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COLOURED COVERING ON ALUMINIUM STUDIED BY MÖSSBAUER SPECTROSCOPY

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Résumé. — La spectroscopie Mössbauer a permis une étude *in situ* de certains revêtements colorés de l'aluminium obtenus par dépôt électrolytique d'étain dans les pores d'une couche d'alumine. Si l'effet de coloration résulte essentiellement des propriétés optiques de petites particules dispersées dans un diélectrique transparent, l'effet Mössbauer montre clairement qu'il existe des échanges entre le métal déposé et l'alumine, conduisant à l'apparition d'une gaine d'oxyde mixte d'aluminium et d'étain, autour des particules de métal.

Abstract. — Mössbauer spectroscopy was used to study *in situ* some coloured coverings on aluminium, made of a thin layer of porous alumina containing electrodeposited tin inside the pores as single crystal whiskers or small sticks. When the colouring results primarily from the optical properties of small particles it can be clearly shown from Mössbauer data that some exchange processes between the electrodeposited tin and the alumina layer lead to the appearance of mixed Al-Sn oxide encasing the tin whiskers.

1. **Introduction.** — Aluminium is now a very common metal among other materials used in building, cars, modern art, etc... In order to protect it against corrosion as well as to modify its external aspect by finishing the surface various processes are used to plate aluminium with some coloured coverings. Most of these processes are protected by patents. In some of them (for instance Eurocolor 800 or Eurocolor 300 [1]) the coloured covering is obtained from the optical properties of small particles in a transparent material. First, porous anodic oxide films are formed on aluminium in sulphuric, phosphoric or chromic electrolytes. Then, a suitable metal is electrodeposited inside the pores. Various colourations can be obtained by changing the deposited metal but the same deposited metal can produce various colourations as well, depending on the size of the particles and even on other experimental conditions which are more or less well defined. Table I give a few examples of colourations obtained under various conditions [2].

The morphology and the mechanism of formation of the porous anodic oxide films formed on aluminium by anodizing in acid electrolytes are now well known [3]. Optical observations and electron micrographs show that the anodic films are thick outer layers, containing fine, regular, almost cylindrical, parallelsided pores, perpendicular to the macroscopic surface of the specimen, penetrating a close-packed cellular structure and extending from the outer surface as far as a thin, compact, scalloped, barrier layer which separates the porous layer from the metal. The diameter of the oxide cells is approximately twice the barrier layer

TABLE I

Various colourations obtained from electrodeposited metal in pores of anodic film on aluminium

Electro-deposited Metal	Electrolytes		Colouration
—	anodic film	deposition	—
Ag	sulphuric	sulphate nitrate nitrate	bright yellow brown light yellow
Cu	{ sulphuric sulphuric chromic	sulphate sulphate sulphate	red black green or brown red
Se	{ sulphuric sulphuric chromic chromic	selenite Na + SO ₄ Cu selenite Na acid Se selenite Na	red gold gold red orange
Co	sulphuric	sulphate	black ; navy-blue
Te	sulphuric	tellurite Na	dark-gold
Mn	sulphuric	MnO ₄ Na	dark-yellow
Zn	chromic	sulphate	dark-brown
Cd	chromic	sulphate	dark-brown
Pb	{ sulphuric chromic	acetate acetate	black dark brown
Ni	{ chromic chromic chromic sulphuric sulphuric	sulphate	bronze black blue bronze light blue
Cr	sulphuric	sulphate	green

thickness, each cell containing a single star-shaped pore. The steady-state barrier-layer thickness, cell diameter and pore diameter are all directly proportional

to the formation voltage. With a sulphuric acid electrolyte, for instance, the thickness of the anodic films can easily reach 15 to 20 μ . These anodic films are transparent, but can be coloured if a metal is electrodeposited, from suitably chosen electrolytes, inside the pores. From optical observations, electron microscopy and diffraction [1], it appears that these small particles of electrodeposited metal are single crystal whiskers, globules or small sticks, having almost the same crystallographic orientation, which produce colouration by changing the variation with wavelength of the extinction, scattering and absorption of the light versus the wavelength [4].

