



Brief Report Application of Secondary Ion Mass Spectrometry for Analysis of Decorative Coatings on Fancy Goods Accessories

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Abstract: The results of a secondary ion mass spectrometry (SIMS) study on Ag and ZrN decorative coatings on nickel and white bronze substrates for fancy goods accessories are presented. It was found that for Ag coatings, an intense diffusion of Cr from the adhesion layer between the coating and the substrate is observed, and corrosion testing in an acetic salt (CH₃COOH+NaCl) atmosphere leads to the almost complete degradation of such coatings. ZrN coatings on white bronze turned out to be the most resistant to Cr diffusion and corrosion processes.

Keywords: decorative coatings; secondary ion mass spectrometry (SIMS); silver; zirconium nitride; sputter depth profiling



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1. Introduction

Decorative coatings based on precious metals are quite widely used in the modern fashion industry to improve the quality of accessories for haberdashery products from the world's leading manufacturing companies (see, for example, [1]). As an alternative, more economical coatings made from nitride compounds of non-jewelry metals, such as Ti and Zr, should be put forward. ZrN imitates the color of silver and white gold quite well, which is why it is often called mock silver. Nitride coatings came to the fashion industry from industrial metalworking, where they had long been successfully used to produce wear-resistant coatings for metal-cutting tools.

At present, the main technologies for the production of decorative coatings are electroplating and physical vapor deposition (PVD). Electroplating [2] is a well-developed and approved technology, but at the same time, it is quite energy-intensive and environmentally unsafe, both for operating personnel and for the environment. PVD provides an application of decorative coatings [3] comparable in hardness and corrosion resistance to electroplating and is an environmentally friendly technology.

The main goal of our work was to demonstrate the potential of secondary ion mass spectrometry (SIMS) [4,5] for studying the degradation of thin decorative coatings made of 925-assay silver and mock silver (ZrN) on Ni and white bronze substrates under the corrosion test in an acetic salt (CH₃COOH+NaCl) atmosphere. SIMS was chosen as the research method since it has proven itself to be a highly sensitive technique for the determination of elemental composition, with the unique possibility of carrying out sputter depth profiling of the near-surface region of the samples studied. This technique is widely used in microand nanoelectronics, the semiconductor industry, geology, criminalistics, etc., and in our view, it could also be successfully applied in traditional handicraft technologies like jewelry and fancy goods production.

2. Materials and Methods

Two sets containing two samples were studied, which were Ag and ZrN coatings on Ni and white bronze substrates (Cu 60%, Sn 39%, Zn 1%). The coatings were deposited by PVD, but the details of the technological process were commercial know-how and were not divulged by the manufacturer of the fancy goods accessories (Top Finish, Florence, Italy). According to the data provided to us by manufacturer, the thickness of the silver coating was 0.02 μ m, and the thickness of ZrN was 0.2 μ m. To improve adhesion between the metal substrate and the decorative coating, a thin layer of Cr with a thickness of about 0.01 μ m was deposited to each sample via PVD. The corrosion test was carried out in a special chamber for 24 h in an acetic salt atmosphere (CH₃COOH+NaCl) in accordance with ISO 9227:2022 [6].

SIMS measurements were carried out under high-vacuum conditions (10^{-6} Pa) by means of a dedicated instrument based on the standard commercial components. A detailed description of this setup can be found, for example, in [7,8]. Briefly, a DP50B duoplasmatron (VG Fison, London, UK) was used as an ionbeam source, which generated a mass-separated beam of primary ${}^{16}\text{O}_2^+$ ions (3 keV, 200 nA). This beam was scanned on the sample surface within a rectangular raster of 0.5 mm², and the crater effect, i.e., the influence of the walls of the sputtering crater on the useful signal, was suppressed by an "electronic diaphragm", which ensured the collection of the secondary ions only from the central part of the crater (15% of the raster area). Secondary ions were analyzed using an EQS 1000 Mass Energy Analyzer (Hiden, Manchester, UK), and the depth of the sputtering craters was measured using a Stylus Profiler P-10 (Tencor, Milpitas, CA, USA).

