CHARACTERIZATION OF ELECTRODEPOSITED NICKEL-COBALT SELECTIVE BLACK COATING USING ELECTRON PROBE MICRO ANALYSIS

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This paper reports on the method of characterization of electrodeposited nickel-cobalt selective black coating through the method of Electron Probe Micro Analysis (EPMA). Qualitative and quantitative elemental analysis have been carried out to identify and estimate elements present in the coating. In this study the ratio between the K_α and K_β X-ray peak intensities of an element has been taken as a representative of the chemical state of the element in a sample. This analysis reports that the nickel-cobalt selective black coating has the elements nickel, cobalt and oxygen as major constituents and sulphur in traces. It has been found that nickel and cobalt are in mixed state, i.e. elemental as well as oxidized state.

Keywords: Selective coatings, black nickel-cobalt, solar energy, thermal energy conversion, electron probe micro analysis.

INTRODUCTION

An absorber plate surface which exhibits the characteristics of a high absorptivity value for incoming solar radiation and a low emissivity for outgoing radiation are called 'selective' surfaces. Such surfaces are desirable because they maximise the absorption of solar energy and minimise the emission of the radiative loss. Hence, they yield higher collector efficiencies than are obtained when the absorptivity and emissivity are equal as in the case of black parts [1-5].

Selective surfaces with high solar absorptance and low thermal emittance are not naturally occurring but are prepared artificially. In our earlier study we have reported on the production of selective coatings based on nickel-cobalt alloy by the electrode position technique. In this paper we report on the characterization of such coatings using electron probe microanalysis.

EPMA is one of the most important surface analytical techniques to analyse elements which are present in a specimen surface. In this technique the specimen is irradiated with a focused energetic intense beam of electrons. During irradiation of electron beam specimen is emitting X-rays. These X-rays are of two types namely continuous and characteristic X-rays. The characteristic X-rays are carrying informations about their origin. Hence EPMA could be successfully employed in the case of elemental analysis in a micro-area of sample. This analysis can be done in three ways namely (a) point analysis in which elemental informations at a point on the sample surface is analyzed, (b) line analysis in which the elemental informations on a line is analyzed and (c) area mapping in which an elemental mapping in a micro-area on the sample surface is carried out. EPMA has been carried out on nickel-cobalt black coating to determine (a) elemental distribution of nickel and cobalt in grains of black coating, (b) quantity of nickel, cobalt and oxygen and (c) chemical state of nickel and cobalt.

EXPERIMENTAL

Nickel cobalt black coating was cathodically deposited using an electrolyte containing nickel sulphate 10 g/l, cobalt sulphate 10 g/l and ammonium acetate 10 g/l at a pH of 6.2 Electrodeposition was carried out under a current density of 3.53 A.dm^{-2} for 30 seconds at a temperature (303-308 K) on pre- treated copper cathode of size 100 mm x 100 mm. This pretreatment involves mechanical polishing, degreasing, alkaline cleaning, washing in distilled water, acid pickling, washing in tap water and rinsing in distilled water. Pretreated copper sheets were given an undercoating of nickel to a thickness of 10 μm using Watt's nickel bath. The schematic cross section of black coating with substrate is shown in Fig. 1.

EPMA studies have been carried using WDS attachment with JEOL JSM 35 CF Scanning Electron Microscope which is attached with the double dispersion spectrometer with Rowland circle radius 140 mm. X-rays emitted by the specimen were analyzed using LiF crystal. The accelerating voltage was chosen as 15 KV. The absorbed electron beam current was kept as constant at 10 nA and the beam diameter was 1 to 5 μm. For EPMA studies the deposit must be very thick to avoid the interference from the substrate. As the black coating is relatively a thin film the experi- ment was carried out in two stages. In the first stage nickel-cobalt black coating was analysed with substrate. In the second stage a pellet of the black powder separated from the substrate was taken for EPMA studies.

To determine the quantity of the constituent elements, i.e. nickel, cobalt and oxygen, the sample was replaced with the standards of them in which the weight percentage of them had been known. The relative intensity of elements was obtained by comparing the X-ray intensity at the peak position of K$_\alpha$ emission of elements in sample and standards. Then by applying suitable ZAF (atomic number, absorption and fluorescence) correction to have relative intensity, the exact weight percentage of elements was found [10-11].

