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Initial stages of cobalt oxidation by FTIR spectroscopy

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Abstract. — The behaviour of specular reflectance of cobalt oxides on metal has been studied theoretically (CoO/Co system) and experimentally (Co₃O₄/Co system; the thin films are obtained by chemical spray pyrolysis) in the infrared region. CoO may be identified by a LO mode at 585 cm⁻¹ and by a TO mode at 345 cm⁻¹. Co₃O₄ is characterized by five bands respectively at 690 (LO), 660 (TO), 605 (LO), 560 (TO) and 390 cm⁻¹. These experimental results allow the characterization of CoO and Co₃O₄ grown on metal during the initial stages of thermal oxidation (400–750 °C). For film thicknesses in the range 10-1000 nm, the amounts of CoO and Co₃O₄ in the duplex structure layers may be estimated by FTIR reflectance spectroscopy. FTIR and XRD studies reveal a cyclic behaviour in the growth of the Co₃O₄/CoO/Co system.

1. Introduction.

The purpose of this work is to determine the nature of oxide films on cobalt in the initial oxidation period during which a non parabolic behaviour prevailed.

The feasibility of employing reflectance infrared spectroscopy to analyze the composition, thickness, and growth of thin films on metal surfaces has been discussed and demonstrated by several investigators.

2. Experimental.

Cobalt plates (12.5 × 12.5 mm) were cut from Co foils (0.125 mm thick, 99.9%, impurities: Fe 180 ppm; Ni 800 ppm; C 30 ppm; S 150 ppm, Goodfellow). The various treatments to which the metal was subjected are as follows: mechanical polishing (3 μm grade diamond paste), ultrasonic cleaning under alcohol and heating in air laboratory. Heat treatments in order to thermally oxidize pure Co were performed in the range 400 – 700 °C, for times between 2 and 60 minutes.

Thin Co₃O₄ films on cobalt plates cleaned with ethyl alcohol and just dried, were obtained by chemical spray pyrolysis of a 0.3 M Co(NO₃)₂·6H₂O (Merck 2536) aqueous solution, acidified with 1 ml l⁻¹ of HNO₃. The experimental set up used in the preparation of the films was described elsewhere [1]. The solution was sprayed with an aerograph (Paasche VLS), on the cobalt plates being placed on the hot platform of a cylindrical furnace. The furnace was

regulated to give a constant temperature of 420 ± 20 °C just above the plate surface during the spray process. Air was employed as the carrier gas at a 2 bar pressure. The flow rate of the solution was adjusted to 4 ml mn^{-1} with a peristaltic pump. The deposited mass was weighed and the film thicknesses were estimated from the theoretical crystallographic density. All samples were checked by X-ray diffraction patterns recorded on a Philips diffractometer or a near grazing incidence X-ray diffraction Inel equipment.

A 710 Nicolet Fourier transform spectrophotometer equipped with reflectance attachments was used to obtain infrared reflectance spectra. The angle of incidence and the reference were 16° and an aluminium mirror, 80° and a gold mirror for the accessories from Perkin Elmer and Spectra Tech respectively. The incident beam was unpolarized. The surface morphology of oxidized Co samples and thin Co_3O_4 films deposited by spray pyrolysis was examined with a scanning electron microscope (Jeol).

3. Results.

3.1 CHARACTERIZATION OF COBALT OXIDES THIN FILMS ON METAL BY FTIR REFLECTANCE SPECTROSCOPY.

System CoO/Co: The interpretation of reflection spectra of thin oxide films on metal is based on reflectance calculations. Equations derived from reference [2] including the interactions of absorption bands with interference fringes for different angles of incidence have been used to study the systems: NiO/Ni [3], $\text{Cu}_2\text{O/Cu}$ [4], $\text{Cr}_2\text{O}_3/\text{Cr}$ [4] and $\text{Fe}_2\text{O}_3/\text{Fe}$ [5].

