JOURNAL OF MATERIALS SCIENCE 15 (1980) 2761–2770

Microanalytical examination of coloured anodized oxide layers

ÁGNES CSANÁDY, IRÉN IMRE-BAÁN, EDITH LICHTENBERGER-BAJZA, ENDRE SZONTÁGH, FERENC DÖMÖLKI
Aluterv-fki, Research, Engineering and Prime Contracting Centre of the Hungarian Aluminium Corporation, Budapest, Hungary

Based on microanalytic and micromorphologic examinations of the dyes of anodic oxide layers coloured by two metals the following observations could be made. The metal particles from the different metal salt electrolytes incorporate into the channels of the oxide layer in the form of crystallized metallic rods. If the colouring electrolyte contains two kinds of metals, the metallic rods will also contain both metallic components. If colouring of the two metals is done successively, a layered structure located perpendicularly to the layer plane inside the anodic oxide will be formed. The majority of the porechannels available were filled by the metal used initially, followed by the second metal, which continued to fill the already replenished channels. Employing a morphological investigation combined with microanalysis, i.e. a combination of the modern electron beam methods, any coloured structure made by any structural technology could be identified.

1. Introduction

Electrolytic colouring processes of conventional, achromatic anodic oxide layers usually involve treatment in a.c. in various electrolytes containing metallic salts [1, 2]. The colour obtained depends on the metallic salt used, while the layers display a multitude of good characteristics, such as excellent corrosion resistance and adequate colour fastness. Over the last decade there has been a growing worldwide interest in questions associated with the electrolytical colouring of metals. This is due primarily to their more economical application, which lies in the lower price of chemical used for electrolytes and in their greater productivity as compared to integral colour anodizing. A rather wide range of colours have been made possible by electrolytic colouring, the hue depending on the composition of the electrolyte and its metal component. A further extension of the colour range is conceivable by the electrolytic colouring of not one, but two metals. A great variety of colours and tints could result, depending of course on the amount and proportion of the two metals used. Colouring with two metals could be obtained in only one electrolyte containing the salts of both metals, or treating separately the anodically oxidized surface in two separate electrolytes, each containing one type of metallic salt. The structure of the anodic oxide films formed during electrolytic colouring have repeatedly attracted scientific interest in recent years [3] and have been examined by X-ray diffraction, infrared spectroscopy as well as conventional electron beam microanalysis [4–6].

The newly initiated electron microscopic investigations [7] demanded further microanalytical examinations with a much greater spatial resolution of oxide layers structures coloured electrolytically by two kinds of metals. The present study was undertaken in an attempt to explore more clearly the spatial distribution of colouring as regards to the thickness and plane of anodically oxidized layers treated simultaneously and successively with alternate metals. Other than that, our microanalytical study has at all times been pursued with the hope of elucidating the principles of the colouring mechanism itself.

0022–2461/80/112761–10$03.00/0

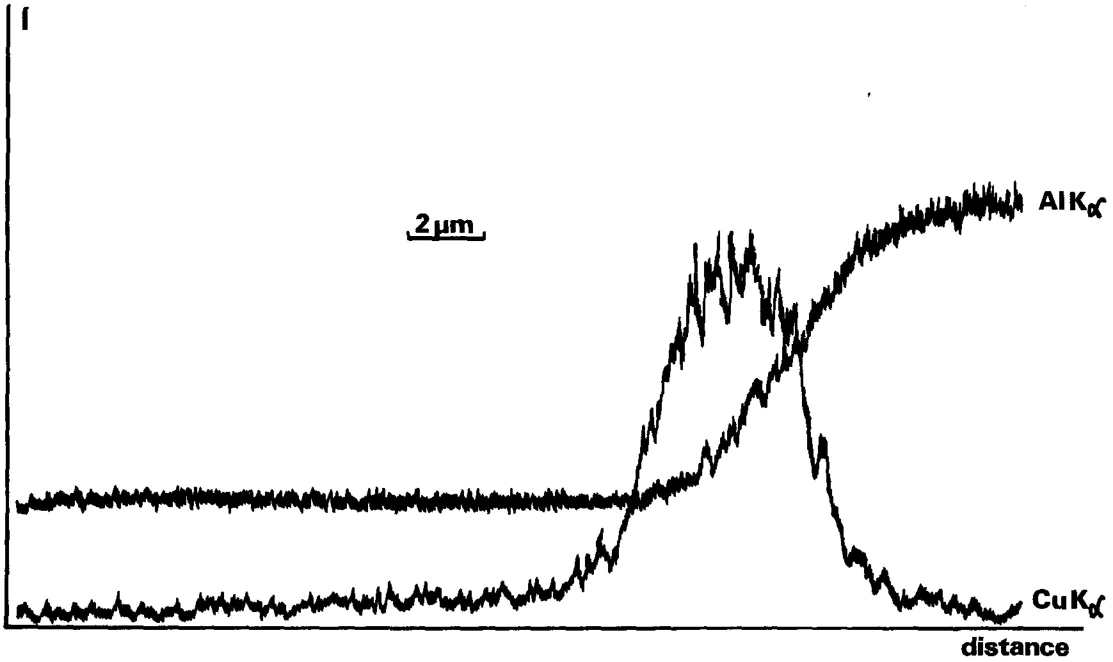

Figure 1 The copper and aluminium line profile of an anodic oxide layer coloured with copper.