The chemical environment of elements present in the sample was analysed by comparing the ratio of K$_\alpha$ and K$_\beta$ X-ray intensity in different specimens in which the elements are in different chemical state or environments. To analyse the chemical state of the nickel and cobalt in the black coating the experiment was carried out in five stages. In the first stage the analysis was done on the nickel-cobalt black powder, in which chemical state of constituent elements was unknown. In the second and third stages the standards of nickel and cobalt (supplied by M/s JEOL Japan) as pure element were respectively analysed. In the fourth stage, a stable compound of nickel (nickel sulphate) with conducting coating was analysed. In the fifth stage a stable compound of cobalt (cobalt sulphate) with conducting coating was analysed [12,13].

RESULTS AND DISCUSSION

The results of the electron probe microanalysis carried out on the nickel-cobalt black coating deposited on nickel undercoated copper substrate is shown in Fig. 2. Normally, using that result, one may enter into a wrong conclusion that the coating has more amount of nickel than cobalt, because the higher amount of nickel might have
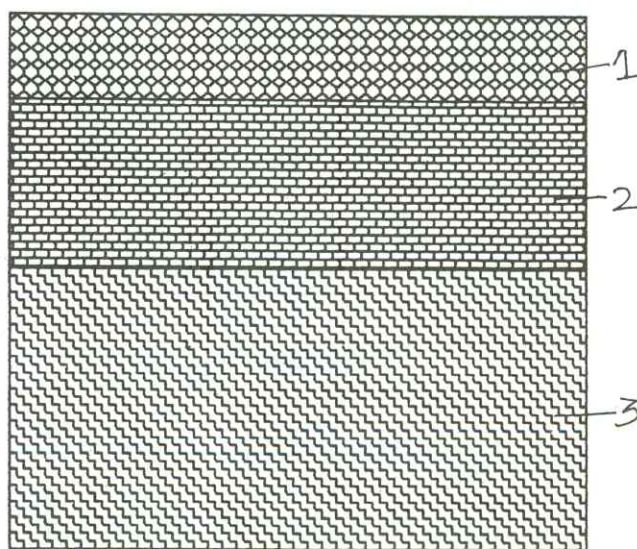

Fig. 1: Schematic diagram of cross section of selective black coating with nickel undercoated copper substrate
(1) Nickel cobalt black coating
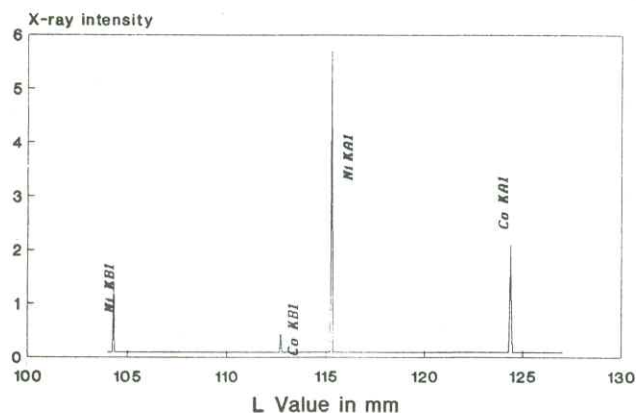(2) Nickel undercoating   (3) Copper substrate

Fig. 2: EPMA on Ni-Co selective black coating with substrate

come from the undercoating. So the analysis has been carried out on the black powder separated from the substrate to get a clear idea about the coating material. The result obtained on the analysis of black powder is shown in Fig. 3. It shows that nickel and cobalt present in the coating with almost equal concentration. On comparison of the K_α X-rays peak intensities obtained for nickel, cobalt and oxygen for the black powder with their corresponding standards, the relative intensities of the elements have been obtained. For nickel and cobalt pure standards are available and for oxygen calcium oxide, which is one of the very stable compound of oxygen is taken as a standard. The true concentration of elements have been obtained using ZAF correction method and are tabulated in Table I.

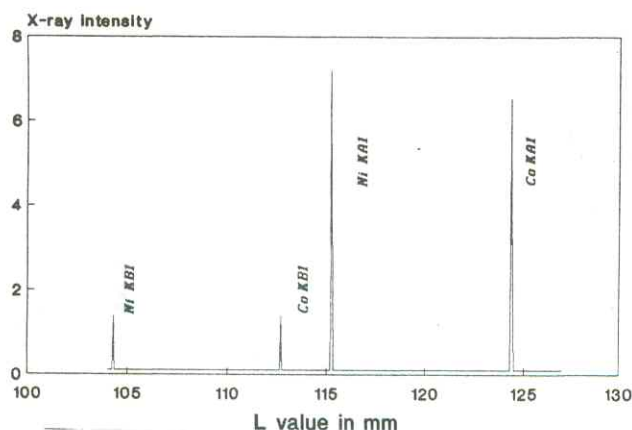To identify the chemical state of nickel in black coating, the K_α and K_β X-ray intensities and their

