA discharges ignited on Re and NiCr.

For plasma ignition, the TVA gun filament used for Re rod has been heated using a 100 A current. The conditions of the stable discharge during deposition of Re TVA are I_{arc} = 1.2 - 1.5 A and U_{arc} = 1400 – 1500 V. For the NiCr plasma ignition the filament was heated with 37 A. The stable conditions during deposition of the NiCr TVA are I_{arc} = 1.1 – 1.29 A and U_{arc} = 700-550 V. The thickness of the film has been measured during the deposition with a Cressington equipment, which uses the quartz oscillators. The deposition has been interrupted when the indicated thickness was of 500 nm. The Cu and ceramic substrates were heated at 250°C. During deposition the support of the substrates was rotating. After termination of the deposition, the anode voltage and the applied current to the TVA gun filaments have been reduced to zero. The samples have been kept in the deposition chamber, under high vacuum for about 120 minutes, in order to cool down the chamber and substrate temperatures.

The XRD measurements were performed using a Szimadzu 6000 in the thin film configuration with a very small incidence θ angle of 1.2°. In order to understand the deposition of Re-NiCr we made first a pure Re film deposition onto Cu and ceramic substrates.

Surface morphology of the thin films was observed by non-contact mode atomic force microscopy (AFM, PARK XE-100 SPM system). The root-mean-square roughness (RMS) and the peak-to-valley roughness (R_{pv}) of the surfaces were estimated over the area of 1×1 μm^2.

3. Results and discussions

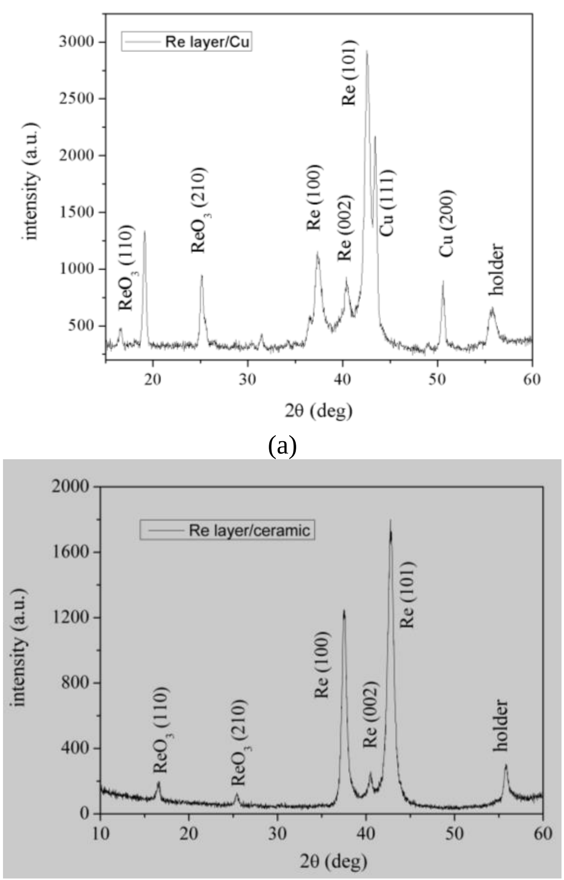
The XRD measurements of the pure Re film deposited on Cu and ceramic substrates are shown in the figures 2a and b.

As we may see from the figure 2, the upper and lower spectra indicate a very clear hexagonal crystalline structure of Re. The strongest lines of the pure Re layer are identified at 2θ positions: 37.634° (100), 40.489° (002) and 42.928° (101). The lines at the 2θ positions, 16.566° (110) and 25.457° (210) are attributed to the hexagonal structure of Re oxide, ReO$_3$. The oxidation might be formed at the film surface after deposition by exposure in ambient air. The peak at position of 56° belongs to holder of the XRD device.

The diffractogram of Re-NiCr layers are presented in figure 3 and figure 4. The diffractograms in figure 3 correspond to Re-NiCr deposited on copper and glass substrates and the solid line belongs to the Cu substrate. The diffractogram presented in figure 3 shows a partial crystalline structure of the layer deposited on Cu and a disordered amorphous layer on the glass. The line (100) of crystalline hexagonal Re is not presented on the glass substrates. This could be a proof that Re-NiCr layer grows in an amorphous structure.

The amorphous characteristic of the layer on glass substrate is proved by the broadening of the peaks (around 39°- 44°) in curve (●) from figure 4. This aspect demonstrates the participation of Cr and Ni to the Re-NiCr composite as disordered form at atomic scale.