Previous studies of spatial elemental distribution have stressed the importance of conventional electron beam analysis [4, 5]. However, with regard to microanalytical observations of certain layers coloured with two kinds of metals, our observations are at a variance in one respect with those so far reported: conventional microanalytical methods using electron beam are not sufficient in this area since only a limited amount of information can be obtained in this way. As the resolution of regular microanalysers is > 1 μm, interfaces are generally shown to be 1 μm or greater. The line profile outline of an oxide layer coloured electrolytically by one kind of metal demonstrates this problem (Fig. 1). Transmission electron microscopic pictures (Fig. 2) reveal that oxide metal transition measuring a couple of nm is shown by the microanalyser only as a transition developing in a long of size 1 μm or larger. Due to such physical restrictions photos of the distribution of elements could not reveal more either, especially if the amount of colouring agent, i.e. the place taken up by it, does not exceed 1 μm. Unfortunately, it also does not provide any significant information about the periodical arrangement of the colour in the plane of the layer, if the periodic distance is less than 1 μm. Such hindrances are even more perceptible if one wished to examine the spatial distribution of colour in the coloured layers or the mechanism of colouration.

2. Experimental procedure

To circumvent the difficulties described above, two experimental solutions have been developed.

Dyeing for 8 min of samples coloured either concurrently with two kinds of metals (Sample A)

Figure 2 Transmission electron micrograph of an ultrathin section of an aluminium oxide layer.

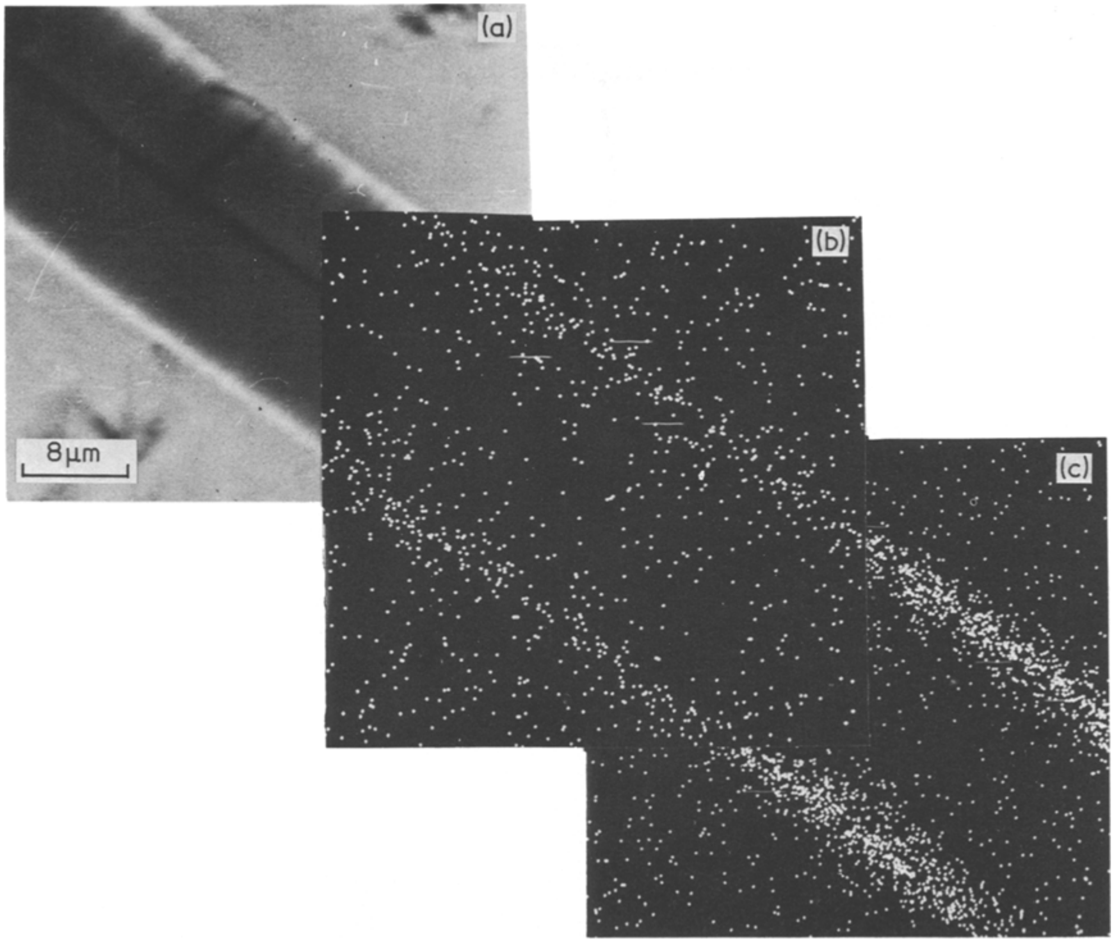

Figure 3 Micrographs made by the electron beam microanalyser on a cross-section of the simultaneously coloured anodic oxide layer of Sample A (a) backscattered electron picture; (b) X-ray picture of one metal; (c) X-ray picture of the other metal.

or successively (Sample B) was chosen so that the parts of oxide layers filled with colour could exceed the 1 μm resolution reached by microanalysis. From the samples coloured this way, cross-sectional polished surfaces were produced and examined by linear distribution and by investigation of the distribution of elements by way of X-ray pictures.

As a new method, but also using a microanalyser, considered as a direct function of probing-beam energy, perpendicularly orientated, in-depth examinations of the element distribution were carried out. Experiments previously described demonstrated the effectiveness of this method and also in studies of thin layers [8]. Our examinations included careful observations of the air–oxide and metal–oxide direction with regard to the boundary surface. Only where the depth of penetration of the electon beam was nearly identical, could the layers coloured by metal-pairs be successfully investigated by probing-beam energy.