ratio have been obtained for pure nickel, black coating and nickel sulphate. The results are shown in Fig. 4. The peak positions of K_α and K_β radiations are shown in Figs. 5 and 6 respectively in an expanded scale. In these graphs X-axis represents the L value

$$L = \frac{2R}{2D}\, n\lambda \tag{1}$$

The representative of wavelength of the emitted X-radiation and the Y axis represents X ray intensity in relative units. To obtain these curves the X ray intensities obtained for pure nickel sample and black coating have been suitably attenuated to compare with the intensity obtained for nickel sulphate. The K_α intensity is kept equal in all the three curves. The K_β intensity increases with the level of oxidation. The width of X ray peaks is also found to be a function of chemical state of an element. The ratio between the nickel K_α and K_β X-ray intensities obtained for black coating, pure nickel and nickel sulphate are 5.143, 5.258 and 4.496 respectively. On analysing the above results and from the concentration obtained in the EPMA studies it can be concluded that nickel present in the nickel cobalt black coating must be in a mixed state, i.e. part of nickel in element state and the rest of it in oxidized state. On looking at Fig. 6, it could be seen that the K_β X ray peak due to black coating is more closer to that of pure nickel than that of nickel sulphate. Hence, it can be concluded that the black coating

Fig. 3: EPMA on Ni-Co black powder

TABLE I: EPMA results obtained on Ni-Co black powder

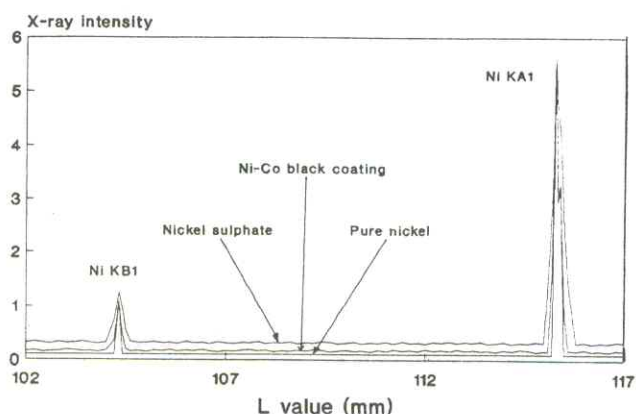| Element	X-ray intensity specimen	(CPS) Std	Relative intensity	Wt%
Nickel	2517.6	5206	0.483595	48.68459
Cobalt	2251.6	4536	0.496384	50.22487
Oxygen	25.6	564	0.012949	1.09054
Total			0.992930	100.0000

301

Fig. 4: Chemical state of nickel in
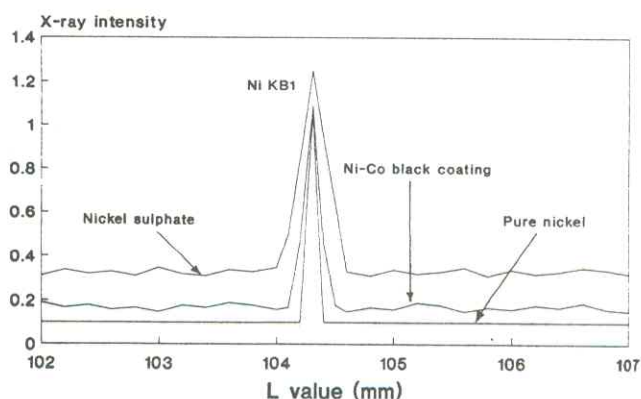pure nickel, black coating and nickel sulphate

Fig. 6: Peak position of nickel K_β radiation in nickel,
Ni-Co black coating and nickel sulphate in expanded scale

has more nickel in the atomic state than in the ionic state [12-13].