In the diffractrogram from figure 4, the large peak could be a disorder structure of Re alloys as: CrRe$_2$, Cr$_3$Ni$_2$, the last one being formed since Ni and Cr are melted in the same pool. In order to clarify this experimental observation we made an attempt to search these compounds on the database in the region of our interest. It was found that Re alloys as CrRe$_2$, Cr$_3$Ni$_2$, and hexagonal Re have the main diffraction lines as presented in the figure 4 in arbitrary units, for a better view.



(a)

(b)

Fig. 2. The XRD structure of pure Re film deposited on Cu (a) and ceramic (b) substrates. The peak at 19.17° could not be assign.

As it may be seen from figure 4 the pure Ni and Cr crystallographic phase cannot be observed for the metallic Re-NiCr films prepared in TVA plasma, the only crystalline phase being exhibited by CrRe$_2$ and Cr$_3$Ni$_2$. The lack of the Ni and Cr as pure elements in the layer is a result of the alloying phase formation during the deposition process by TVA.

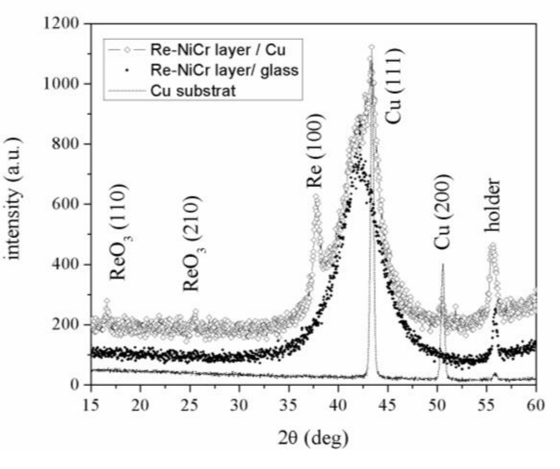


Fig. 3. The XRD spectra of Re-NiCr film deposited on the Cu (-○-) and glass substrates (●). The solid line spectrum corresponds to the substrate cubic Cu.

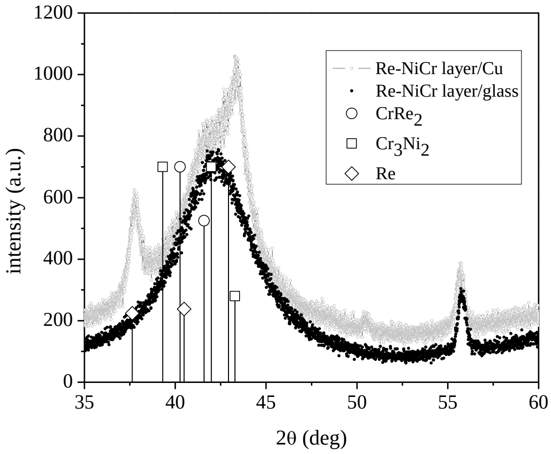


Fig. 4. The XRD spectra of Re-NiCr and those of Re and the alloys $CrRe_2$, Cr_3Ni_2, from the database (in arbitrary units).

The 3D topographic AFM image from Fig. 5 suggests that using TVA technique we obtained surface layers quite smooth, without cracks and compact, with a very small roughness (around 4nm). The surface roughness analysis in PSD terms are shown in figure 6 (for glass substrate) and figure 7 (for Cu substrate). The maximum "peak-to-valley" values are found to be 28nm for Re-NiCr film deposited on glass substrate and 38nm for Re-NiCr film deposited on Cu substrate.

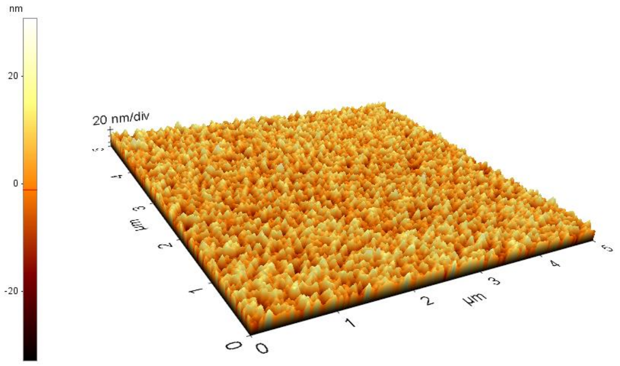
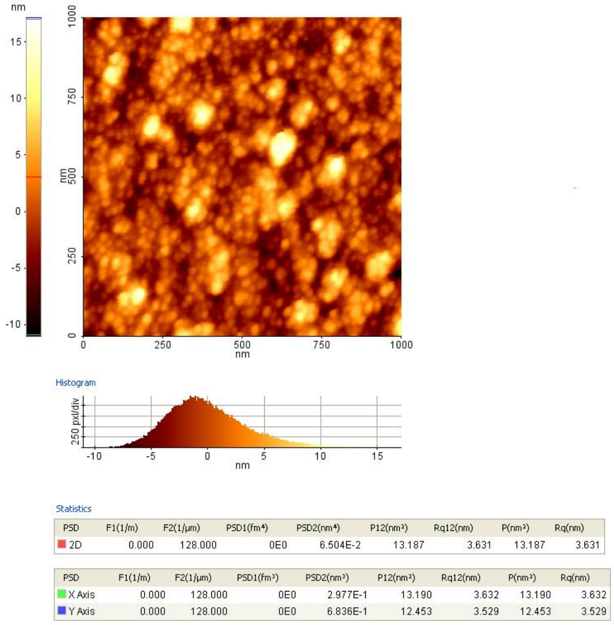