In the light of our findings, the following tentative scheme for obtaining better spatial resolution is suggested. First in order to familiarize ourselves with the intricate mechanism of metal desposition, elemental analysis of colour rods formed in the channels of anodic oxide layers had to be completed. This meant, that an elemental analyser connected to a scanning transmission electron microscope was needed. The colour rods found periodically in the channels of anodic oxide layers (Fig. 3) were analysed in ultra-thin sections and in samples fractured in liquid nitrogen.

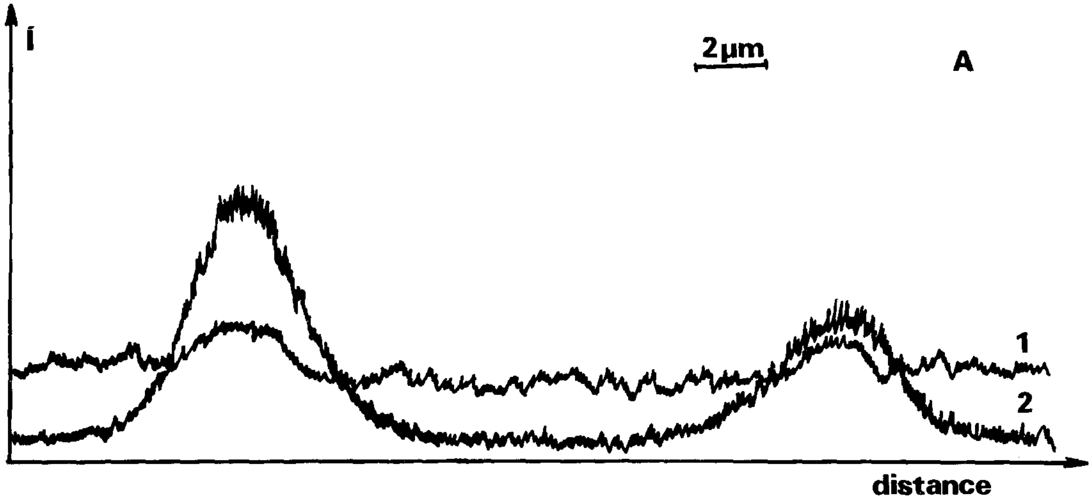

Figure 4 Line profile of the two metals of Sample B.

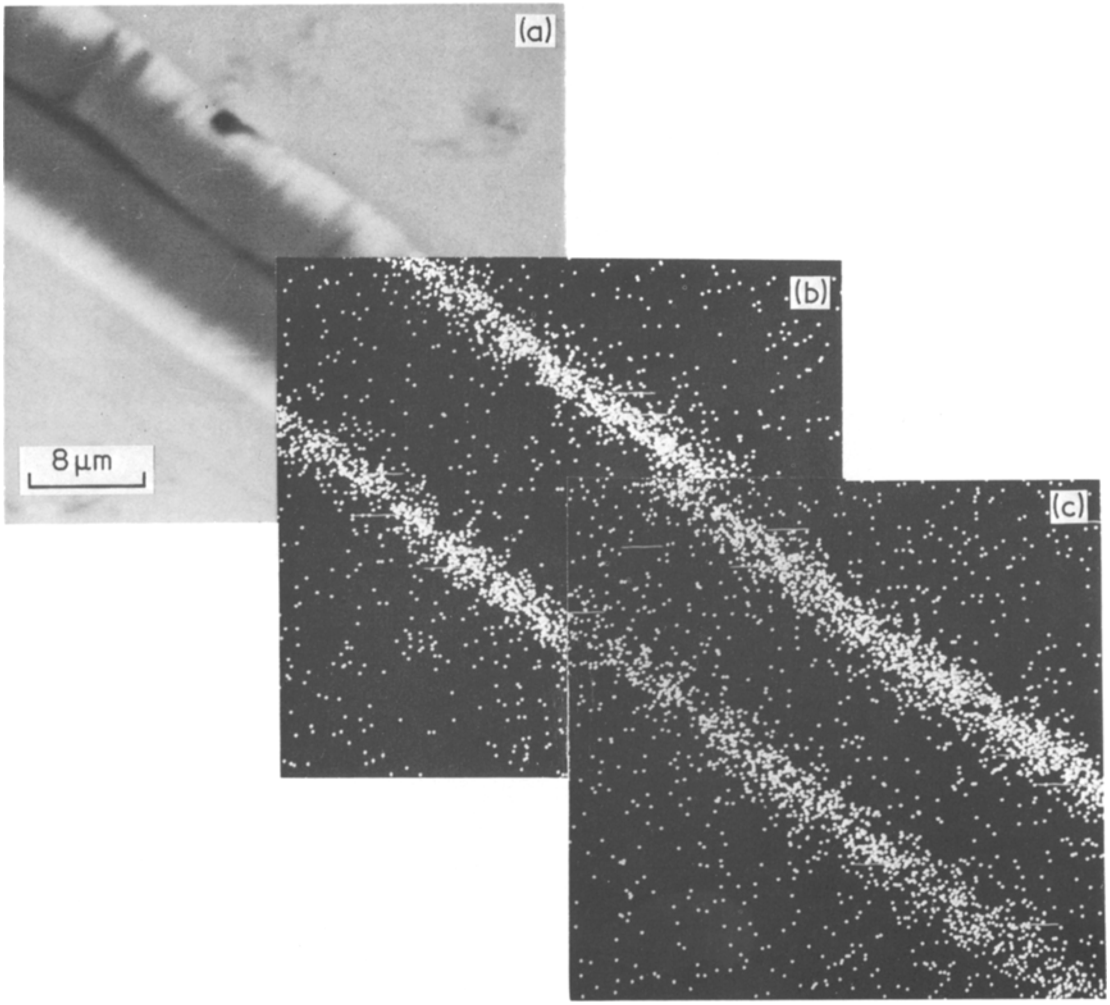

Figure 5 Micrographs made by the electron beam microanalyser on a cross-section of the anodic oxide layer of Sample B (a) backscattered electron picture; (b) X-ray picture of the primary deposited metal; (c) X-ray picture of the secondary deposited metal.