To identify the chemical state of cobalt in nickel-cobalt selective black coating, the K_α and K_β X-ray intensities and their ratios have been obtained for pure cobalt, black coating and cobalt sulphate. As in the case of nickel the results obtained for cobalt are shown in Fig. 7. The peak positions of cobalt K_α and K_β radiation in an expanded scale are shown in Figs. 8 and 9 respectively. The ratio between K_α and K_β intensities for black coating, pure cobalt and cobalt sulphate are 4.678, 4.928 and 3.6 respectively. On analysing these results obtained in the EPMA studies it can be concluded that cobalt presents in nickel-cobalt black coating must be in a mixed
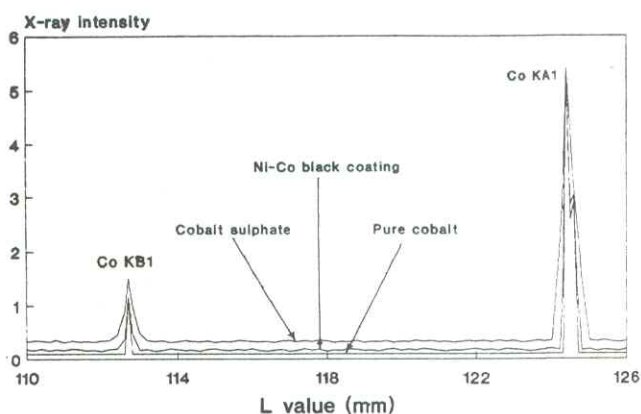

Fig. 7: Chemical state of cobalt in
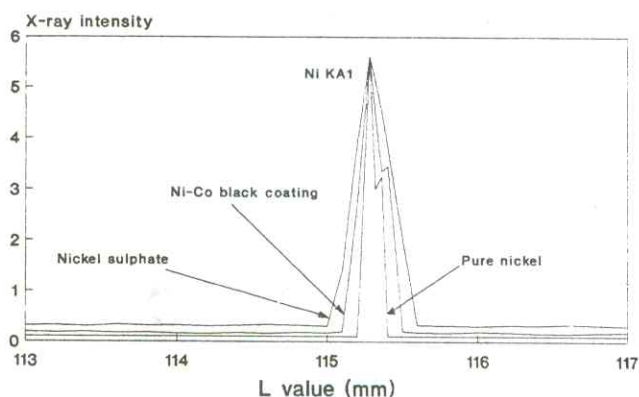pure cobalt, black coating and cobalt sulphate

Fig. 5: Peak position of nickel K_α radiation in nickel,
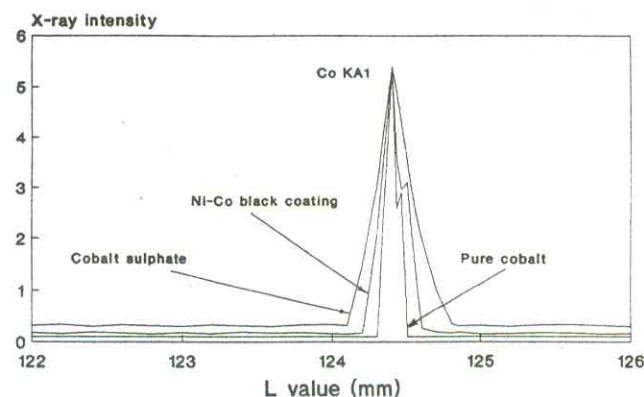Ni-Co black coating and nickel sulphate in expanded scale

Fig. 8: Peak position of K_α radiation in cobalt,
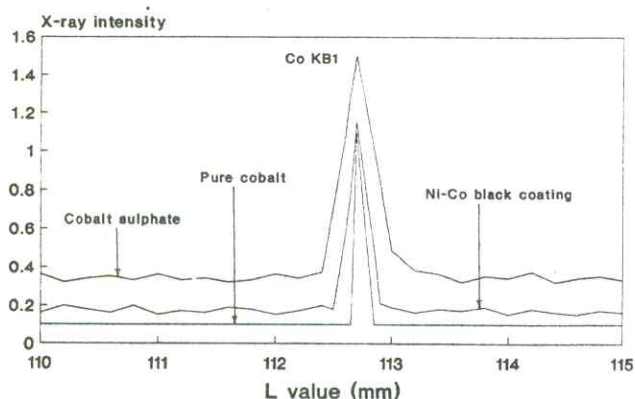Ni-Co black coating and cobalt sulphate in expanded scale

Fig. 9: Peak position of cobalt K_β radiation in cobalt, Ni-Co black coating and cobalt sulphate in expanded scale

Fig. 10 shows SEM micrograph and the elemental mapping of nickel and cobalt obtained from he nickel-cobalt black coating. This clearly shows that nickel and cobalt are in a finely mixed form. From the earlier discussions also we can arrive at a conclusion that the material must be either a very fine mixture of alloy and oxide grains or very fine cermets having metallic core and ultra thin oxide envelope.

state i.e, part of cobalt in element state and the rest of it in oxidised state. On looking at Fig. 9, it could be seen that the K_β X-ray peak due to black coating is more closer to that of pure cobalt than that of cobalt sulphate. Hence, it can be concluded that the black coating has more cobalt in the atomic state than in the ionic state. Table II gives details about constituent elements, their K_α and K_β X-ray peak intensities, K_α/K_β ratio and their corresponding chemical states [12,13].

