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Cathodic reduction and infrared reflectance spectroscopy of basic copper(II) salts on copper substrate

J. Y. MALVAULT, J. LOPITAUX, D. DELAHAYE, M. LENGLET

Université de Rouen, Laboratorie d'Analyse, de Spectroscopie et de Traitement de Surface des Matériaux, IUT, 76821 Mont-Saint-Aignan Cedex, France

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Infrared reflectance spectroscopy and cathodic reduction have been used for the characterization of copper corrosion products formed by atmospheric corrosion. The following basic copper(II) salts were synthesized: atacamite and paratacamite ($Cu_2Cl(OH)_3$), brochantite ($Cu_4SO_4(OH)_6$), posnjakite ($Cu_4SO_4(OH)_6.H_2O$), malachite ($Cu_2CO_3(OH)_2$), gerhardite ($Cu_2NO_3(OH)_3$). The samples for analysis were obtained by incrustation of submicron particles of the compound on the surface of OFHC copper coupons. Infrared reflectance spectroscopy shows that, unlike copper oxides, the reflection spectra of thin layers of basic copper(II) salts on copper are similar to those obtained by the usual KBr-pellet method for the location of the bands. However, some differences occur in the intensities of the bands between the two modes. Infrared reflectance spectroscopy allows an easy identification of basic copper(II) salts: chlorides can be identified by their Cu–O–H bending modes; sulfates, sulfite, nitrate and carbonate by the internal mode of the corresponding anion (ν_3 region). The cathodic reduction analyses of the salts on copper display only a wide peak in the range from −0.6 to −0.55 V vs SCE, indicating that one step is involved. The potential of this cathodic reduction peak is distinguishable from the one of copper(I) oxides (−0.9 V vs SCE). Thereby the relative proportions of copper(II)) salts and copper(I) oxides present in the corrosion layer can be determined.

1. Introduction

The interaction of metals with the atmosphere and the growth of surface films of corrosion products have important consequences for technology. The formation of thin films on metals and alloys used in electronics and electrical contacts may influence the electrical and magnetic properties of the components and lead to failure.

The analysis of corrosion films requires highly sensitive surface techniques. The characterization of atmospheric corrosion products developed on copper can be carried out by nondestructive methods like low angle X-ray diffraction for the determination of crystalline phases and optical methods. Photon based techniques (i.r. and Raman spectroscopy) possess important advantages over physical methods, like XPS, SIMS and electron microprobe, based on electrons or ions as probing particles. Optical methods do not require high vacuum conditions during the analysis and therefore can be used at ambient atmospheric conditions. These techniques allow *in situ* studies [1, 2].

Cathodic reduction of oxides formed on copper has been described by Evans and Miley [3]. These authors suggest that the initial part of the potential–time curve is related to the reduction of cuprous oxide and the second part to the reduction of the cupric oxide. Pops and Hennessy [4] have proposed a galvanostatic method, based on the same conclusions, for determining oxides formed on copper in the wire industry. The cathodic reduction technique of oxide thickness determination is currently used in industry as part of the quality control testing program and the aforementioned interpretation has been included in a standard specification [5]. It is now well established that the specifications of the ASTM standard B49-50 result in substantial errors due to an incorrect identification of the two oxides CuO and Cu_2O, [6–8]. Coulometric reduction is a technique used for quantitative measurements of the total amount of corrosion products. However, the potential associated with reducing each corrosion species includes considerable electrochemical overlap. The purpose of this study is to characterize the copper(II) salts formed on copper during atmospheric corrosion by electrochemical and optical methods.

2. Experimental details

The basic copper(II) salts were prepared according to procedures previously published: chlorides [9], carbonate [10], nitrate [11] and sulfates [12]. The samples obtained were characterized by X-ray diffraction. Copper oxides were formed by thermal oxidation of copper coupons. Powder copper oxides were commercial products which were ground, the submicronic particles being separated by sedimentation.