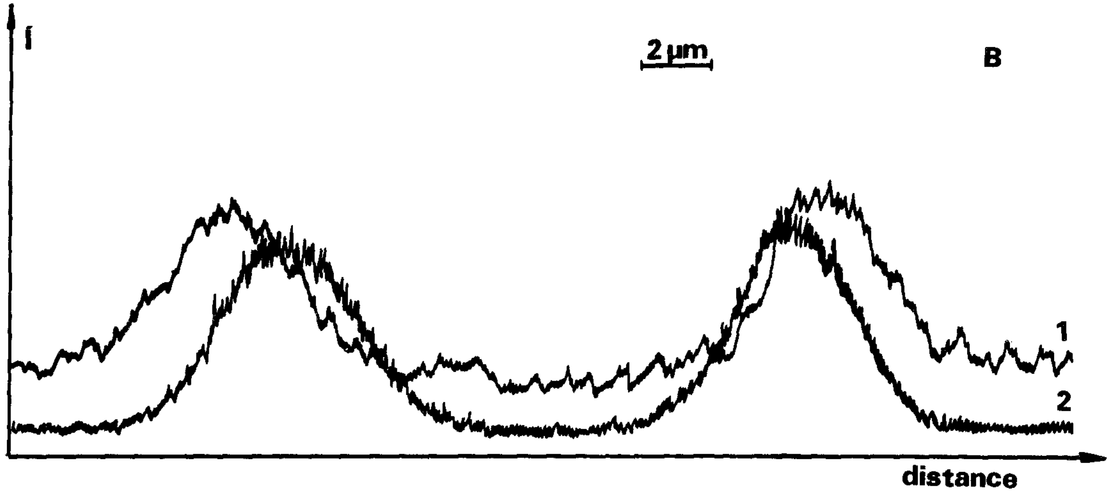

Figure 6 Line profile of the two metals of Sample B.

3. Results

3.1. Examinations with an electron beam microanalyser

For traditional electron beam microanalysis a JEOL JXA-5 microanalyser was employed. Figs. 3 and 4 show the microanalytic results obtained on cross-sectional polished surfaces of simultaneously coloured layers of Sample A. Figs. 5 and 6 show some cross-sectional photographs of Sample B that were coloured successively with two kinds of metals. Electron images of all the samples are presented in Fig. 3a and Fig. 5a as well as X-ray pictures of the elemental distribution of the two metals shown in Fig. 3b and c and Fig. 5b and c. At the same time, Fig. 4 and Fig. 6 display the linear distribution of metal particles.

Although the electron images do not provide sufficient information as to the differentiation of the two types of metals, they can be useful in the determination of the thickness of the oxide layer and colouring. The nature and degree of these alterations are summarized in Table I. Based on a comparison of electron pictures, associated X-ray tests and evaluations of linear distribution curves, the following conclusions were made.

(a) For simultaneous colouring with two metals, both deposit in the same zone. On the basis of a qualitative evaluation a rather inhomogeneous distribution could be observed within the zone.

(b) For successive colouring of metals the maximums did separate, while the bulk of the metal added second was farther from the oxide layer boundary. In fact, three different zones could be noted here. The first contains the earliest colouring metal, the next embraces both metals, while the third zone incorporates only the colouring metal added second.

Experiments taken as a function of probe-beam energy supported these observations.

The above observations were also verified on the basis of cross-sections appearing with the maximums detected by investigations taken perpendicularly at the air–oxide boundary surface as well as from the metallic side. For the examinations obtained from the direction of the air–oxide boundary, the samples were thinned by polishing, while parts of the unfilled oxide layers impeding the test have been removed. An electron beam measuring 20 μm in diameter and a test current of 1.9×10^{-8} Å were used. Fig. 7 shows the depth distribution of the elements considered from the air–oxide direction of the boundary surface, for both samples. The distribution of elements as viewed from the metallic side is shown in Fig. 8. For measurements of the latter, aluminium was removed from the oxide layer by a bromic–methanol dissolvent.

Owing to the heterogeneity of the coloured oxide structure these data can only be regarded as

TABLE I

	Sample	
	A	B
Oxide layer thickness	8.0–9.5	7.5–8.2
Dyestuff thickness	2.0	2.8–3.5