TABLE II: EPMA results regarding chemical state of nickel and cobalt in pure samples, black coating and their sulphates

Speci-men	Ele-ment	X-ray intensity K_α	X-ray intensity K_β	K_α/K_β	Remark
A	Nickel	5206	990	5.258	Nickel atom
B	Nickel	1978	440	4.496	Nickel ion
C	Nickel	2517	489	5.143	Ni in mixed state
C	Cobalt	2252	481	4.678	Co in mixed state
D	Cobalt	1724	479	3.604	Cobalt ion
E	Cobalt	4536	921	4.928	Cobalt atom

A = Nickel standard   B = Nickel sulphate
C = Ni-Co black powder   (d) Cobalt sulphate
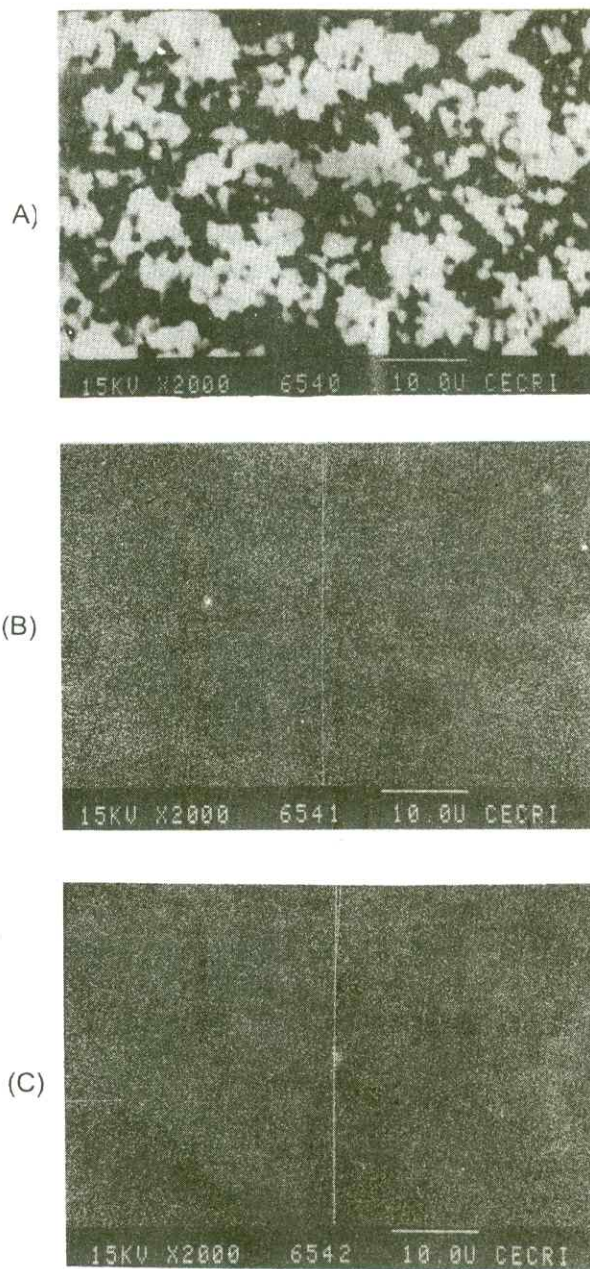(e) Cobalt standard

A)

(B)

(C)

Fig. 10: (a) SEM (secondary electron image) micrograph of nickel cobalt selective black coating
(b) nickel mapping and (c) cobalt mapping

CONCLUSION

Electron Probe Micro analysis could be successfully carried out on nickel-cobalt selective black coatings. Nickel, cobalt and oxygen are the elements identified in large scale and sulphur is found in trace level. The concentration of constituent elements, i.e. nickel, cobalt and oxygen have been estimated by comparing their K_α peak intensity with that of their suitable standards.

The chemical state of the elements have also been identified using different samples in which the elements are in different chemical states. Finally it is concluded that the black coating material must be either a very fine mixture of metal and metal oxide grains or very fine cermets with metallic core and ultra thin oxide envelope.

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