USE OF INFRARED SPECTROSCOPY TO INVESTIGATE THE CORROSION PRODUCTS OF COPPER

I. A. Efimov, B. N. Rybakov,
L. A. Knizhenko, G. V. Maslova,
and Yu. Ya. Kharitonov

UDC 620.193.01

Establishment of the phase composition of the corrosion products aids in a correct evaluation of the mechanism of the corrosion process. At the present time x-ray [1-3], electron diffraction [4], and thermogravimetric [5, 6] methods of phase analysis are widely employed. Infrared spectroscopy is much more rarely used, although it has a number of advantages when compared to the other methods. Among these advantages, we must above all bring out the possibility of investigating small amounts of any given compounds, independently of their degree of dispersion of form (crystalline or amorphous) [7, 8]. Use of this method permits establishing the presence of functional groups in a compound and, in certain cases, also its phase composition. In addition, infrared spectroscopy may be used also for quantitative determinations.

In the present work a study was made of corrosion products formed on the surface of copper, heat treated at 600°C, in a moist atmosphere containing SO_2 in the amount of ~ 20 mg/m^3, under laboratory conditions, and of the corrosion products of copper ingots after natural tests in atmospheres with different degrees of aggressivity.

Powdered corrosion products were removed from the surface of the samples using a wood spatula, and were then carefully washed in an agate mortar. To record the infared spectra, emulsions of the corrosion products (weighed portion 0.03 g) were prepared in a vaseline oil. The spectra were recorded in a UR-10 spectrometer in the region from 400-4000 cm^{-1}. For purposes of comparison, parallel x-ray investigations were carried out. X-ray photos of the powders were recorded in a DRON-1 diffractometer under FeK_α-irradiation, using a manganese filter. As an example, Table 1 gives the results of the identification of the corrosion products of copper, obtained under laboratory conditions.

It is evident from Table 1 that, in the presence of sulfur dioxide, the main corrosion products are: $3CuSO_4 \cdot 2H_2O$; $CuSO_4$; $3Cu(OH)_2$; Cu_2O; CuO; judging from the intensity of the lines on the diffractogram, the content of Cu_2O and CuO is considerably smaller than that of the other compounds.

Figure 1 gives the infrared absorption spectrum for these same corrosion products. Comparison of this spectrum with the spectra of the corresponding copper compounds confirms the conclusion drawn previously with respect to the phase composition of the corrosion products (Table 2).

TABLE 1. Identification of the Corrosion Products of Copper after Laboratory Tests

Experimental data		Handbook data		Compounds identified	Experimental, data		Handbook data		Compounds identified
d, Å	I_c, %	d, Å	I_c, %		d, Å	I_c, %	d, Å	I_c, %	
6,81	5	6,80	11	$3CuSO_4 \cdot 2H_2O$	2,27	5	2,27	13	$3CuSO_4 \cdot 2H_2O$
5,40	48	5,40	58	$CuSO_4 \cdot 3Cu(OH)_2$	2,13	30	2,13	69	"
					2,07	5	2,07	10	"
4,86	60	4,86	100	$3CuSO_4 \cdot 2H_2O$	1,80	3	1,81	12	"
3,91	55	3,91	100	$CuSO_4 \cdot 3Cu(OH)_2$	1,55	7	1,55	15	"
					1,50	60	1,51	50	Cu_2O
3,34	6	3,34	16	$3CuSO_4 \cdot 2H_2O$					
2,50	40	2,51	100	CuO					
2,45	100	2,45	100	Cu_2O					

Translated from Zashchita Metallov, Vol. 7, No. 4, pp. 439-441, July-August, 1971. Original article submitted February 6, 1970.

TABLE 2. Wave Numbers of Absorption Maxima, Found in the Infrared Spectrum of the Corrosion Products of Copper and Their Attribution

Position of maximum, cm^{-1}	Attribution of vibrations to groups of atoms	Literature source
3580	Valence vibrations of the OH-group	[7, 8]
880, 637, 515, 490	Deformation vibration of the OH-group	[8-10]
3500, 3400	Valence vibrations of the crystalline water of hydration of the copper sulfate molecule (II)	
1630	Deformation vibrations of the crystalline water of hydration of the copper sulfate molecules (II)	
1120	Valence vibration of the SO_4^{2-}-group	[10]
605	Deformation vibrations of the SO_4^{2-}-group	
1090, 795	Vibrations of the Cu—O bonds of cuprous oxide	[11]
990, 950	Valence vibrations of the Cu—O bonds of cupric oxide	[12]
425	Deformation vibrations of the Cu—O bonds of cupric oxide	

TABLE 3. Dependence of the Phase Composition of the Corrosion Products of Copper on the Aggressivity of the Atmosphere