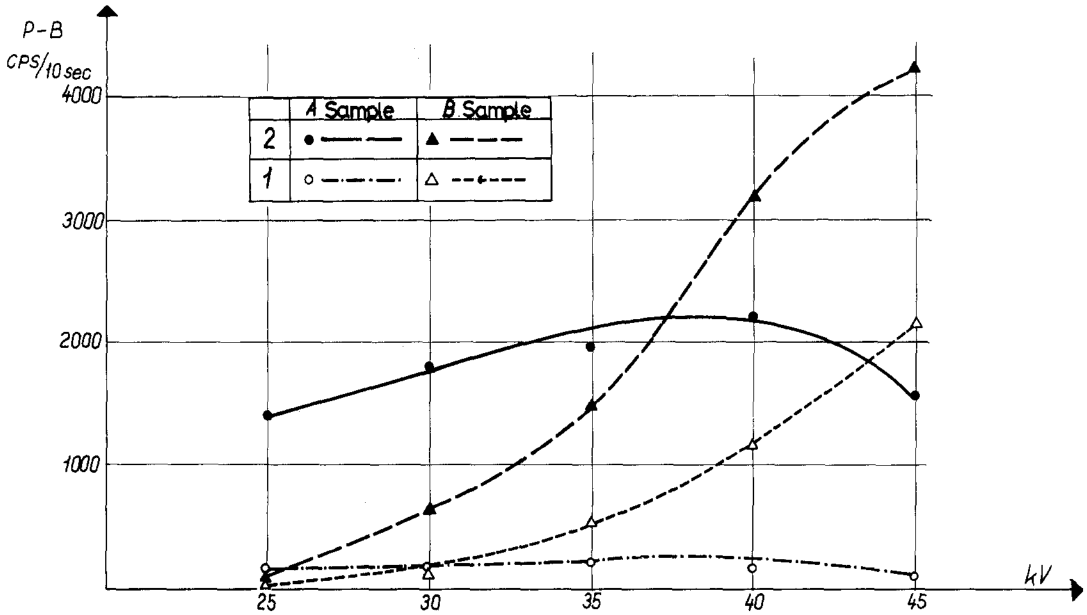

Figure 7 Depth profiling concerning the two metals in the case of Sample A and Sample B from the air–oxide boundary direction.

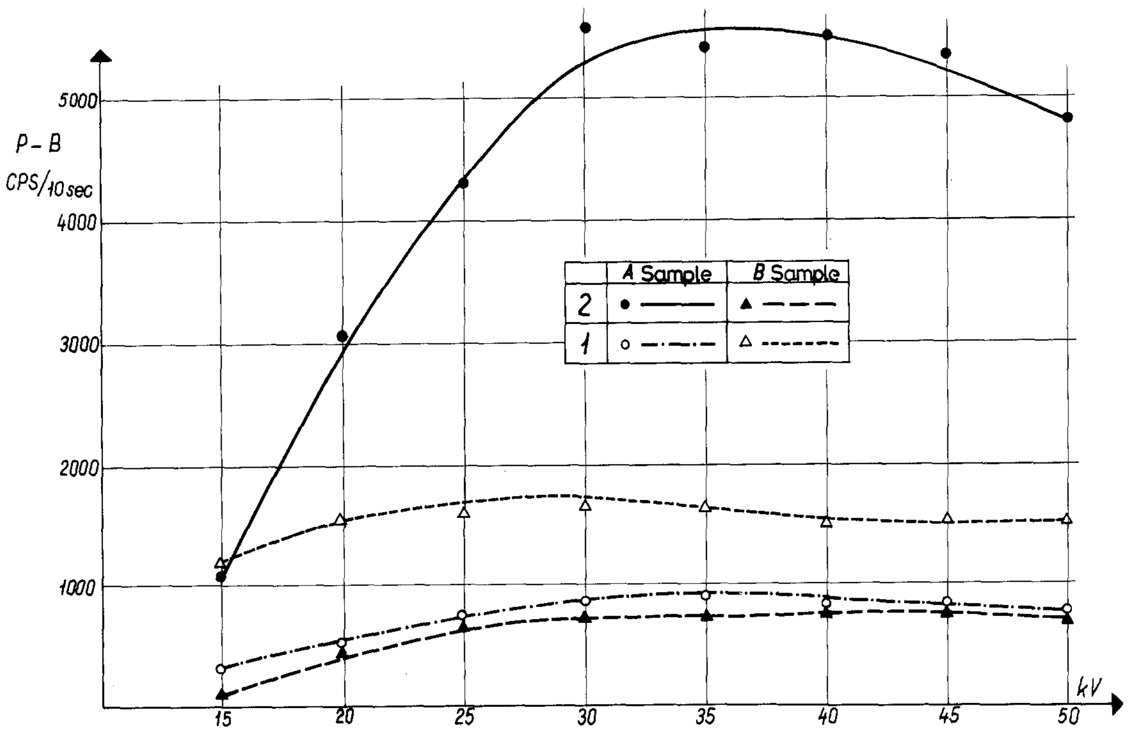

Figure 8 Depth profiling concerning the two metals in the case of Sample A and Sample B from the metal–oxide boundary direction.

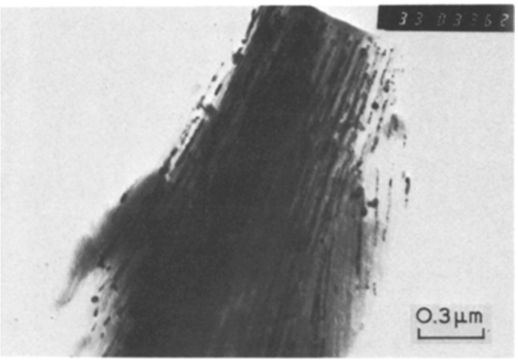

Figure 9 Low magnification transmission electron micrograph of a thin section made from Sample A.

semi-quantitative. However the data do seem to be characteristic of the tendencies observed.

