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GRAIN SIZE AND GRAIN SHAPE EFFECT OF ZINC SULPHIDE STRUCTURE AND OF OXIDIZING PROCESS CONDITIONS

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ABSTRACT

The results in this paper give information about the influence of the zinc sulphide structure and the oxidation conditions on the shape of the crystallites in the oxide phase. Zinc sulphide has regular and hexagonal structures. The cross-sections of the samples have been observed before and after the oxidation at 1223 K.

The reaction products are dependent of the temperature, the flow-rate of gases and the oxygen pressure. Showing these dependences the shape of zinc oxide crystallites has been investigated when the oxidation of regular zinc sulphide was already finished. It was also taken into consideration that the growth of the grain of the sulphide may change the rate of oxidation. The results obtained agree with all the mentioned parameters of the shape of zinc oxide crystallites allowing to interpret the kinetic curves.

1. INTRODUCTION

The oxidizing process on the interfacial surface between ZnO and ZnS produces the transformation of the sulphide phase in an increasingly oxidized layer. When the sulphide phase has a structure similar to the new oxide phase growing up, then the transformation runs according to the orientation and dimension principle[1]. The transformation must proceed in such a manner, that only small lattice translations occur. The lattice of the new phase can be considered as the continuation of the old phase lattice. When the lattice parameters of the new and old phase, i.e., of the sulphide and new oxide phase are quite different, the deformation is much larger. Such reasoning is correct in the first stage of the process, when the layer of the new phase is still thin and when the stresses due to volume changes are still relatively small. If the stresses could not be neglected the new phase lattice has the previous orientation relative to the matrix only in the volume close to the reaction zone. At some distance from this zone the crystals decrease and a new growing phase is appearing.

Cannon and Denbigh[2] dealt with the influence of single-crystal anisotropy of sphalerite on the oxidizing rate.

Prior to the investigations some additional faces on monocrystals of sphalerite have been polished every 5° between (the (110)-faces) joining at 60°. In this way some new planes have been obtained, the most inclined to the (110) plane forming an angle of 30° with it.

After the oxidation at 780°C it has been found that the oxide layer increases for increasing angle values between the given plane and the (110)-plane and its thickness attains the maximum value for the 30°-plane being about 35% thicker than for the (110)-plane. The same oxidation time of ZnS-monocrystals with the (100)-plane corresponds to the about 10%-thicker layer than on the (110)-plane. Therefore the conclusion can be drawn, that there are considerable changes of the oxidation rate due to the oxidized plane orientation, with a minimum value for the (110)-plane. Consequently the ZnS-crystallites having a suitable orientation, i.e., with their active plane parallel to the oxidizing (reaction) front will grow faster than others. As a result a so-called "crystal growth texture" will be obtained, independent of the initial phase orientation.

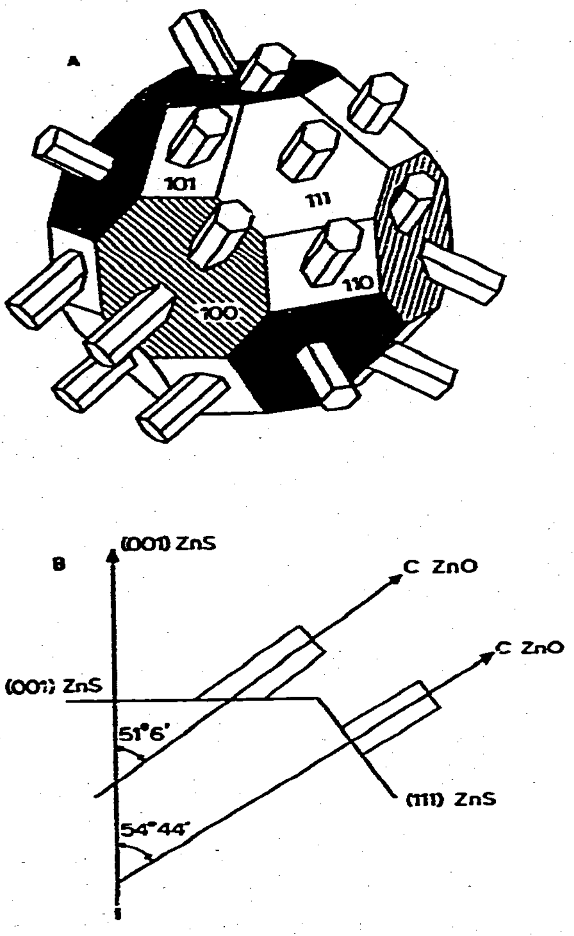


Fig. 1. (a) Schema of the variations of hexagonal prisms position; the prisms being produced on various ZnS-planes[3]. (b) Variations of the angle between C-axis of ZnO and [001] ZnS-axis, when the orientation of the oxidized plane changes[3].