In this work, we have studied the coloured coverings *in situ* by Mössbauer spectroscopy, without the necessity of removing the layer from its aluminium support as necessary for optical or diffraction studies. One of the aims was to identify the nature and the composition of a thin layer of amorphous material which seems to encase the metal whiskers inside the pores [1] and which cannot be a single metal oxide since it appears even under reducing conditions (electrodeposition by direct current). An other point to be explained was the remaining colouration after removing the metal from the pores by heating, which left a yellowish material independent of the metal first electrodeposited, as if coloured center process would occur.

2. Experimental results. — The samples studied were aluminium with coloured coverings made of tin electrodeposited from a sulphate electrolyte in the pores of a sulphuric anodic oxide film. The thickness of the anodic film was about 10 μ , the pore diameter ranged from 150 Å to 280 Å and the total thickness of the samples was about 100 μ . Various colouration ranging from clear bronze to black were obtained by changing the duration and the current intensity of electrodeposition, as given in table II, while the formation voltage was kept constant (16 V).

The Mössbauer experiments were done with a spectrometer operating in the constant acceleration mode and transmission geometry. The 5 mCi source used was the ^{119m}Sn in a BaSnO_3 matrix. A Li-drifted Ge crystal detector gave good resolution of the 23.88 keV

TABLE II

Coloured coverings studied by Mössbauer spectroscopy

Sample	Colour	Electrodeposition	
		t (mn)	i (A/dm ²)
1	black	5	0.8 \sim
2	brown	3	0.8 =
3	bronze	1	0.4 =
4	bronze	1	0.4 \sim

(\sim alternating current).
(= direct current).

γ -ray from the 25.04 and 25.27 keV X-rays. A natural β -Sn absorber gave a peak half width of 0.46 mm/s. The peak positions are determined in mm/s with respect to a BaSnO_3 absorber, with a + sign if the energy of the observed nuclear transition is larger than for tin in BaSnO_3 . The accuracy of the peak positions is about 0.02 mm/s and their relative intensities are evaluated with an error of a few per cent.

Figure 1 shows the Mössbauer spectra obtained from the four coloured aluminium samples. All four of them exhibit a typical spectrum with two peaks at about + 2.56 mm/s and - 0.09 mm/s, with respect to the BaSnO_3 peak. The table III summarizes the Mössbauer data obtained from the spectra: the first column gives the peak positions with respect to BaSnO_3 , the second column contains the peak half-width and the third column gives the relative intensities of the peaks. We will explain further the meaning of the figures in columns four and five.

3. Interpretation and discussion. — The line with isomer shift of 2.56 mm/s can be clearly assigned to β -Sn deposited in the pores. For a relative large abundance of deposited metal, as in black and brown samples (1 and 2), the main part of the coloured covering comes obviously from β -Sn in pores of the alumine film, while a second phase, assigned to the line with isomer shift of 0.09 mm/s, take relatively greater importance for small abundance of deposited metal (see bronze-like samples, 3 and 4). This second line,

TABLE III

Mössbauer data obtained from coloured aluminium

	(mm/s)	Γ (mm/s)	H (%)	Sn fraction (%)	Sn/ <i>it</i>
1 (black)	+ 2.56	0.47	2.8	99	0.74
	- 0.09	0.80	0.2	1	
2 (brown)	+ 2.56	0.49	2.5	98	1.00
	- 0.09	0.80	0.4	2	
3 (bronze)	+ 2.56	0.55	0.2	95	0.52
	- 0.09	0.80	0.1	5	
4 (bronze)	+ 2.56	0.57	0.3	93	0.77
	- 0.08	0.70	0.2	7	