The parameters of classical oscillators used to calculate the optical constants of CoO are issued

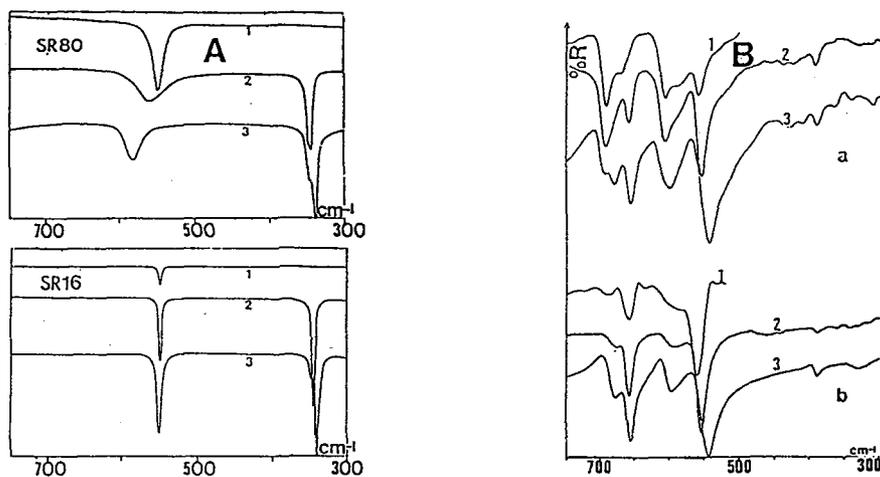


Fig. 1. — A) Calculated infrared reflectance spectra of CoO films on cobalt at various thicknesses: 1) $0.1 \mu\text{m}$; 2) $0.5 \mu\text{m}$; 3) $2 \mu\text{m}$; and angles of incidence: a) 80° ; b) 16° ; B) Experimental infrared reflectance spectra of Co_3O_4 films at various thicknesses: 1) $0.25 \mu\text{m}$; 2) $0.5 \mu\text{m}$; 3) $2 \mu\text{m}$ and angles of incidence a) 80° ; b) 16° (Absorption at $\sim 585 \text{ cm}^{-1}$ and 330 cm^{-1} are respectively due to LO and TO modes of CoO).

from reference [6]:

$$\epsilon_{\infty} = 5.3; \epsilon_0 = 13.0; \omega_T = 350 \text{ cm}^{-1}; \gamma = 3 \text{ cm}^{-1}.$$

Optical data for Co metal from Ordal [7] were used with a linear interpolation procedure between experimental points. The evolution of the spectrum with incidence angle and thickness values (Fig. 1A) is similar to that observed for the system NiO/Ni. The observed band near 550 cm^{-1} is attributed to the longitudinal optical mode (LO) of CoO. The low-frequency band at 345 cm^{-1} is due to the transversal optical mode (TO). A shift to larger wavenumbers 550 to 585 cm^{-1} is theoretically observed for the LO band at 80° , with increasing thicknesses in the range 0.1 - $2 \mu\text{m}$. An experimental shift has been observed (from 585 cm^{-1} : LO band of a 50 nm film to 620 nm for a $10 \mu\text{m}$ layer).

System $\text{Co}_3\text{O}_4/\text{Co}$: The infrared spectrum of the normal II-III spinel Co_3O_4 obtained in the transmission mode consists of four bands at 672 , 590 , 392 and 220 cm^{-1} [8].

The lack of the parameters of classical oscillators system used to calculate the optical constants of Co_3O_4 leads us to study the experimental spectra of thin Co_3O_4 films on cobalt.

Scanning electron microscopy studies indicate that the oxide films follow the shape of the Co substratum. The morphology of surfaces is identical to that of Co samples oxidized in the range 500 - 750°C , [9] and this study. On thin Co_3O_4 films prepared by spray pyrolysis some granulations ($\leq 1 \mu\text{m}$) are noticed. A similar result has been obtained for thin Co_3O_4 films on Ti [10]. The analysis of the experimental spectra (Fig. 2B) is presented in table I.

Table I. — Analysis of the experimental infrared reflectance spectra of the $\text{Co}_3\text{O}_4/\text{Co}$ system.