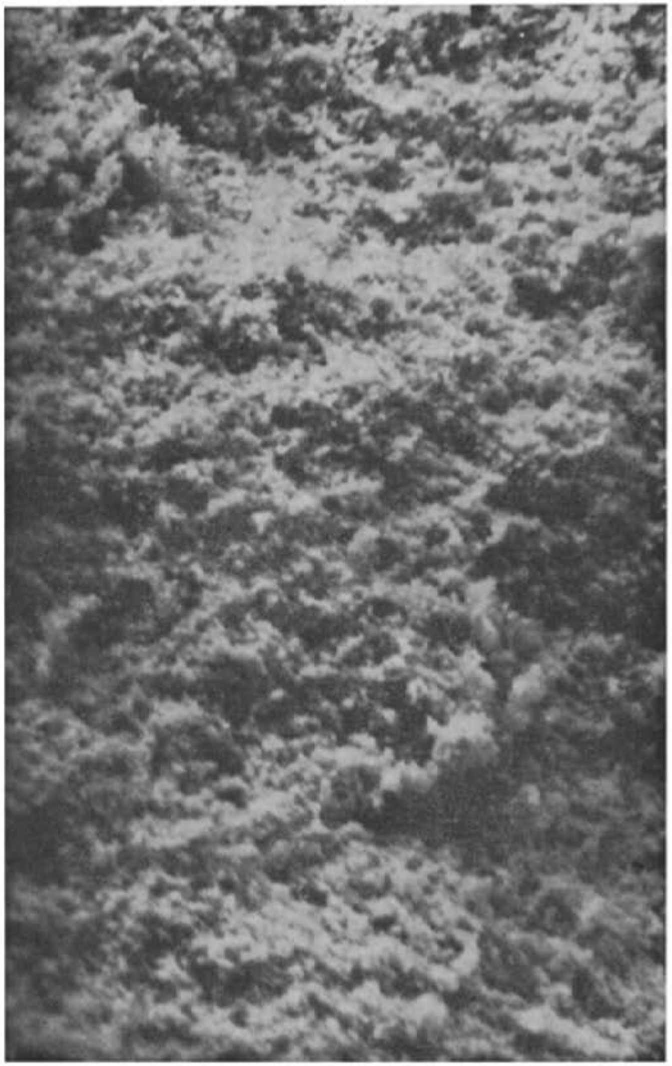
Aminoff and Broome[3] considered theoretically the oxide phase crystals formation on appropriate crystal planes of the sulphide phase. From a detailed, theoretical work the authors concluded that generally the basic plane of the hexagonal ZnO-system lies parallel to the (111)-plane of ZnS having a regular structure. These two planes with maximum Zn-ions packing are gradually arranged to coincide with the directions of maximum package. A scheme has been established relative to the observed phenomena in order to show how the prismatic ZnO-crystals are arranged on different ZnS-planes (Fig. 1a and b).

2. EXPERIMENTAL

2.1. *The grain shape of the oxide phase in relation to the sulphide phase structure*

According to many references, it can be stated that the crystalline structure of zinc sulphide affects its behaviour to a high degree during the oxidation process[4-6]. To confirm these references two kinds of zinc sulphide have been used, namely, a synthetic one (B.D.H.) and a natural kind (from Olkusz mines in Poland), called brunckit. The primary material and the final product, after oxidation, were submitted to the X-ray analysis, by the Debye-Scherer method carried out on a "TUR M-62" diffractometer with copper-tube having a nickel filter. The diffractograms obtained showed both the regular face-centered structure of synthetic zinc sulphide and the hexagonal structure of the natural zinc sulphide. The oxidation products of both types of sulphide showed the hexagonal structure, the lattice parameter of the regular ZnS-system being $a_0 = 5.412$ Å, whereas the lattice parameters of hexagonal ZnS are as follows: $a_0 = 3.881$ Å and $c_0 = 6.234$ Å[4,6-8]. The oxidation products obtained from both sulphide modifications had the hexagonal structure with the following values of lattice parameters: $a_0 = 3.249$ Å and $c_0 = 5.180$ Å[4,6-8]. Thus the oxidation of zinc sulphide with regular structure causes a great volume change of the elementary cell due to the reaction from sulphide to oxide with a change of lattice type. When the hexagonal modification of zinc sulphide is submitted to oxidation, then the volume change is considerably smaller due to the reaction from ZnS to ZnO. Therefore, the new structure is similar to the primary one. In such a case the lattice transformation should develop according to the orientation and grain size principle, in relation to the individual grain size in the sample submitted to the investigations. The polymorphic modifications of the investigated zinc sulphide had nearly the same value of the average grain diameter, as determined by the Fisher-device, i.e., for zinc sulphide with regular structure, 0.90 μm and 1.25 μm for the hexagonal lattice-structure.