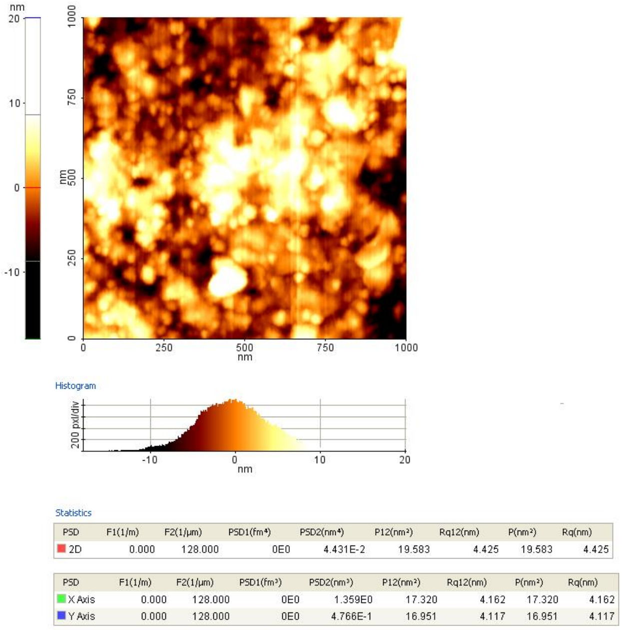
Fig. 5. Surface morphology of Re-NiCr film deposited on glass substrate, measured with AFM. Scanned area is 5×5 µm^2.



PSD	F1(1/m)	F2(1/µm)	PSD1(fm⁴)	PSD2(nm⁴)	P12(nm²)	Rq12(nm)	P(nm²)	Rq(nm)
🟥 2D	0.000	128.000	0E0	6.504E-2	13.187	3.631	13.187	3.631

PSD	F1(1/m)	F2(1/µm)	PSD1(fm³)	PSD2(nm³)	P12(nm²)	Rq12(nm)	P(nm²)	Rq(nm)
🟩 X Axis	0.000	128.000	0E0	2.977E-1	13.190	3.632	13.190	3.632
🟦 Y Axis	0.000	128.000	0E0	6.836E-1	12.453	3.529	12.453	3.529

Fig. 6. PSD data conducted over 1×1 µm^2 area of Re-NiCr film onto glass substrate.



PSD	F1(1/m)	F2(1/µm)	PSD1(fm⁴)	PSD2(nm⁴)	P12(nm²)	Rq12(nm)	P(nm²)	Rq(nm)
🟥 2D	0.000	128.000	0E0	4.431E-2	19.583	4.425	19.583	4.425

PSD	F1(1/m)	F2(1/µm)	PSD1(fm³)	PSD2(nm³)	P12(nm²)	Rq12(nm)	P(nm²)	Rq(nm)
🟩 X Axis	0.000	128.000	0E0	1.359E0	17.320	4.162	17.320	4.162
🟦 Y Axis	0.000	128.000	0E0	4.766E-1	16.951	4.117	16.951	4.117

Fig. 7. PSD data conducted over 1×1 µm^2 area of Re-NiCr film onto Cu substrate.

5. Conclusions

Using the Thermoionic Vacuum Arc technique we reveal that materials as Re and NiCr could be deposited in the same time. By AFM investigations we observed that the films are pure and have a compact, cracks free, homogeneous and very smooth surface. By XRD measurements we have found that: first, Re films were grown in crystalline structures both on metallic and non-metallic substrates and second, the Re-NiCr films grown crystalline on metallic substrate but amorphous on non-metallic substrate.

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