The samples, analysed by infrared (i.r.) reflectance spectroscopy, were obtained by incrustation of

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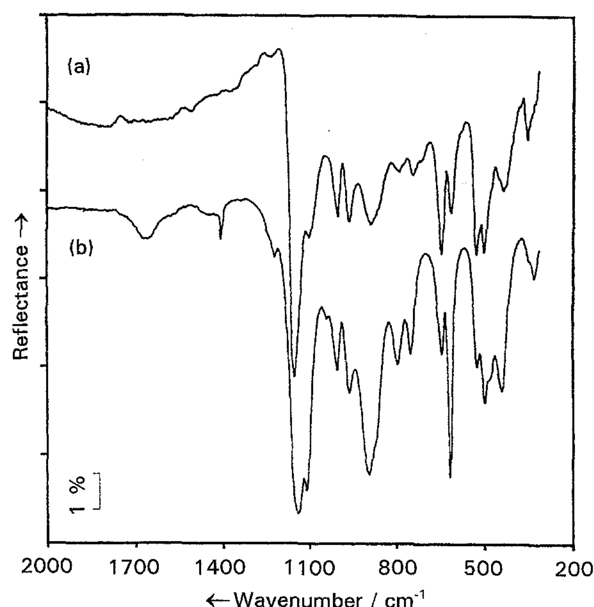


Fig. 1. Infrared spectra of $Cu_4(OH)_6SO_4$: specular reflectance of a thin layer of bronchantite at 80° (a) and transmission in KBr pellet (b).

submicronic particles of the compound in the surface of OFHC copper coupons. The bulk metal specimens were mechanically polished (1 μm grade diamond paste). The layer formed was checked with a low angle X-ray diffractometer using CuK_α radiation (Inel equipment, incidence angle: 5°). The vibrational spectra were recorded on a Nicolet FTIR 710 spectrophotometer (analyzed range 5000–225 cm^{-1}). Two techniques were used: the standard KBr pellet technique and the specular reflection technique for surface analysis (incidence angle: 80°).

For electrochemical analysis, circular copper electrodes, 0.5 mm thick with 1.13 cm^2 surface area, were used. The electrochemical reduction curves were determined using a sample holder, an electrochemical cell fitted with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. Before each run the electrolyte (0.1 M $Na_2B_4O_7$; at pH ~9, the solubility of the different copper compounds, oxides and hydroxides in this solution is minimal) was carefully purged with nitrogen. The reduction speed was 0.5 mV s^{-1}.

3. IR reflectance spectroscopy of basic copper(II) salts

The behaviour of the specular reflectance of thin oxides films on metals has been studied theoretically and experimentally in the infrared region. The optical constants and absorption bands are calculated by using the model of a system of independent adsorbed harmonic oscillators. This model is deduced from the classical theory of bound electrons applied to dielectric materials. An excellent agreement between calculated and experimental spectra is observed for the Cu_2O/Cu system [13]. The spectra are closely dependent on the angle of incidence of the radiation on the surface and on the thickness of oxide on the metallic substrate but not on the nonstoichiometry of the cuprous oxide (the reflectance spectrum of Cu_3O_2 is similar to that of Cu_2O [14, 15]). Nevertheless, the interpretation of reflectance spectra is more difficult for such systems than that of transmission spectra, since the effects of radiation incidence angle, thickness of oxide films, optical constants of surface products and phase changes during the reflection process are critical considerations in reflectance spectroscopy. The reflectance spectra differ in band locations and band intensities from the transmission spectra for the oxide–metal systems.

The feasibility of employing reflectance infrared spectroscopy to study the composition of complex films on metal surfaces like chromate conversion coatings has been demonstrated [16]. A previous study of the $ZnCrO_4/Fe$ and $CrPO_4/Fe$ systems has shown that the CrO_4^{2-} and PO_4^{3-} ions are easily identified by infrared reflectance spectroscopy under a near grazing incidence by the longitudinal optical components of the ν_3 vibration, i.e., at 960 and 1080 cm^{-1}, respectively [17]. It appears that the interpretation of the reflectance spectra for these systems is not

Table 1. Transmission and specular reflectance i.r. spectra of brochantite $Cu_4(OH)_6SO_4$

