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INFRARED ABSORPTION SPECTRA OF METAL CARBIDES, NITRIDES AND SULFIDES

O. Kammori, K. Sato and F. Kurosawa

Translation of "Kinzoku Tankabutsu, Chikkabutsu oyobi Ryukabutsu no Sekigai Kyushu Supekutoru," Japan Analyst, Vol. 17 (1968) pp. 1270-1273

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16. Abstract The infrared absorption spectra of 12 kinds of metal carbides, 11 kinds of nitrides and 7 kinds of sulfides, a total of 30 materials, were measured and the application of the infrared spectra of these materials to analytical chemistry was discussed. The measurements were done in the frequency (wave length) range of (1400 - 400 cm^{-1}(7 - 25μ). The carbides Al_4C_3, B_4C, the nitrides AlN, BN, Si_3N_4, WB, and the sulfides Al_2S_3, FeS_2, MnS, NiS and PbS were noted to have specific absorptions in the measured region. The sensitivity of Boron nitride was especially good and could be detected at 2 - 3μg in 300 mg of potassium bromide.

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INFRARED ABSORPTION SPECTRA OF METAL CARBIDES, NITRIDES AND SULFIDES

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The infrared absorption spectra of 12 kinds of metal carbides, 11 kinds of nitrides and 7 kinds of sulfides, a total of 30 materials, were measured and the application of the infrared spectra of these materials to analytical chemistry was deiscussed. The measurments were done in the frequency (wave length) range of (1400-400 cm^{-1} (7-25μ). The carbides Al_4C_3, B_4C, nitrides AlN, BN, Si_3N_4, WB, and the sulfides Al_2S_3, FeS_2, MnS, NiS and PbS were noted to have specific absorptions in the measured region. The sensitivity of Boron nitride was especially good and could be detected at 2-3μg in 300 mg of potassium bormide. /1270*

1. Introduction

Interposed material and effluents in steel plan an exceedingly important role. At the present time many attempts are being made to explain the behavior of these materials by extracting, separating and measuring them. Recently, in addition to the usual electrolytic and wet methods, other methods such as the machine analytic method, derivatography, X-ray diffraction, electron beam diffraction, and X-ray micro analyser (EPMA) have come into wide use. However, all of these methods have their merits and short comings and none of them are definitive. Therefore, we thought it would be interesting to apply the infrared absorption method which has been very little used for inorganic analysis.

The infrared absorption method has the advantages of a) the sample can be less than 1 mg, b) there is no reaction or dissolution as in derivatography and c) detection can be made even in non-crystalline material. If used with proper samples, good results should be expected, though not important reports have appeared thus far. There is almost

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*Numbers in the margins indicate pagination in the foreign text.

no accumulation of information concerning the absorption and spectra of the inorganic materials of this report, though part of them appeared in Ramdas report [1].

The authors are doing research on the application of infrared spectra to the analysis of steel [2-6], and this report continues from our report on oxides [2]. Here we investigate the absorption spectra of carbides, nitrides and sulfides.

2. Experiments

2.1 Measurement

A Perkin-Elmer 521 model diffraction grating spectrophotometer was used. The experiments were done by the potassium bromide disk method. The 1 mg samples (20 μg in the case of BN) were weighed /1271
out with microscales and mixed with 300 mg of potassium bromide powder. After this was uniformly mixed in an agate mortar, disks of 13 mm diameter and 1 mm thickness were prepared in a disk molding vessel. The area of measurement was 1400-400 cm^{-1} (7-25 μ).

2.2 The Samples

The 12 carbide samples are shown in Table I, the 11 nitride samples in Table II, and the 7 sulfide samples in Table III.

3. Experimental Results and Discussion

Of the 12 kinds of carbides two, Al_4C_3, and B_4C were noted to have specific absorption in the frequency area measured. Of the 11 kinds of nitrides, four, AlN, BN, Si_2N_4 (α-Si_3N_4 and β-Si_3N_4), and WN, were noted to have specific absorption in the frequency area measured. Of the 7 kinds of car sulfides, five, Al_2S_3, FeS_2, β-MnS, MiS and PbS were noted to have specific absorption in the frequency area measured. Figures 1-3 show the absorption spectra with the absorption positions. Below we will discuss the relationship between the absorption spectra and the structure of these materials.