3. Results and Discussion

Three measurements in the randomly selected points were carried out for each sample. In Figures 1–4, the representative SIMS depth profiles of Ag and ZrN coatings on Ni and white bronze are presented before and after the corrosion test. The mass peaks of positive ions $^{107}Ag^+$, $^{53}Cr^+$, and $^{58}Ni^+$ (for Ni substrate) and $^{107}Ag^+$, $^{90}Zr^+$, $^{14}N^+$, $^{53}Cr^+$, $^{63}Cu^+$, and $^{152}(SnO_2)^+$ (for white bronze substrate) were chosen as characteristic of the coatings and substrate materials, and the surface and near-surface contamination was monitored by the intensity of the $^{23}Na^+$ mass peak. The depth profiles, which are dependencies of the maximal mass peak intensities versus time of sputtering, were automatically measured using EQS MASsoft Ver. 3 control software (Hiden, Manchester, UK).



Figure 1. SIMS depth profiling of Ag coatings on Ni substrate: (a) initial sample; (b) after corrosion test.



Figure 2. SIMS depth profiling of ZrN coatings (mock silver) on Ni substrate: (**a**) initial sample; (**b**) after corrosion test.



Figure 3. SIMS depth profiling of Ag coatings on white bronze substrate: (**a**) initial sample; (**b**) after corrosion test.



Figure 4. SIMS depth profiling of ZrN coatings (mock silver) on white bronze substrate: (**a**) initial sample; (**b**) after corrosion test.

It is worth recalling that the intensities of the mass peaks are related to the concentration of the corresponding chemical elements, but their magnitude in the SIMS method is drastically influenced by the efficiency of the ionization of the sputtered atoms, which depends on the ionization potential of these atoms. This explains the high intensity of ²³Na⁺ (the ionization energy of Na is 5.139 eV [9]). The depth scale in all figures was calculated from the sputtering times, and crater depths were measured by a Stylus Profiler P-10 (Tencor, Milpitas, CA, USA) after the end of the SIMS analysis, assuming a constant sputtering rate over the whole analyzed depth.

From the SIMS depth profiles presented in Figure 1a, one can conclude that Cr is present on the surface and throughout the whole thickness of the Ag coating of the initial sample. The thickness of this coating was found to be within 0.1–0.15 μ m, which is an order of magnitude greater than what was indicated by the manufacturer based upon the time of the coating deposition. Additional SEM studies showed that the surface of the Ag coating is rough, and the arithmetic mean deviation R_a of the roughness profile measured by a profilometer turned out to be comparable with the thickness of the coating itself. After the corrosion test (Figure 1b), in addition to Cr, Ni was observed on the coating surface, which diffused from the substrate material through the Cr layer. The intensity ratio of the ⁵⁸Ni⁺ mass peaks on the coating surface before and after the corrosion test exceeded 10², and for the ⁵³Cr⁺ mass peak, this ratio was equal to 2.

As for the ZrN coating on the initial sample with the Ni substrate (Figure 2a), the Cr penetration from the adhesion layer onto the surface of this coating was much less pronounced than in the case of the Ag coating (Figure 1a). This can be explained by the greater thickness of the coating, which, according to the results of SIMS depth profiling, was found to be 0.25–0.3 μ m, which approximately coincides with the data provided by the manufacturer. The corrosion test (Figure 2b) also caused intense diffusion of Ni onto the surface of the ZrN coating, and the intensity ratio of the ⁵⁸Ni⁺ mass peak before and after the corrosion test reached 10³, which is approximately five times greater than for the Ag coating on the same substrate. At the same time, the intensity of the ⁵³Cr⁺ mass peak remained at the level of the initial sample. Note that the low intensity of the ¹⁴N⁺ mass peak could be explained by the low efficiency of positive ionization of the sputtered N atoms (the ionization energy of N is 14.534 eV [9]).