The cross-sections of compressed samples were submitted to microscopic observations, in order to examine the shape and distribution of individual grains. A Joel-electron-scanning microscope was used for this purpose and the obtained microphotographs of sample cross-sections, after fracture, are given in Figs. 2 and 3. There are no very important structure variations, although some discontinuities can be found. The synthetic zinc sulphide samples are more homogeneous than the natural ZnS. From microscopic observations of fractured samples the conclusion can be drawn, that there is no doubt as to the homogeneity of sample structure.



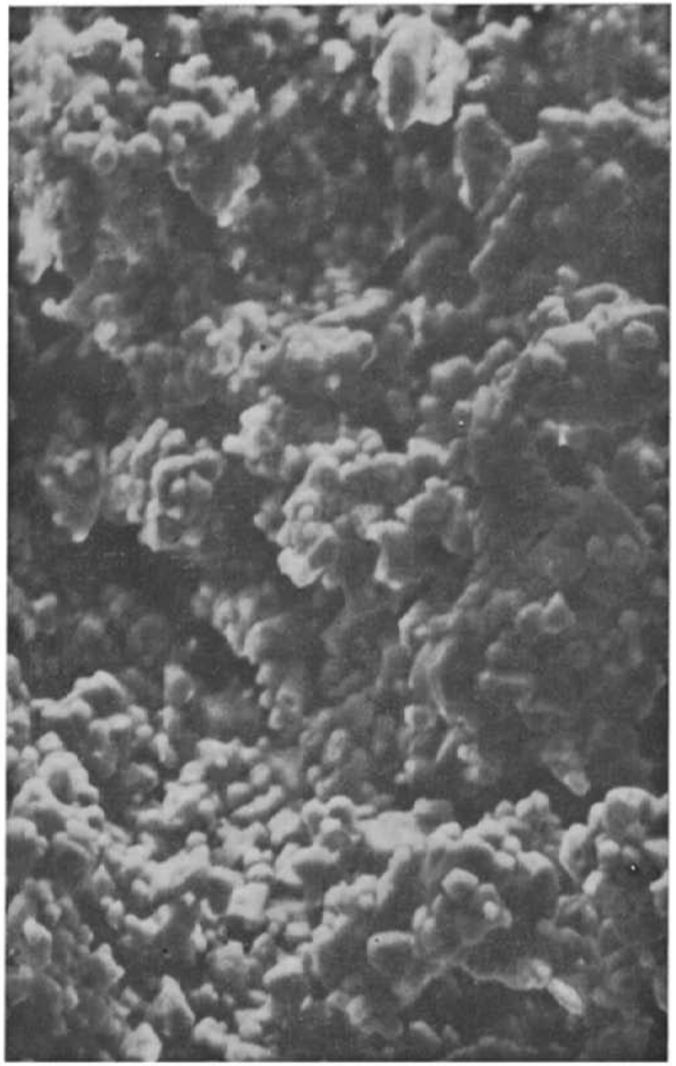
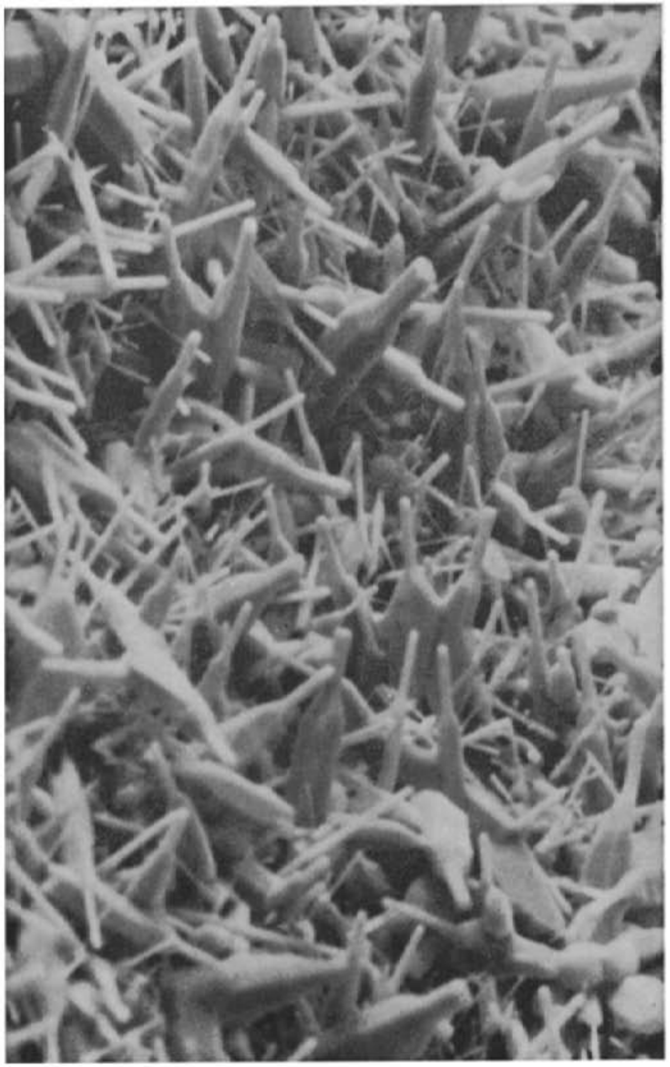