3.2. Examinations with transmission electron microscope

TEM investigations of the specimens were carried out with a JEOL 100 C scanning transmission electron microscope combined with an ORTEC ED analyser. For the transmission electron microscope investigations ultra-thin sections have been made using a diamond knife [7]. Fig. 9 shows Sample A in lower magnification. Clearly, the coloured area remains under 3 μm wide (see Table I). For evaluations of individual colour-rods very high magnification is recommended, possibly at a small analysing area of the examination of about 100 nm^2. A high intensity electron micrograph of the colour is presented in Fig. 10. Successful analysis also required an area of investigation where the colour-rods do not overlap each other, i.e. where the section is adequately thin.

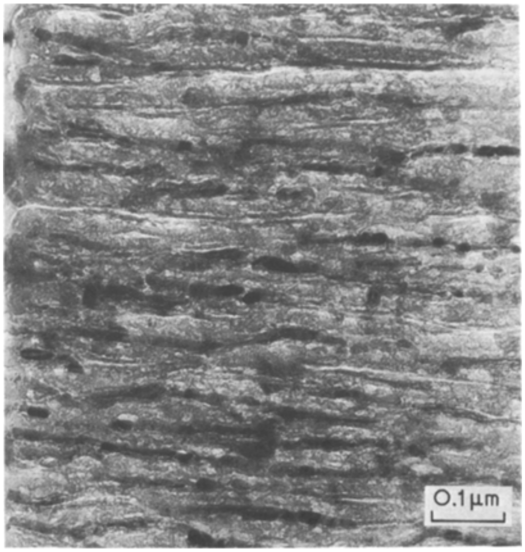

Figure 10 High magnification transmission electron micrograph of a thin section.

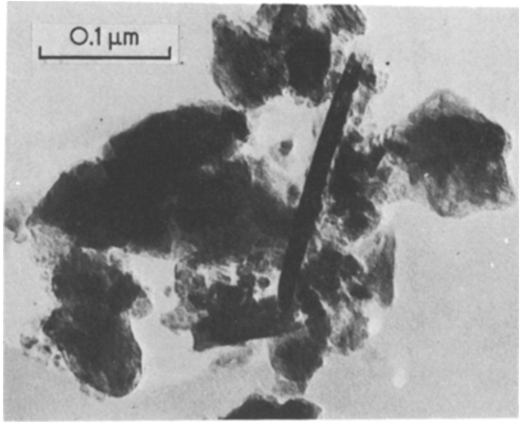

Figure 11 Transmission electron micrograph of a metal rod found in a specimen crushed in liquid nitrogen.

The samples of the aluminium oxide layers, fractured in liquid nitrogen, extracted from the support aluminium via a bromic–methanol dissolution are also suitable for the individual examination of colour-rods (Fig. 11). However, the original site of these rods may be difficult to determine later, and consequently investigation depending on the site could also become harder. In spite of this, this method is still more conceivable than previously used isolation techniques, where all the oxide matrix was chemically separated from the metal. The possibility of problem-causing selective dissolving must be considered in these investigations.

Prior to energy dispersive analysis careful verifications have been made. The samples were examined only on grids that were different from the metal tested, e.g. Pt grids. In Fig. 12 the X-ray spectrum of a pure, colour-free aluminium oxide layer is seen. The spectrum of aluminium shown in Fig. 13 shows the area derived from the aluminium support. The grid holding the samples was made of copper.

A layer coloured simultaneously by copper and silver is noticeable in Fig. 14. The sample was tested on a Pt grid. The area chosen for closer scrutiny involved a copper–silver rod embedded into the aluminium oxide layer, directly at the metal–oxide boundary surface. As the X-ray spectrum reveals, both metals are easily detectable.

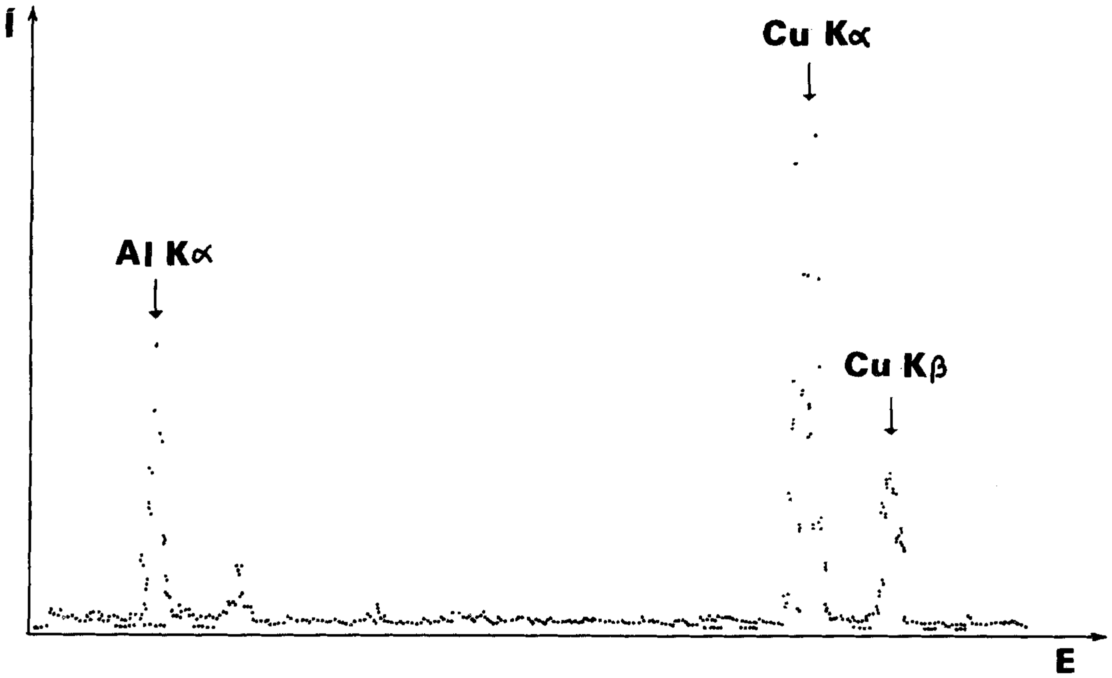

Figure 12 Energy dispersive X-ray spectrum of an anodic aluminium oxide specimen without metal colouring; the sample holder was copper.