	OH stretching frequencies/cm^{-1}				*Cu–OH bending energies*/cm^{-1}						*Ref.*
T	*3596*	3572	*3704*	*3388*	3272	990	945	*878*	780	734	[18]
	3590	3569	*3404*	*3389*	3278	986	945	*873*	776	734	[19]
	3584	3563		*3385*	3274	985	944	*876*	780	734	*
R		3556		*3382*	3272	987	947	873	781	743	*

	Internal vibrations of the SO_4^{2-} ions/cm^{-1}										*Cu–O stretching* [17]		*Ref.*
	ν_3				ν_1	ν_4		ν_2 *or Cu–O* [18]					
T	*1129*	*1123*	*1117*	*1090*	995	630	*604*	513	485	420	338	318	[18]
		1119		1088	986	629	*602*	510	485	420	338	315	[19]
		1119		1089	985	628	*602*	510	484	425	335	318	*
R	*1130*			1082	987	632	600	513	487	421	337		*

T, R transmission or reflectance spectrum.
3596, *1129* main bands.
* This study.

Table 2. Specular reflectance i.r. spectra of basic copper(II) salts in the 1500–300 cm^{-1} region

$Cu_2(OH)_3Cl$ Paratacamite	Atacamite		$Cu_4(OH)_6SO_4, H_2O$ Posnjakite		$Cu_2(OH)_3NO_3$ Gerhardite	$Cu_2(OH)_2CO_3$ Malachite	
						1501	ν_3
					1419	1425	
					1356	*1391*	
			1121	ν_2		1098	
			1072		1048 (m)	1049 (m)	
985	987 (m)	Cu–O–H	980				
	948 (m)						
921	*917*						
	897						
863			875		877	878	
830	*848*					817 (m)	
	741					753	
			691 (m)		697		
			629 (m)				
585	600 (m)		601 (m)			587	
520	519		509 (m)		510 (m)	523	
	482 (m)					505	
455	448						
405	415					427	
						364	
						330	
						303	

complicated by distorted band shapes and frequency shifts for thin films, when compared to absorption spectra of the pure bulk materials.

Consequently, one purpose of this paper is a systematic study, by this technique, of the main products formed during the atmospheric corrosion of copper. The transmittance and reflectance spectra of the $Cu_4(OH)_6SO_4$ compound (brochantite) are presented in Fig. 1. An excellent agreement is observed concerning the vibrational frequencies of OH stretching modes, internal modes of the SO_4^{2-} ions and Cu–O–H bending modes (Table 1). Nevertheless, the intensity of the Cu–O–H bending modes and Cu–O stretching modes decrease on the reflectance spectra.

The transmission spectrum presented in this study is in agreement with those previously published [18, 19]. According to Lutz [19], the internal vibrations of the SO_4^{2-} (ν_1, ν_2 and ν_4) ions in brochantite are overlapped, and even overlaid, as well as partly coupled with the vibrations of the six crystallographically different OH also present in that region.

This spectroscopic study of brochantite allows us to conclude that, unlike oxide systems, the spectra of thin films of basic copper(II) salts on copper obtained in the reflection mode are similar to those recorded by the usual KBr pellet method.

In this study a similar analysis has been extended to other copper(II) compounds (Table 2). From the vibrational frequencies of the copper sulfite $Cu_2(I)SO_3Cu(II)SO_3, H_2O$ it is evident that the formation of sulfites may be characterized by i.r. spectroscopy [21]: Vibrational frequencies for sulfite ions in copper sulfite [21] 1025, 1008, 977, 912, 636, 564 and 519 cm^{-1}.

In conclusion, the different basic copper(II) salts developed on copper during atmospheric corrosion may be identified by i.r. reflectance spectroscopy. Specific frequencies are assigned as follows: (i) Chlorides: Cu–O–H bending modes; (ii) sulfite, sulfates, nitrate, carbonate: internal modes of the corresponding anion (ν_3 region). The OH stretching mode region cannot be used because of a large overlap observed for different components in the spectra of different compounds.