TABLE I METAL CARBIDE SAMPLES

Table I Metal carbide samples

No.	Sample	X-ray diffraction
1	Aluminum carbide, Al_4C_3	Al_4C_3†·††
2	Boron carbide, B_4C	B_4C†
3	Chromium carbide, Cr_3C_2	(Cr_3C_2) [illegible]††
4	Hafnium carbide, HfC	HfC
5	Molybdenum carbide, Mo_2C	Mo_2C
6	Niobium carbide, NbC	NbC
7	Nickel carbide, NiC	NiC
8	Tantalum carbide, TaC	TaC
9	Titanium carbide, TiC	TiC
10	Vanadium carbide, VC	VC
11	Tungsten carbide, WC	WC
12	Zirconium carbide, ZrC	ZrC

† Involves graphite ; †† Involves unknown material

TABLE II METAL NITRIDE SAMPLES

Table II Metal nitride samples

No.	Sample	X-ray diffraction
1	Aluminum nitride	AlN
2	Boron nitride, BN	BN
3	Chromium nitride, $Cr_2N(CrN)$	β-Cr_2N, CrN(Cr)†
4	Hafnium nitride, HfN	HfN(HfO_2, Hf)†
5	Niobium nitride, NbN	NbN(NbNO, (NbN)4H)†
6	Silicon nitride, Si_3N_4	α-Si_3N_4, β-Si_3N_4
7	Tantalum nitride	TaN††
8	Titanium nitride, TiN	TiN
9	Vanadium nitride, VN	VN
10	Tungsten nitride	β-WN(W, WO_3)†
11	Zirconium nitride, ZrN	ZrN

† Minor components ; †† Unknown material is involved.

TABLE III METAL SULFIDE SAMPLES

Table III Metal sulphide samples

No.	Sample	X-ray diffraction
1	Aluminum sulphide, AlS	Al_2S_3(Al, etc.)†
2	Cuprous sulphide	CuS·$4Cu_2S$(CuS)**
3	Ferrous sulfide, FeS	FeS(α-Fe)††
4	Pyrite, FeS_2	FeS(FeS_2, Fe_3O_4)**
5	Manganese sulphide, MnS	β-MnS*††
6	Nickel sulfide	Amorphous
7	Lead sulphide	PbS

* Many impurities are involved ; †† Minor components ;
††† Unknown materials are involved.

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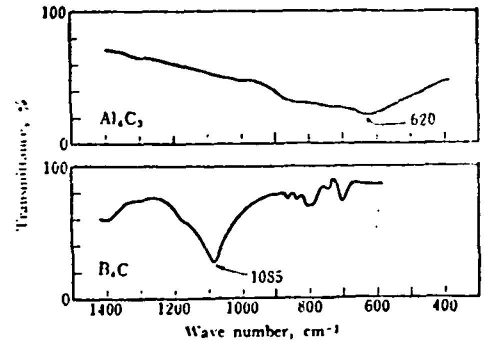

Fig. 1 Infrared absorption spectra of metal carbides

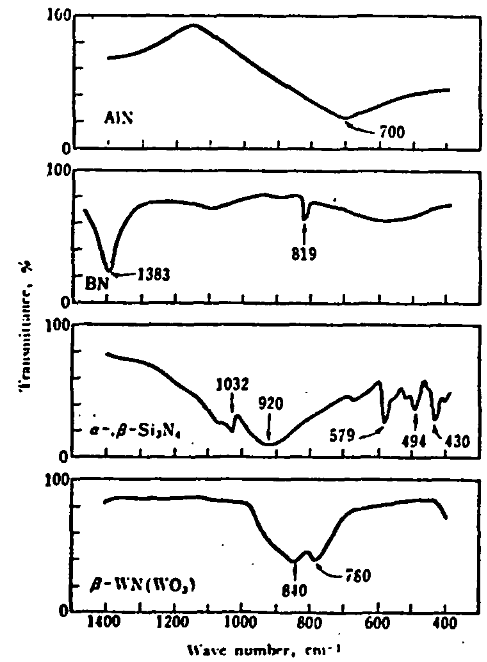

Fig. 2 Infrared absorption spectra of metal nitrides

3.1 Carbides /1272

The crystalline structure the carbides [7] were in general of the interstitial type, as for example, HfC, NbC and TaC. Most of the carbides tended to become berthollide. Al_4C_3 was similar to salt and Cr_3C_2, NiC and WC each had their peculiar structure. Only two kinds of carbide were noted to have specific absorbency and it is supposed that the others have absorption bands in the far infrared region. Consequently, it would be difficult to attempt a study with only these results.

From the analytic point of view, B_4C had a specific absorbency of 1085 cm^{-1}. The authors have already used this for separative measurement of boron effluents in steel obtaining a calibration curve of fairly good linearity [5,6].

3.2 Nitrides

The crystalline structure of the nitrides [7] was mostly of the NaCl type as seen in HfN, NbN and TiN. Consequently, these materials had only one absorbency, Since the absorption band was not inside the area measured, it was assumed that it was in the low frequency far infrared section below 400 cm^{-1}.