Thickness (μm)	0.25	0.5	2	Assignment	
Band positions (cm^{-1})		690 (670 sh.)	691	694	ω_L
			658	655 *	ω_T
	RS 80°	605	606	607	ω_L
		559	553	543	ω_T
			394	388	$\omega_L ?$
		661	657	655 *	ω_T
	RS 16°	559	552	548	ω_T
			390	388	

3.2 STUDY OF THE INITIAL STAGES OF COBALT OXIDATION AT $p_{\text{O}_2} = 0.21 \text{ atm}$. IN THE RANGE 400 - 750°C . — The kinetics of oxidation of cobalt at low temperature has received little attention. Between 400 and 1400°C a parabolic relationship is obeyed with some initial deviations in the range 400 - 800°C . According to the stability diagram for the Co-O system, oxidation of cobalt in air under 1 atm pressure at temperatures below 900°C would yield a layer comprising CoO and Co_3O_4 if formation of these phases were not prevented by nucleation or kinetics constraints. Each oxide would exist as a separate layer, the CoO being adjacent to the metal

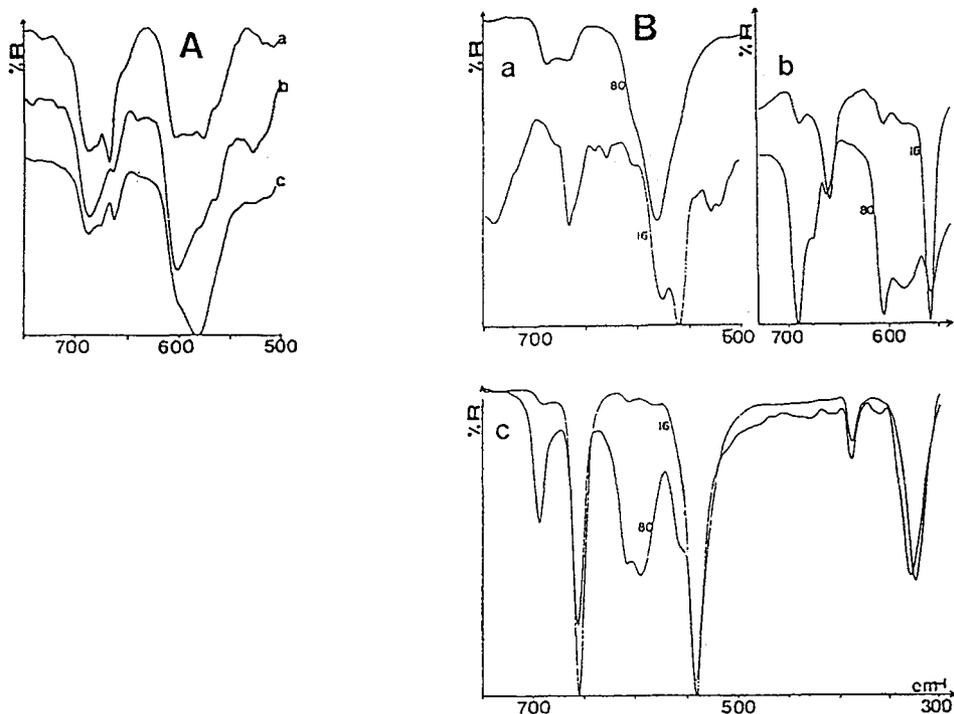


Fig. 2. — A) IR reflectance spectra at 80° off-normal of Co samples oxidized at 400°C : a) 5 min; b) 15 min; c) 60 min; B) IR reflectance spectra at 80° and 16° off-normal. Samples oxidized at 500°C : a) 2 min; b) 5 min; c) 60 min.

and the Co_3O_4 being adjacent to the gas phase. This type of scale morphology has, in fact, been observed by many investigators [9, 11-13].

X-ray diffraction. — Table II shows a comparative analysis of X-ray diffraction measurements for CoO and Co_3O_4 . The experimental Bragg intensities measured on a polycrystalline Co_3O_4 sample using a diffractometer and on thin Co_3O_4 films analyzed with a near grazing incidence equipment are in excellent agreement. Values too large of the I_{220}/I_{111} and I_{220}/I_{222} intensity ratios for the spinel phase (Tab. II) indicate orientation effects owing to the enhancement of the 220 peak as mentioned by Païdassi [9]: this is observed for layers thicker than $1\ \mu\text{m}$.

FTIR reflectance spectroscopy. — The preliminary study of calculated reflectance spectra of the CoO/Co system and of experimental reflectance spectra of the $\text{Co}_3\text{O}_4/\text{Co}$ system allows the use of FTIR reflectance spectroscopy in view of a better understanding of the early stages of cobalt oxidation (Fig. 2).