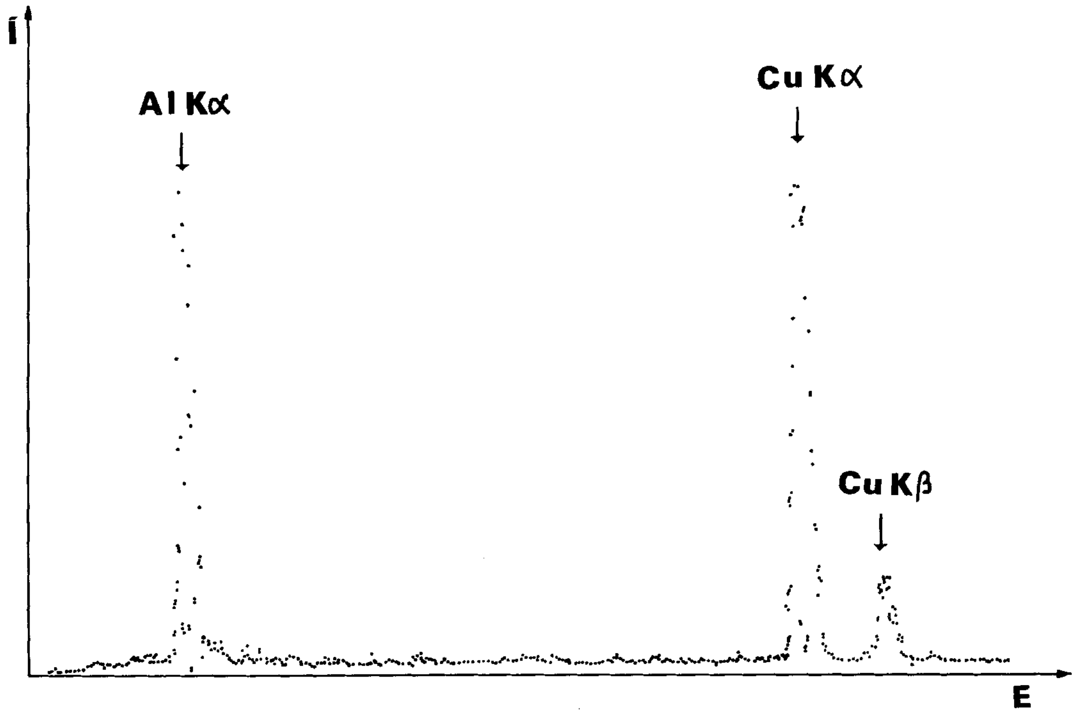

Figure 13 Energy dispersive X-ray spectrum of aluminium; the sample holder was copper.

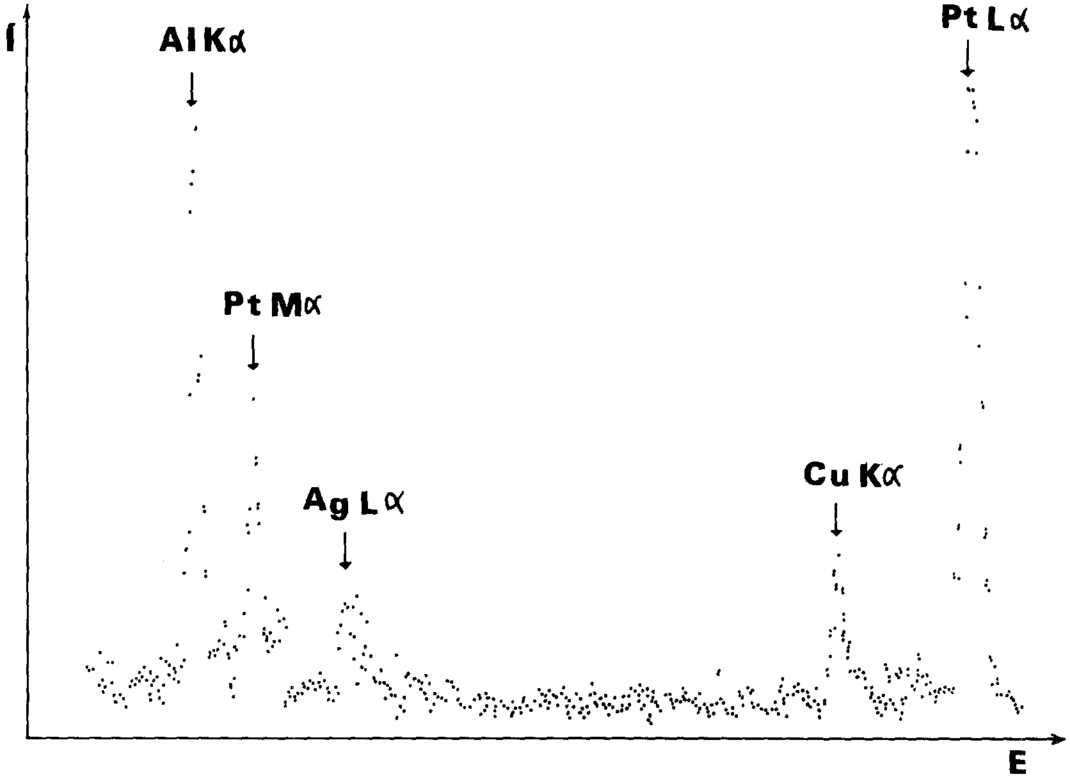

Figure 14 Energy dispersive X-ray specturm of a metal rod formed during simultaneous colouring with copper and silver near the oxide–metal boundary; the sample holder was platinum.