Region in which natural tests were made	Concentration of SO_2 in atmosphere, mg/m^3	Time during which the surface of the metal was wet, h/year	Phase composition of corrosion products	Content of components in mixture, %
North Kazakhstan Region	0,25	1 700	$3CuSO_4 \cdot 2H_2O$ $CuSO_4 \cdot 3Cu(OH)_2$ Cu_2O CuO	~35 ~55 ~3 ~5
Moscow	0,5	2 230	$3CuSO_4 \cdot 2H_2O$ $CuSO_4 \cdot 3Cu(OH)_2$ Cu_2O CuO	~60 ~30 ~5 ~3
Donets Region	2,0	1 000	$3CuSO_4 \cdot 2H_2O$ $CuSO_4 \cdot 3Cu(OH)_2$ Cu_2O	~70 ~20 ~8

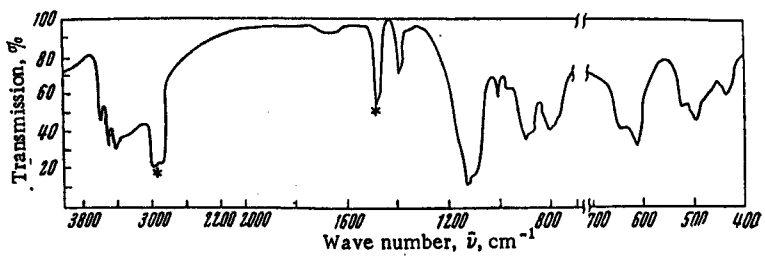

Fig. 1. Infared absorption spectrum of the corrosion products of copper after laboratory tests (the absorption bands of the vaseline oil are marked with asterisks).

The results of interpretation of the powder diffractogram and the infrared spectrum (Table 2) are in agreement with the literature data of [13], in accordance with which the corrosion of copper in electrolytes containing dissolved SO_2 is accompanied by the formation of $CuSO_4 \cdot 3Cu(OH)_2$, identified as brochantite, on the surface of the metal.

Comparison of the relative intensities of the absorption bands has permitted an evaluation of the content of each component in the mixture of corrosion products (%): $3CuSO_4 \cdot 2H_2O \sim 60$, $CuSO_4 \cdot 3Cu(OH)_2 \sim 30$, $CuO \sim 3$, $Cu_2O \sim 15$.

Exactly the same methods were used to determine the phase composition and to evaluate the quantitative content of the components in the products of the atmospheric corrosion of copper (Table 3). The criterion for evaluation of the effect of climatic and meteorological factors on the corrosion was the time during which the surface of the metal was wet [14].

As is evident from Table 3, the phase composition of the products of atmospheric corrosion is basically identical to the composition of the products obtained in accelerated tests. The quantitative ratios are determined by the actual climatic and meteorological conditions, as well as by the sulfur dioxide content in the air.

The data obtained agree well with the results of work in which it was established that, with the atmospheric corrosion of copper objects, a patina is formed [15] consisting mainly of copper sulfates, basic and hydrated to various degrees.

LITERATURE CITED

1. M. I. Hunter, J. Electrochem. Soc., 103, No. 9, 482 (1956).
2. F. Keller, Metall. Protect., 54, 195 (1948).
3. M. N. Ronzhin, A. I. Golubov, and G. M. Fedorova, Corrosion and Protection of Structural Alloys [in Russian], Izd. Akad. Nauk SSSR, Moscow (1966).
4. B. K. Vainshtein, Structural Electron Diffraction [in Russian], Nauka, Moscow (1956).
5. W. W. Wentlandt, Analyt. Chim. Acta, 27, 309 (1962).
6. H. I. Borchard and F. H. Daniels, J. Phys. Chem., 61, 917 (1957).
7. I. M. Hunt, M. P. Wisherd, and L. S. Bonham, Analyt. Chem., 22, No. 12, 1478 (1950).
8. K. Nakomoto, Infrared Spectra of Inorganic and Coordination Compounds [Russian translation], Mir, Moscow (1966).
9. O. Glemser and E. Hartert, Z. Anorgan. und Allgem. Chem., 283, 111 (1956).
10. I. Gamo, Compt. Rend., 252, 2402 (1961).
11. E. F. Cross and N. A. Karryev, Dokl. Akad. Nauk SSSR, 84, 261 (1952).
12. M. V. Akhmanova, Uspekhi Khimii, 28, No. 3, 312 (1959).
13. M. Pourbaix, Werkstoffe und Korrosion, 20, No. 9, 772 (1969).
14. A. I. Golubev and M. Kh. Kadyrov, Proceedings of the III International Congress on the Corrosion and Protection of Metals [in Russian], Vol. 1, Mir, Moscow (1969).
15. G. Geneslay, Bull. Soc. Chim. France, 5, No. 4, 111 (1937).