For very thin films ($\sim 0.1\ \mu\text{m}$) at an 80° incidence angle, Co_3O_4 is easily characterized by the two longitudinal optical modes (LO) at 690 and $605\ \text{cm}^{-1}$, CoO by its LO band at $580\ \text{cm}^{-1}$ (Figs. 2A, B(a)). The change of incidence angle reveals the spinel phase by the TO bands at 660 and $560\ \text{cm}^{-1}$ in thin films where the monoxide is largely predominant (Fig. 2B(a)).

Table IV. — Energy and assignment of bands observed on spectra recorded at 80° and 16° (687 band of maximum intensity).

T (°C)	400				500				600				Assignment
Time (min.)	5	60	2	5	15	60	2	3.5	5	15	Co ₃ O ₄	COO	
RS 80°	687	687	688	690	692	695	695	695	695	696	ω _L		
	668	665	667	664	660	656	661	656	656	658	ω _T		
	602			606	607	608	608	609	609	614	ω _L		
	577	582	581	584	587	595	593	597	595	598		ω _L	
	564			559	553	541	549	540	546		ω _T		
					389	390	392	392	391	388		ω _L	
Band positions (cm ⁻¹)			661	659	658	655	658	655	658		ω _T		
			577									ω _L	
			561	559	555	542	550	540	546		ω _T		
RS 16°					389	389	390	390	390		ω _L		
						324	328	322	324			ω _T	
Approximative thickness (μm)	0.1	~0.3		0.2	0.5	1	0.8	1	1	2.15			

Table V. — Analysis of the duplex structure of oxide layers formed during thermal oxidation of cobalt by X-ray diffraction and FTIR reflectance spectroscopy (spectra recorded at 80°).

Temperature		Exposure time (minutes)						
		2	3.5	5	10	15	60	
500°C	RX	I _{CoO₂₀₀} /I _{Co₃O₄111}			2.77		4	9.2
		I _{CoO₂₀₀} /I _{Co₃O₄220}			1.21		1.40	3.03
	FTIR	I ₆₀₅ /I ₅₈₅			0.87		0.98	1.07
		I ₃₃₀ /I ₃₉₀						3.30
		Main phase	CoO		Co ₃ O ₄		Co ₃ O ₄	CoO
		Thickness (μm)			~ 0.2		~ 0.5	1
600°C	RX	I _{CoO₂₀₀} /I _{Co₃O₄111}	7.2	10			7	3.6
		I _{CoO₂₀₀} /I _{Co₃O₄220}	2.17	3.4	2.54		~ 1.8	~ 0.75
	FTIR	I ₆₀₅ /I ₅₈₅	0.98	1.07	0.98		†	†
		I ₃₃₀ /I ₃₉₀	2.61	3.71	3.05		†	†
		Main phase	CoO, Co ₃ O ₄	CoO	CoO, Co ₃ O ₄		Co ₃ O ₄	Co ₃ O ₄
		Thickness (μm)	~ 0.8	1	~ 1		~ 2.15	3.6
750°C		I _{CoO₂₀₀} /I _{Co₃O₄220}	1.5		1.36		0.86	
		Main phase	Co ₃ O ₄		Co ₃ O ₄		Co ₃ O ₄	
		Thickness (μm)	~ 2.6		3.6		4	

† For layers thicker than 1 μm, the FTIR reflectance spectra become too complex because of the superimposition of interference fringes.

1.8 : the I_{CoO₂₀₀} / I_{Co₃O₄220} ratio is reduced owing to the enhancement of the 220 peak of the spinel phase due to orientation effects [9].

(If [CoO] = [Co₃O₄], the ratios I_{CoO₂₀₀} / I_{Co₃O₄111} and I_{CoO₂₀₀} / I_{Co₃O₄220} are respectively 6.5 and 2.5).

determination of oxides in duplex structure layers.

In the temperature range 500-600 °C, different steps are observed in the initial transient stage of cobalt oxidation during which the monoxide and the spinel phase are successively

the main phase.

This cyclic behaviour may be partly explained by the important change of the Co_3O_4 non-stoichiometry [14] involving different values of the diffusion coefficient of cations in spinel phase. The variation of Co_3O_4 UV-Vis-NIR diffuse reflectance with temperature and time exposure supports this hypothesis [15].

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