APPLICATION OF X-RAY SPECTRAL MICROANALYSIS TO
THE STUDY OF POWDER METALLURGICAL MATERIALS

A. V. Skoblo

Chemical microanalysis of materials with the aid of an electron microprobe is based on measurements of the intensity of the characteristic x-ray radiation emitted by the specimen under the action of an electron beam.

A narrow (~1 μ) electron beam from a microprobe focused onto a certain area on the specimen surface excites the characteristic x-ray radiations of the elements present in the volume under investigation (~1 μ³) [1-3]. At angles of emergence greater than 30°, the intensity (as a function of this angle) changes only negligibly (~2%), although an appreciable correction is required at small (under 10°) angles of emergence and with strong radiation absorption by the specimen material.

Little has been published in the literature on the application of x-ray spectral microanalysis to powder metallurgy [4].

A study was made, using an MS-46 electron microprobe,* of sintered powder metallurgical specimens prepared from iron with copper, sulfur, and graphite additions. The raw materials chosen for the study were PZh3M2 iron powder† produced by the Brovarsk Factory, PM-2 copper powder, elemental sulfur, and 3KA pencil-grade graphite. From these materials, charges of the following compositions were prepared: 2.1% graphite, balance iron; 4% sulfur, balance iron; 2.1% graphite, 2.5% sulfur, 7% copper, balance iron; 0.7% sulfur, 3% copper, balance iron.

After mixing for 2 h, specimens 10 × 10 × 50 mm in size were compacted under a pressure of 5.5 tons/cm². Sintering was conducted in a cracked ammonia atmosphere at 1170°C (the sintering and cooling time was 8 h).

*The instrument was manufactured by the Cameca Company. The present investigation was conducted at the Siberian Branch of the Academy of Sciences of the USSR.
†Fine grade, prepared by the reduction process—Transl.

Fig. 1. Iron—sulfur (4%) composite, ×250: a) electron micrograph (AB is the line along which intensity was recorded); x-ray photographs: b) in FeKα radiation; c) in SKα radiation.

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The greatest interest must attach to the results yielded by the study of the specimens with high (2.5 and 4%) sulfur contents. In recent years, sulfur has been widely employed in sintered materials to improve their antifriction properties and increase their wear and seizure resistance [5], reduce interconnected porosity in gas carburizing [6], etc. There is interest in the character of distribution of sulfur and its compounds in the microstructure of such materials. Sulfur readily mixes with iron powder, exhibiting low viscosity and excellent wetting of iron at 150-250°C. Because of this, it rapidly spreads along all capillaries and over the contact surfaces of adjacent particles. At 200-250°C, FeS begins to form. Liquid FeS, too, wets solid Fe well. As a result, accelerated sintering and blockage of pores and channels occur in very many places. The microstructure of such alloys consists of ferrite grains and ferrous sulfide; the shape of the sulfide inclusions depends on the percentage sulfur content, changing from round to angular as the sulfur concentration rises [7]. Compared with iron, copper exhibits greater affinity for sulfur. During sintering in the presence of copper, the compound Cu₂S forms.

Figure 1a shows an electron micrograph of the microstructure of an iron-sulfur (4%) alloy, in which two phases are clearly visible. The other two micrographs illustrate the same zone of this specimen, as seen in characteristic iron (b) and sulfur (c) x-ray radiations. The white areas (points, spots) in the x-ray photographs are indicative of the presence in these surface zones (in a layer about 1 μ deep) of the element whose characteristic radiation was employed for obtaining the photographs. It is therefore clear that the dark round grains in the microstructure in Fig. 1a represent iron, while the phase precipitated along the boundaries contains iron and sulfur.

To determine the stoichiometric composition of the iron-sulfur phase, use was made of the intensities of the characteristic x-ray radiations FeKα₁ and SKα₁ in the diagram in Fig. 2. This diagram shows the distribution of the FeKα₁ and SKα₁ intensities along the AB line in Fig. 1a. At first the electron beam was moved across an iron grain, so that the intensity FeKα₁ was a maximum and SKα₁ = 0. Next, the beam was directed toward an area of the unknown phase under examination. The intensity of the iron radiation decreased by almost half, while at the same time the intensity of the characteristic sulfur radiation markedly rose. This was followed by another iron grain and so forth. It should be noted that the intensity ratio FeKα₁/SKα₁ at different points within each phase was constant, testifying to the latter's homogeneity. Calculation was based on the relationship between the intensity of characteristic x-ray radiation and voltage [8]:

\[ I = \text{const} (V^2 - V_0^2), \]

where \( V \) is the applied voltage (20 kV) and \( V_0 \) is the K-series excitation voltage (2.5 kV for SKα₁ and 7.1 kV for FeKα₁).

It was found that ISKα₁ = 393.7 and IFeKα₁ = 350.0.