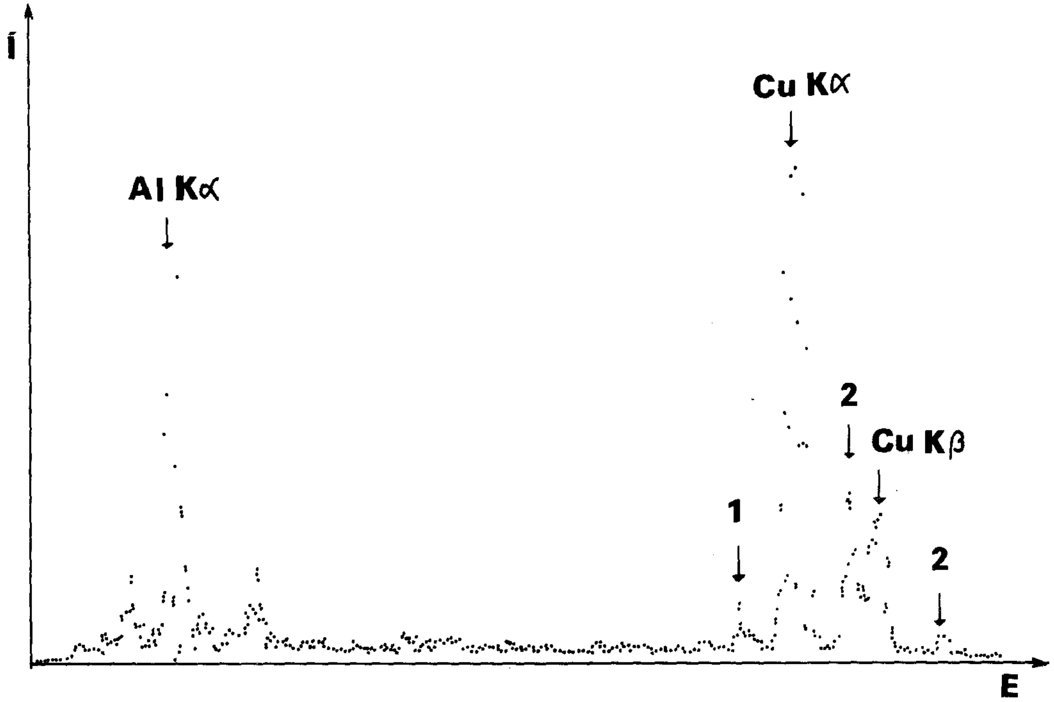

Figure 15 Energy dispersive X-ray spectrum of a metal rod formed during simultaneous colouring with two metals near the oxide–metal boundary in Sample A; the sample holder was copper.

An energy sepctrum of Sample A prepared by two kinds of metals simultaneously on copper is seen in Fig. 15. The rod taken from near the metal–oxide boundary shows characteristics of both metals under X-ray analysis.

Energy dispersive examinations proved that during simultaneously colouring with two metals, deposition of both metals occurs in each of the channels.

4. Summary

Based on microanalytic and micromorphologic examinations of the colour of anodic oxide layers coloured by two metals the following observations could be made. The metal particles from the different metal salt electrolytes incorporate into the pore channels of the oxide layer in the form of crystallized metallic rods. This finding was confirmed by X-ray and electron diffraction [4, 9]. If the colouring electrolyte contains two kinds of metals, the metallic rods will also contain both metallic components. If colouring of the two metals is done successively, a layered structure located perpendicularly to the layer plane inside the anodic oxide will be formed. The majority of the channels available were filled by the metal used initially, followed by the second metal, which continued to fill the already replenished channels. Employing morphological investigation combined with microanalysis, i.e. a combination of the modern electron beam methods, any coloured structure made by any structural technology could be identified.

Acknowledgements

We wish to thank Dr. Gabriella Major for her technical assistance and Dr. Ernö Bácsy for the energy dispersive analysis.

References

1. E. HERRMAN, *Galvanotechnik* 63 (1972) 110.
2. K. R. NARASIMHAN and E. LICHTENBERGER, *Metal Finishing* 71 (1973) 32.
3. G. W. GOAD and M. MOSKOVITS, *J. Appl. Phys.* 49 (1978) 2929.
4. P. GADÓ, E. LICHTENBERGER-BAJZA, F. DÖMÖLKI and I. IMRE-BAÁN, *Acta Technica Academiae Scientiarum Hungaricae*, 80 (1975) 303.
5. E. LICHTERNBERGER-BAZJA, F. DÖMÖLKI and I. IMRE-BAÁN, *Metal Finishing* 71 (1973) 50.
6. W. SAUTTER, G. IBE and J. MEIER, *Aluminium* 50 (1974) 143.
7. Á. CSANÁDY, *J. Mater. Sci.* 14 (1979) 745.
8. Á. CSANÁDY, V. STEFÁNIAY and D. BEKE, *Mater. Sci. Eng.* 38 (1979) 55.
9. L. SANDERA, *Aluminium* 49 (1973) 533.

Received 28 February and accepted 31 March 1980.