4. Electrochemical study

4.1. *Analysis of cuprous oxide films formed by thermal oxidation or by incrustation of submicronic particles*

A brief analysis of the experimental data, previously published [7] shows that the electrochemical reduction of copper oxides in complex layers gives rise to the following reactions:

For CuO

$$\underset{(CuO)}{Cu^{2+}} + e^- \longrightarrow Cu^+ \quad \text{in the range from } -0.60 \text{ to } -0.75\,V \quad (1)$$

$$\underset{(CuO)}{Cu^{+}} + e^- \longrightarrow Cu^0 \quad \text{near } -0.80\,V \quad (2)$$

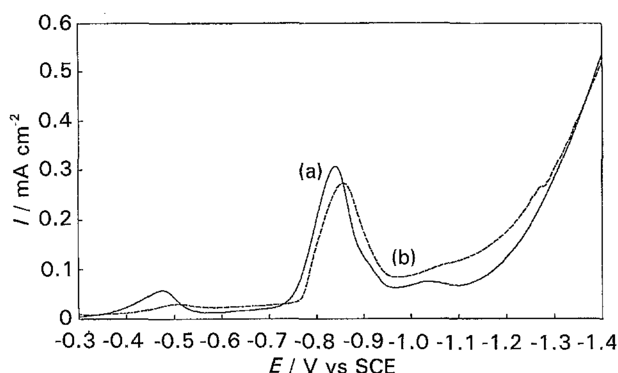


Fig. 2. Electrochemical reduction curves of cuprous oxides formed by thermal oxidation of OFHC copper samples (a) or by incrustation of Cu_2O on bulk copper (b).

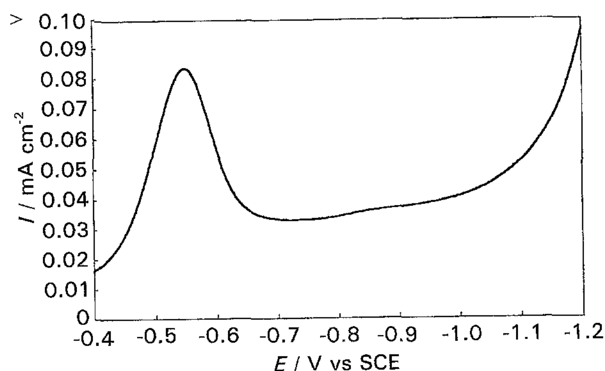
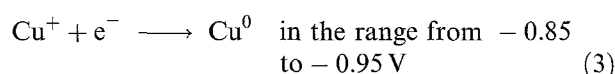


Fig. 3. Electrochemical reduction of a thin layer of brochantite incrusted on bulk copper.

and for copper(I) oxides



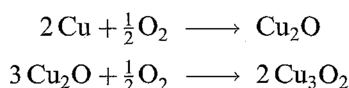
$$Cu^{+} + e^{-} \longrightarrow Cu^{0} \quad \text{in the range from } -0.85 \text{ to } -0.95\,V \qquad (3)$$

$(Cu_2O \text{ or } Cu_3O_2)$

(An overlap of Reactions 2 and 3 may be observed: increasing thickness shifts the peak positions to more negative potentials).

These results, in excellent agreement with those of other authors [6], contradict the conclusions of Pops and Hennessy [4] who mistook CuO for Cu_2O in the study of the reduction of oxide layers formed on copper wires (the same error is observed in the specification of the ASTM standard B49-50 [5]).