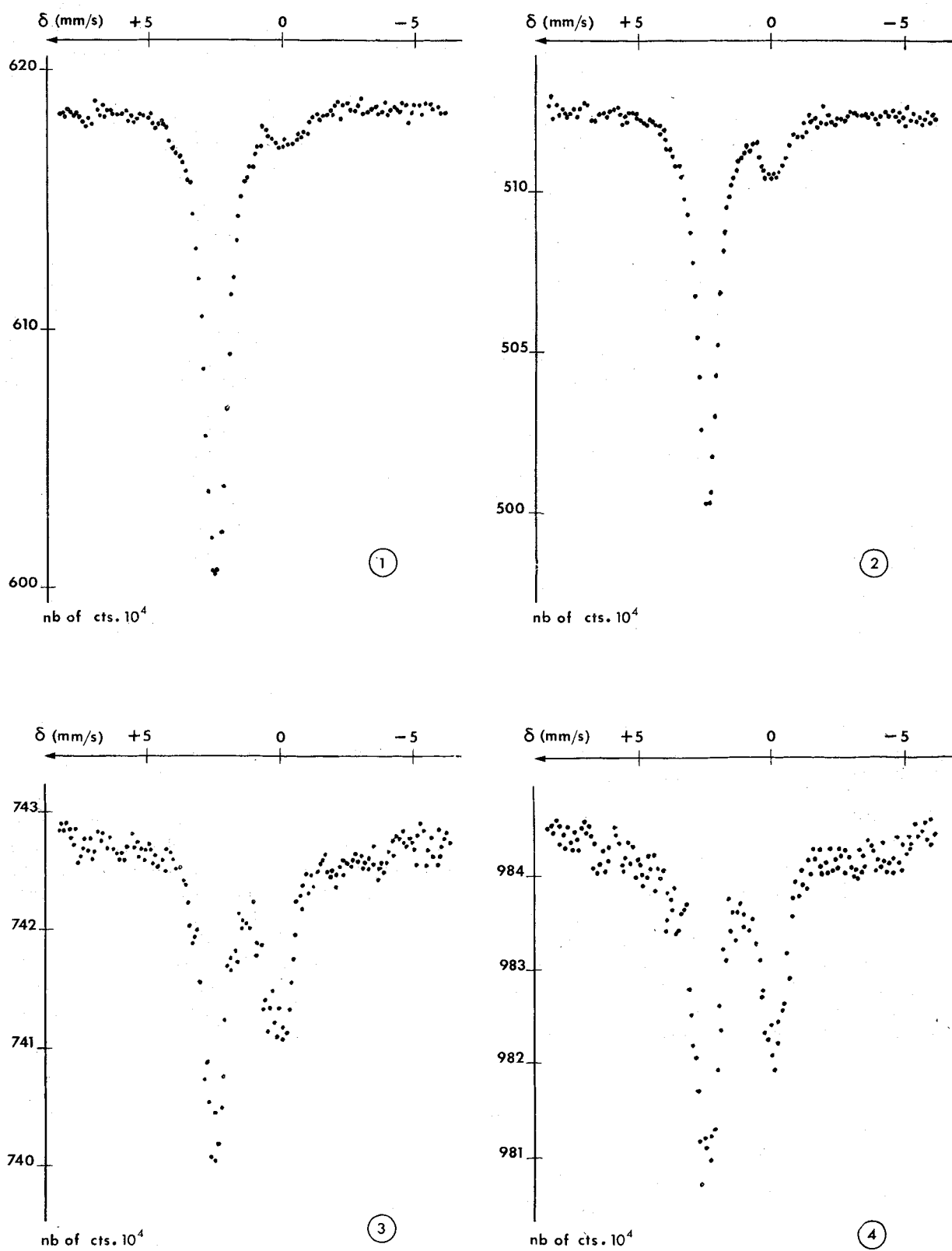


FIG. 1. — Mössbauer spectra of tin coloured covering on aluminium.