Fig. 2. Cross-section of zinc sulphide with regular structure. Enlargement 3000 ×. (sample fracture).

Fig. 3. Cross-section of fractured zinc sulphide sample with hexagonal structure. Enlargement 3000 ×.



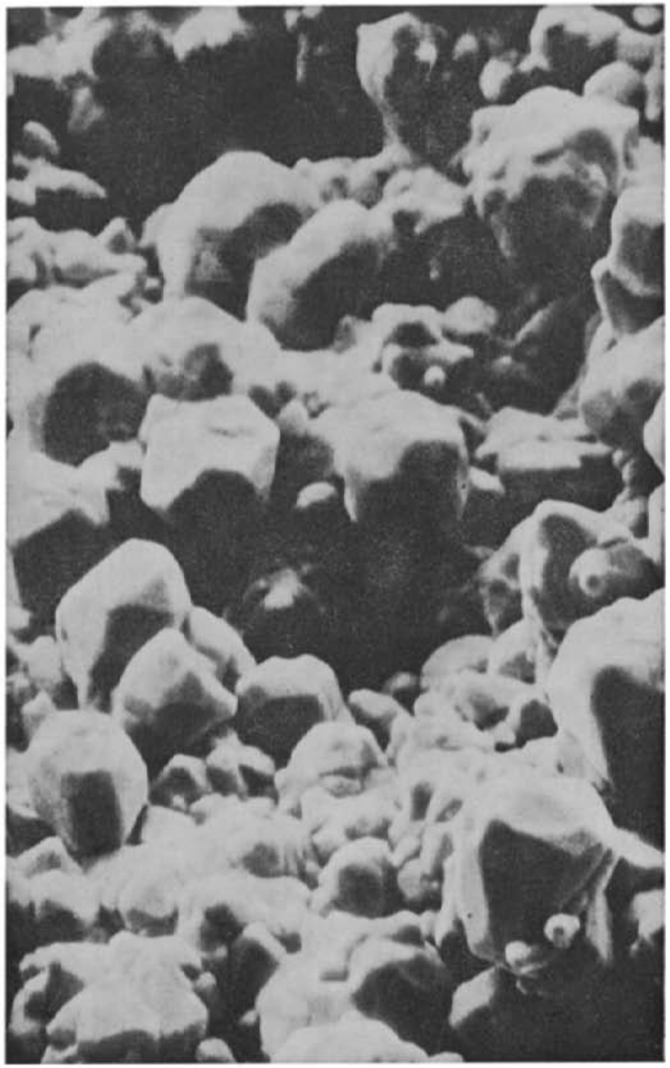


Fig. 4. Fracture cross-section of zinc sulphide sample with regular structure, after oxidation at 1223 K. Air flow-rate 300 Ncm^3 min^{-1}.

Fig. 5. Fracture cross-section of zinc sulphide sample with hexagonal structure, after oxidation at 1223 K. Air flow-rate 300 Ncm^3 min^{-1}.

Separate sulphide grains, on the microphotographs have a nodular structure. Thus the eventual error concerning the means value of grain diameter, as determined by means of the Fisher apparatus could be considered as negligible.

The samples of both zinc sulphide types have been submitted to the oxidizing process, at 1223 K, the air flow-rate in the reaction zone being 300 Ncm^3 min^{-1}. After oxidation the fractures have been observed using a microscope and the respective microphotographs can be seen in Figs. 4 and 5.