Figure 2 presents the electrochemical reduction curves of cuprous oxide films formed by thermal oxidation of OFHC copper samples (a) or by incrustation of Cu_2O submicronic particles in the surface of a circular mechanically polished sheet (b). In the two voltammograms the first minor peak near -0.5 V vs SCE is attributable to the precursor Cu_xO [22] and the major peak at -0.85 V vs SCE to the reduction reaction $Cu^{+} + e^{-} \longrightarrow Cu^{0}$ of the non stoichiometric cuprous oxides. The precursor of cuprite already present on copper substrates has been developed by thermal oxidation. From atom probe, XPS and Auger studies, it can be concluded that the precursor Cu_xO has a mixed valency character containing interstitial Cu^0 scattered in the Cu(I) oxide phase [22]. At 473 K, three steps preceeding the formation of CuO are always observed: formation of the precursor Cu_xO and growth of the cuprous oxides according to reactions:



$$2\,Cu + \tfrac{1}{2}O_2 \longrightarrow Cu_2O$$
$$3\,Cu_2O + \tfrac{1}{2}O_2 \longrightarrow 2\,Cu_3O_2$$

The study of the grazing X-ray diffraction diagrams and the electron probe microanalysis has revealed the successive steps of copper oxidation [23], in agreement with data of reference [24]. Czanderna has obtained a composition $CuO_{0.67}$ (or Cu_3O_2) by low temperature oxidation (120–160 °C) of polycrystalline [25] or ⟨1 0 0⟩ single crystal films of copper [26]. This composition has been considered as a gross defect structure of Cu_2O corresponding to one copper vacancy per unit cell on the average. A deviation from stoichiometry of this magnitude has not been reported previously and, in fact, Cu_3O_2 is probably a unique metastable phase. Cu_3O_2 and Cu_2O may be identified only by grazing X-ray diffraction and by optical methods (mainly photoluminescence measurements) [23]. I.r. reflectance spectra of Cu_2O/Cu and Cu_3O_2/Cu systems are similar and consist of thin oxide layers (0.1–0.2 μm) of one band in the range 660–645 cm^{-1} (LO mode) [14, 15].

The formation of Cu_3O_2 by thermal oxidation at 473 K is very rapid (the EPMA analysis of an ETP copper sample oxidized 30 min at 473 K reveals that the main constituent of the oxide layer is Cu_3O_2).

Consequently, it may be concluded from this study that the differentiation of the two cuprous oxides Cu_2O and Cu_3O_2 by cathodic reduction is impossible.

4.2. *Cathodic reduction of basic copper(II) salts on metallic substrates.*

A voltammogram observed for the reduction of a thin layer of brochantite incrusted in the surface of copper sheet is shown on Fig. 3. The potential scans at 0.5 $mV\,s^{-1}$ in 0.1 M $Na_2B_4O_7$ for the reduction of all basic copper(II) salts incrusted in copper display only one broad peak in the range -0.60 to -0.55 V vs SCE indicating that one step is involved; see Table 3.

Table 3.

Compounds (on OFHC copper)	*$Cu_2(OH)_3Cl$*		*$Cu_4(OH)_6SO_4$*	*$Cu_2(OH)_2CO_3$*
	Atacamite	*Paratacamite*	*Brochantite*	*Malachite*
Peak position /V vs SCE	−0.55	−0.61	−0.56	−0.58

From this study, it may be concluded that techniques based on electrochemical reduction provide valuable means for determining copper(II) compounds and copper(I) oxides. Linear potential sweep voltammetry shows that CuO and basic copper(II) salts are reduced before copper(I) oxides.

5. Conclusion

Cathodic reduction is a technique which has been extensively used for the characterization of products formed during the atmospheric corrosion of copper [27] and the measurement of the corrosion layer thickness. The thickness data are calculated under the assumption of an average density of corrosion products equal to that of Cu_2O. This assumption introduces an error which depends on the deviation of the real film density from the density of Cu_2O (because of a lack of knowledge of the porosity and real film composition). The potentials at which copper compounds are reduced change with the layer thickness and the nonstoichiometry for cuprous oxides. The reduction of copper(II) species like CuO, basic copper(II) salts, takes place before that of cuprous oxides Cu_2O or Cu_3O_2.

Another purpose of this study was to show the contribution of i.r. spectroscopy to the analysis of the surface film formation during metal-atmosphere interaction. Infrared reflection spectroscopy allows easy identification of basic copper(II) salts: the $Cu_2(OH)_3Cl$ chlorides are characterized by their Cu–O–H bending modes and other salts like sulfites, sulfates, nitrates and carbonates by the internal modes of the corresponding anion.

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