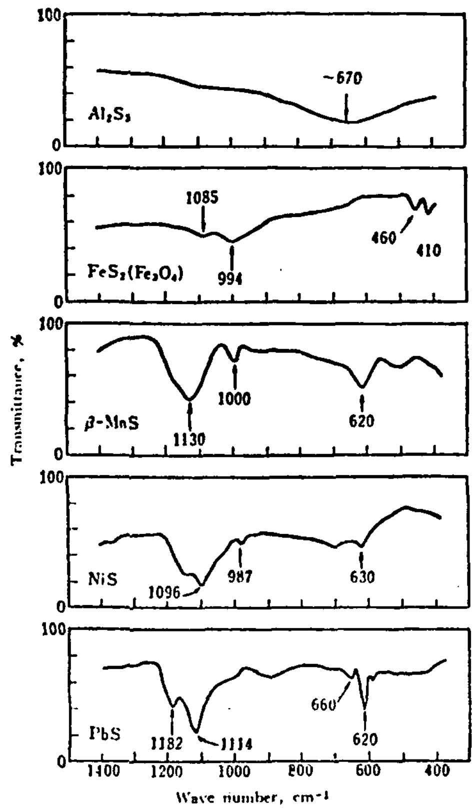

Fig. 3 Infrared absorption spectra of metal sulphides

AlN belongs to the wurtzite type, and is known as a material that plays an important role in certain kinds of steel, such as IN steel. BN was of hexagonal layered graphite-like structure and diamond-like zinc-blende type. Boron is known as a material that enhances the quenching qualities of steel [8], and is beginning to be used in metallurgical research and recently in research by the analysis of state method [5, 6, 9]. BN had specific absorption at 1383 cm^{-1} and 819 cm^{-1}. The 1383 cm^{-1} absorption band was noted to be very strong. The absorbency was about 0.1 under the measuring conditions of our experiment with a 4 µg sample. Since detection is sufficient at under 1 µg, this can be applied to the separation analysis of steel which contains boron. Si_3N_4 was of α-type and β-type. Consequently, there is no clear specific individual adsorption in the absorption spectrum of figure 2. This material is of group IV elements and this nitride is known as one of the few compounds that satisfy the valence law. X-ray diffraction showed that the β-WN contained WO_3 and the origin of the absorption band in figure 2 is not known. This could be resolved if the absorption spectrum of WO_3 were known.

Since only 4 of the nitrides were noted to have specific absorption, the relevance of the absorption spectra to the structure cannot be determined.

3.3 Sulfides

There is a fair amount of diversity in the crystalline structures of sulfides [7]. A defect is that it is very difficult to obtain a pure material. However, of the seven samples specific absorption was noted for five.

Al_2S_3 was multiform and there was $\alpha \rightleftarrows r \rightleftarrows \beta$ mutual transition. Its absorption spectrum was broad and the position of absorption unclear. The FeS_2 sample contained FeS and Fe_3O_4. There was no absorption band for FeS and since that of Fe_3O_4 is in the vicinity of 580 cm^{-1} and 380 cm^{-1} [2, 10], it is assumed that the absorption band in figure 3 is mostly that of FeS_2,

β-MnS, NIS NiS and PbS absorption spectra were very interesting for their very great similarity. However, according to the results of X-ray diffraction, the β-MnS contained impurities and the NiS was noncrystalline. Therefore, these materials must be studied further using other analytical methods.

4. Conclusion

Compared with oxides, there were very vew carbides, nitrides and sulfides which had specific absorptions in the measured region. (1400-400 cm^{-1}). Of the 30 samples measured, specific absorption was noted in only 11 types, and of these, 5 were sulfides. Almost none of the materials of the experiment having absorption bands /1273 outside the measured region had absorptions at high frequencies above 1400 cm^{-1}. Most of them had absorption bands in the low frequency far infrared section below 400 cm^{-1}.

Concerning the crystalline structure, HfC is typical of the carbides and is of the interstitial type. TiN is typical of the nitrides and is of the NaCl type. The nitrides were prone to become berthollide. The sulfides all had their peculiar structures which were diverse. No tendency for linearity between the crystal structure and absorption spectra was noted. However the absorption spectra of these materials can be very useful in the qualitative identification of compounds and can be effective in everyday analysis. BN, especially, can be detected when the quantity is 1/100. In this experiment, 4 μg of BN in 300 mg of KBr gave absorbence of 0.1, which is very sensitive. It is possible to use BN in the quantitative analysis of actual samples.

It is exptected that more interesting information can be obtained concerning these inorganic materials by a study of their infrared absorption in the far infrared section.

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