The fracture cross-section microphotographs reveal an evident influence of matrix phase structure upon the grain shape of the produced oxide phase. Furthermore, the microscopic investigations carried out on the fractured zinc-sulphide samples (Figs. 2 and 3) revealed nodular grain shape, with the only difference, i.e., different structure of the crystal lattice. The oxidation of zinc sulphide with a regular structure produces an oxide layer with a completely different structure from the original one. The new ZnO-crystallites have a well-developed structure, with hexagonal shaped structure components. The fine grain structure of the oxidized sample causes varied crystallite orientation. The oxide layer formed by oxidation of natural zinc sulphide with a hexagonal structure is quite different from the one previously described. There is no well-developed growth orientation and the oxide grain shape is very similar to the sulphide grains shape.

2.2. *Temperature effect*

The zinc sulphide samples have been compressed, then fractured and the obtained cross-sections, being furthermore called simply "cross-sections", have been submitted to the microscopic observations. To show more comprehensively the temperature effect concerning grain shape and grain size the oxidation at 1123, 1223 and 1323 K has been carried out. The microphotographs obtained as an effect of temperature are shown in Figs. 4, 6 and 7, respectively.

If the microphotographs in Figs. 4, 6 and 7 are examined thoroughly and compared with each other, it can be concluded that the oxide phase crystallites, formed at 1123 K, have a well-developed orientation[9] in spite of their fine grain structure. The oxide phase crystallites obtained at 1223 K have a very regular and well-developed prismatic structure with a hexagonal basis. Zinc sulphide, when oxidized at 1323 K (Fig. 7) is transformed to a quite different oxide phase. The structures of the crystallites obtained under such conditions differ from each other, most probably as a result of sintering of separated grains, consequently causing the grain growth.

This study of temperature effect on the shape and size of crystallites in the growing oxide layer, would not be complete without considering the sulphide matrix phase grain growth at different temperatures. In order to investigate this phenomenon some samples have been held at 1123; 1223 and 1323 K in the nitrogen atmosphere during 40 min; then the cross-sections have been submitted to microscopic observations. Figures 8–10 show the respective microphotographs. The examined cross-sections reveal a considerable increase of the sulphide grain size at 1223 K (Fig. 9) in

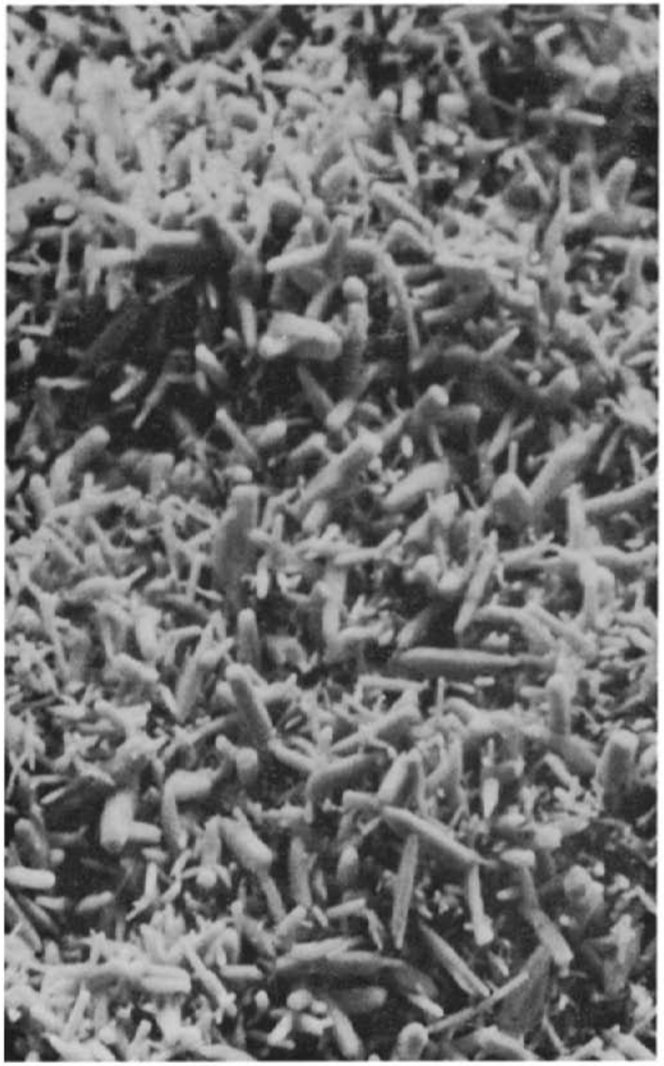


Fig. 6. Fracture cross-section of the sample oxidized at 1123 K. Air flow-rate 300 Ncm^3 min^{-1}.