practically unshifted from BaSnO_3 and showing some broadening, can be assigned to some kind of tin (IV) oxide-like compound. However it cannot be pure SnO_2 because it was never observed by electron diffraction [1], and, above all, because this second phase appears in Mössbauer spectra even for samples 2 and 3 which were obtained under reducing conditions (electrodeposition of tin by direct current). This second phase which appears in the pores is certainly something like a stannate $\text{M}_2\text{Sn}_2\text{O}_7$ (M is a metal) although Al metal is not clearly reported as able to give stannate compound. May be it is better to speak about some mixed Al-Sn oxide of the kind $(\text{Al}_2\text{O}_3, 2 \text{SnO}_2)$ which has been already observed by Mössbauer spectroscopy [5]. The yellowish colouration remaining after evaporating the metal from the pores certainly proceeds from this mixed oxide which also explains the amorphous layer surrounding the metal whiskers as observed by electron microscopy [1].

Taking respectively 0.45 and 0.05 as the recoilless fractions of SnO_2 and $\beta\text{-Sn}$ at room temperature, we can deduce the fraction of Sn which is contained in each of the two phases from the relative intensities of the lines. The results of this calculation are reported in column 4 of table III. The figures in column 5 of table III are obtained by A/Q where :

$$Q = i \cdot t \begin{cases} i \text{ current intensity during electrodeposition} \\ t \text{ electrodeposition duration (sec. table II)} \end{cases}$$

$$A = \frac{H(\text{Sn}) \times 100}{(\% \beta\text{-Sn})} \quad (\text{sec. table III})$$

which allow us to compare the rates of electrodeposited metal per unit of time and electric current.

All of these results lead to the following remarks :

(i) The total abundance of mixed oxide $(\text{Al}_2\text{O}_3, 2 \text{SnO}_2)$ -like is practically the same for all the samples (within the accuracy range) whatever the conditions of the electrodeposition. It means that the amorphous layer has always the same thickness for a well defined kind of porous anodic oxide film on aluminium. Alternating or direct current, total abundance of electrodeposited metal and current intensity seem to have no influence in the growth of this amorphous sheath. We

can thus conclude that the presence of mixed Al-Sn oxide, though responsible of the remaining colouration when the metal is evaporated, does not play the prominent part in the changes of colouration which come mainly from the particle size of the electrodeposited metal, as previously stated [1]. For clear colouration corresponding to a small abundance of tin in the pores, it is obvious that both metal and mixed oxide have comparable influence in the way the colouring occurs (see samples 3 and 4).

(ii) The mechanism of the whisker formation seems to be very simple when alternating current is used, since the total abundance of electrodeposited metal is proportional to $Q = it$, according to the classical Faraday law (see samples 1 and 4). This proportionality law must be given up when direct current is used (see samples 2 and 3) ; in that case the electrodeposition seems to be slower at the beginning (see samples 3) and faster after a while (see samples 2) than with alternating current. If classical laws were valid, the electrodeposition would be twice as fast with the direct current as with the alternative one. The discrepancy certainly lies in the difficulty of penetrating the barrier layer which separated the porous layer from the metal and which seems more easily penetrated by alternating current.

(iii) The constancy of the total abundance of mixed Al-Sn oxide is more strictly observed when alternating current is used. This remark, connected with the preceding one (ii) suggests that the penetrating of the barrier layer influences the formation of the amorphous mixed oxide.

In conclusion, the information obtained from Mössbauer spectroscopy about the morphology and the chemical composition of tin coloured covering on aluminium, show that the presence of some sort of amorphous mixed oxide, though obvious, has only an indirect influence in the way the colouring occurs and is directly connected with the penetrating of the barrier layer between metal and porous anodic layer. These results suggest the possibility of obtaining other colourations by simultaneous electrodeposition of tin and a second metal in the pores under oxidizing conditions in order to produce various mixed oxide whiskers exhibiting colour centers.

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