For the initial sample with an Ag coating on white bronze (Figure 3a), the presence of chromium on the surface and inside the coating was also observed. After the corrosion test (Figure 3b), the intensity of the ${}^{53}Cr^+$ mass peak increased by 1.5 times, and the intensity of the ${}^{63}Cu^+$ mass peak due to diffusion from the substrate material increased by approximately 50 times. As for the ZrN coating on the same substrate (Figure 4a,b), the intensity of the mass peaks of Zr⁺ and Cr⁺ ions after the corrosion test for these samples remained at the level of the initial samples, and the diffusion of Cu from the substrate led to an increase in mass peak ${}^{63}Cu^+$ of approximately 8 times. Another component of white bronze (Sn) was monitored by the molecular ion ${}^{152}(SnO_2)^+$, the intensity of which did not change significantly after the corrosion test.

For quantitative interpretation of the SIMS data, the relative sensitivity factors (*RSF*) can be used [5,10], which are experimentally determined as [5]

$$RSF_i = C_i \frac{I_m}{I_i},\tag{1}$$

where I_m and I_i are the intensities of the mass peaks of the matrix and impurity ions (sum of the isotopes), respectively, and C_i is the concentration of impurity atoms in the matrix.

The RSF method is more suitable for assessing a low concentration of impurities $(C_i < 1 \text{ at.}\%)$, but good results were also obtained for $Si_{1-x}Ge_x$ (0.092 $\le x \le 0.78$) [11]. We used this method to calculate the concentrations of metals on the surface of the decorative coatings studied. The *RSF* values for Ag, Cr, Zr, and substrate metals (Ni, Cu, and Sn) are given in Table 1, and the intensities of their mass peaks of positive ions were obtained from the measured mass spectra of the samples.

Table 1. RSF values for metals entered into the composition of decorative coatings and substrates [9].

Ag	Cr	Ni	Zr	Cu	Sn
500	65	370	40	310	300

We should note that our calculation is semi-quantitative since surface contaminants (alkali and alkaline earth metals, hydrocarbons, water, gaseous impurities, etc.) were not taken into account and the *RSF* values were used for the impurities in the silicon matrix. Estimated concentration calculations were made using the following formula [5]:

$$C_i = \frac{(I \cdot RSF)_i}{\sum_i^n (I \cdot RSF)_i} \times 100 \text{ at.\%.}$$
⁽²⁾

The results obtained for both types of decorative coatings before and after the corrosion test are presented in Table 2.

Table 2. Concentration of metals C_i (at.%) in decorative coatings before and after corrosion test (wb means white bronze).

	Ag on Ni	Ag on wb	ZrN on Ni	ZrN on wb
Initial sample	Ag 20, Cr 80	Ag 10, Cr 90	Zr 83, Cr 11, Ni 6	Zr 88, Cr 12
After corrosion test	Ag 2, Cr 89, Ni 9	Ag 8, Cr 88, Cu 3, Sn 1	Zr 6, Cr 2, Ni 92	Zr 84, Cr 5, Cu 8, Sn 3

4. Conclusions

Based on the results of SIMS depth profiling presented in Figures 1–4 and the metal concentration estimates shown in Table 2, the following conclusions were made:

- Ag coatings on Ni and white bronze substrates, even for the initial samples, contain a large amount of Cr, and the degradation of these coatings progresses after the corrosion test.
- Initial ZrN coatings on Ni and white bronze substrates were less broken due to Cr diffusion from the intermediate adhesion layer placed between the coating and the substrate than in the case of Ag coatings with the same adhesion layer on the same substrates.
- ZrN coatings on a white bronze substrate turned out to be the most resistant to the corrosion test.

To improve the quality of decorative coatings, we recommended that the manufacturer increase the thickness of Ag coatings, reduce the roughness of the substrates, and find a replacement for the Cr adhesive layer to prevent the diffusion of Cr and substrate metals (Ni, Cu, and Zn) into the coatings.

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