Fig. 7. Fracture cross-section after oxidizing at 1323 K. Air flow-rate 300 Ncm^3 min^{-1}. Enlargement 3000 ×.

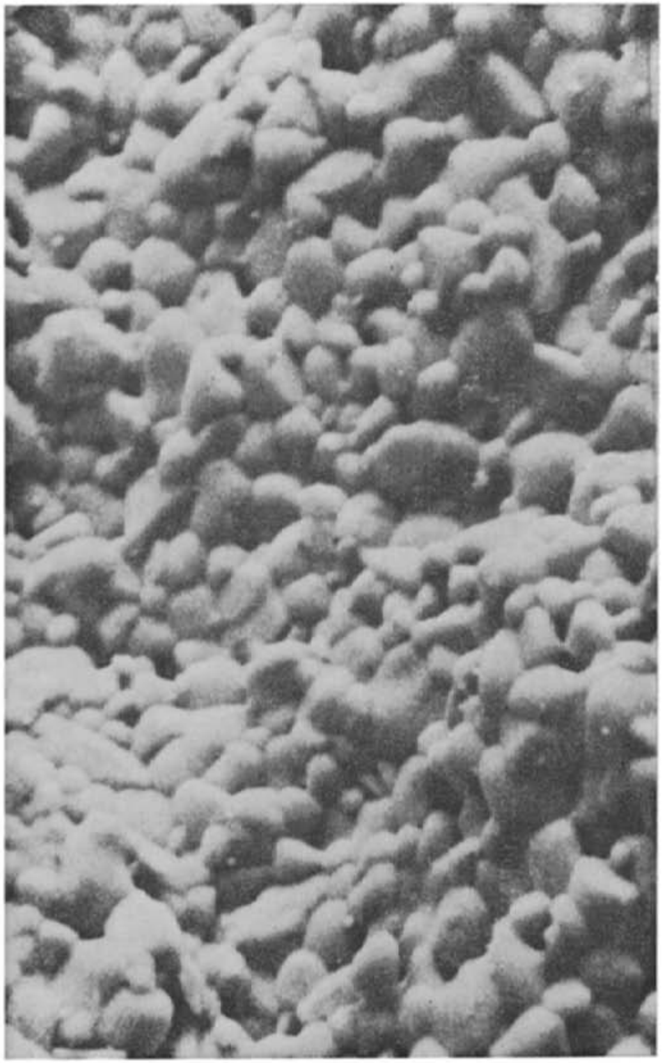
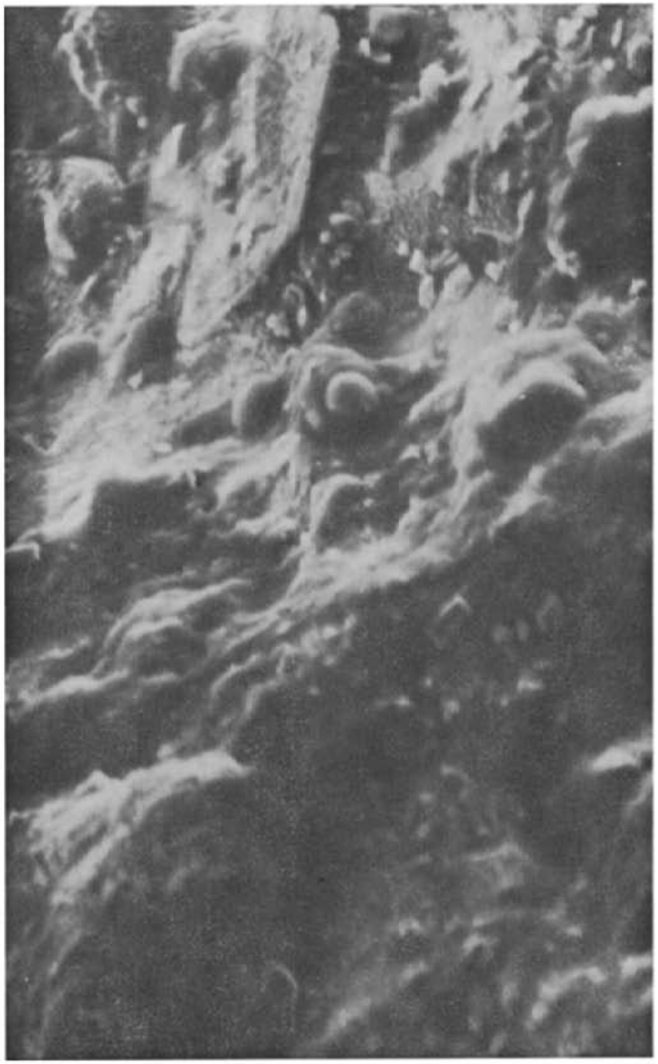


Fig. 8. Microphotograph of zinc sulphide sample cross-section fracture taken at 1123 K in nitrogen, during 40 min. Enlargement 3000 × .

Fig. 9. Microphotograph of fracture cross-section of the zinc sulphide sample taken at 1223 K in nitrogen during 40 min. Enlargement 3000 × .



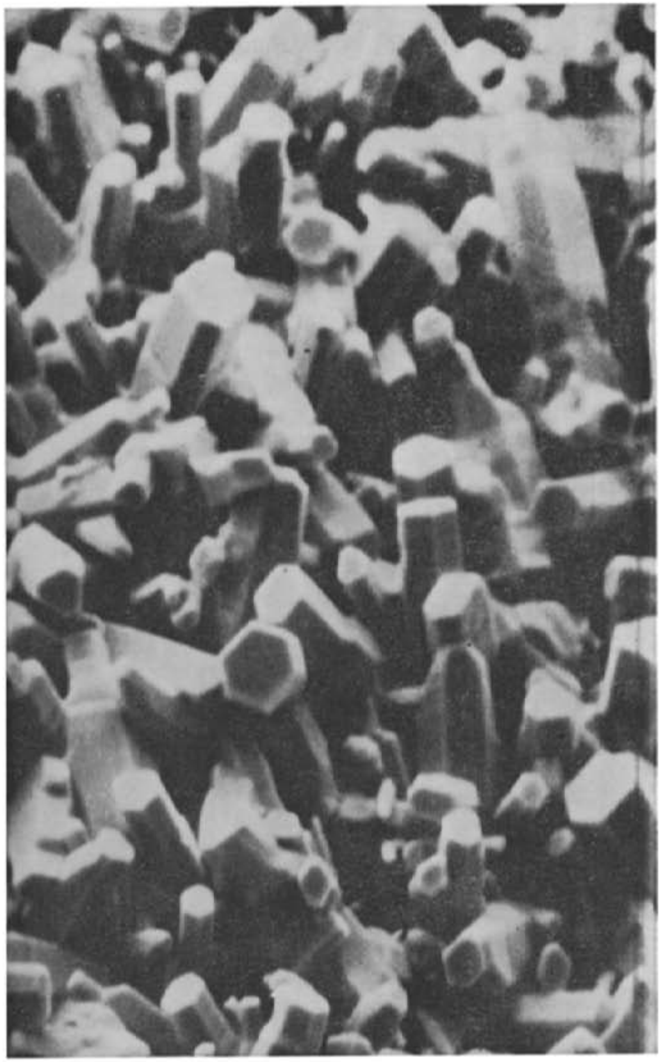


Fig. 10. Microphotograph of fracture cross-section of zinc sulphide sample taken at 1323 K in nitrogen, during 40 min. Enlargement 3000 ×.

Fig. 11. Sample fracture cross-section after oxidizing at 1223 K. Air flow-rate 100 $\text{Ncm}^3\ \text{min}^{-1}$. Enlargement 3000 ×.

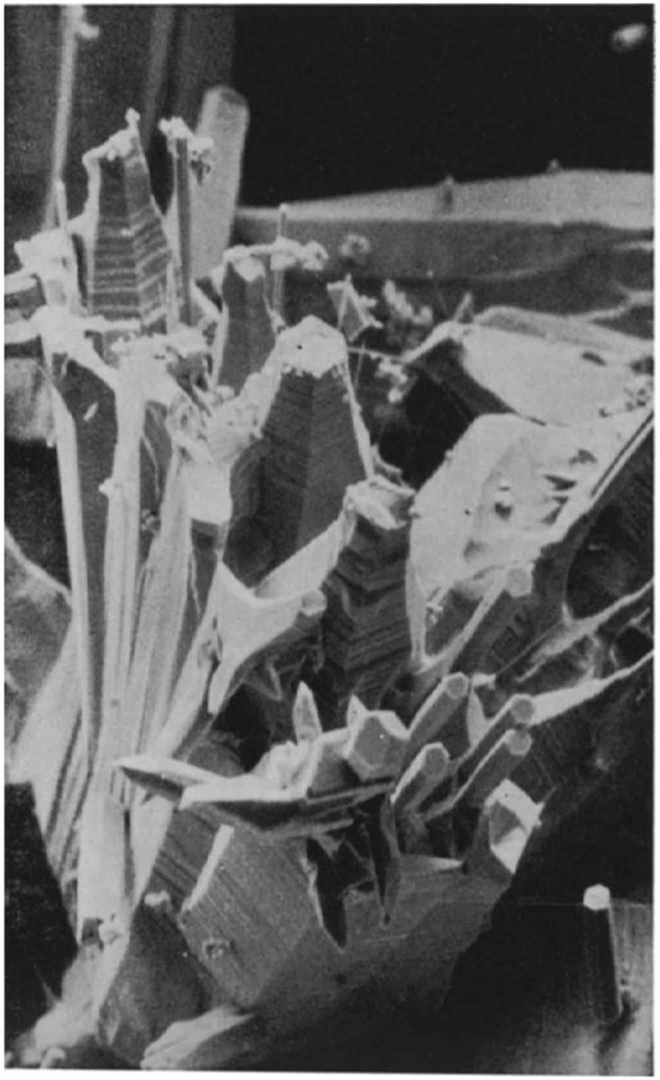


Fig. 12. Sample fracture cross-section after oxidizing at 1223 K. Oxygen flow-rate 300 Ncm^3 min^{-1}. Enlargement 1000 ×.

relation to the grain size obtained at 1123 K (Fig. 8). It should furthermore be stated that the sulphide grains retain their original nodular shape.

With regard to the zonal character of the oxidizing process the deeper situated sulphide grains have a longer time to grow. Thus the oxidation rate decreases monotonically not only because of phases ZnO and ZnS boundary surface decrease but also as a result of matrix sulphide phase grain growth[10]. When the sample was submitted to the temperature of 1323 K, in nitrogen atmosphere a quite different structure of the sulphide phase was obtained (Fig. 10). There is most probably the effect of polymorphic transformation of sphalerite to wurtzite at 1293 K (ref. 7). Because of the less reactive power of hexagonal zinc sulphide in relation to the regular structure form, the oxidizing rate above 1293 K should decrease gradually[8,11]. This decrease should be attributed to the difference between the oxidizing rate and the rate of transformation of sphalerite into wurtzite. The experimental results[10], as obtained at 1223 K, confirmed the above conclusion.

2.3. *Effect of activity and of gaseous phase flow-rate*

For a more complete analysis of effects resulting from different oxidizing process parameters and producing structure changes of the oxide layer, microscopic observations have been carried out, concerning the samples oxidized at 1223 K, by varying the flow-rate of the gaseous phase having different oxygen content. The microphotographs are shown in Figs. 4, 11 and 12, respectively.

Analysis of the obtained fracture microphotographs (Fig. 4, 11 and 12) leads to the conclusion that the amount and activity of the gaseous phase affect the structure of the oxide layer produced[9]. The oxidation by air stream at a low flow-rate producing very regular and very uniform crystallites contributes to the development of a homogeneous structure (Fig. 11). The increase of flow-rate from 100 to 300 Ncm^3 min^{-1} activates considerably the oxidizing process. Therefore, the ZnO-grains have a varied, non-uniform shape (Fig. 4). The activity of the gaseous phase affects the oxide layer structure to a high degree, which can be seen on fracture microphotographs (Figs. 4 and 12).

In the oxygen atmosphere the process rate is many times higher in comparison with the process rate in air. Therefore, the zinc oxide crystallites have a very varied structure. There are fine, regular, prismatic crystallites as well, as coarse grains having the shape of hexagonal pyramide could be found. Furthermore, a sandwich structure and very coarse grains can be observed.

3. CONCLUSIONS

From microscopic observations of zinc sulphide samples under different oxidizing conditions the following conclusions can be drawn:

(1) The shape and size of oxide phase crystallites are related to both the original structure and to the process conditions. The grain shape of the oxide phase obtained at 1223 K by oxidation of synthetic zinc sulphide with regular structure

corresponds to the theoretical pattern established by Aminoff and Broome. It may be said: the higher the temperature and process intensity, the less regular the shape of growing ZnO-crystallites.

(2) Above 1293 K the oxidizing rate of ZnS is essentially dependent of the sphalerite–wurtzite transformation and the sintering phenomenon. It is consequently associated with a longer reaction time. For this reason and taking into account the sulphide phase grain growth, the process should be carried out at relatively low temperatures.

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