G. SMOŁA*,♯, A. POCZEKAJŁO*, Z. GRZESIK*

REDUCTION KINETICS OF NiS SULPHIDE

KINETYKA REDUKCJI SIARCZKU NIKLU NiS

Reduction mechanism and kinetics of NiS nickel sulphide obtained during the process of nickel sulphidation, have been studied as a function of temperature (723-873 K). It has been found that the reduction process follows linear kinetics with activation energy of 103 kJ/mol. It is important to note that during nickel sulphidation and after the reduction of nickel sulphide, the product sample shows highly developed surface, creating thus the potential possibilities to be applied in heterogeneous catalysis.

Keywords: NiS sulphide, sulphidation, sulphide reduction, kinetics

Przeprowadzono badania mechanizmu oraz kinetyki redukcji siarczku niklu, NiS, w funkcji temperatury (723-873K). Siarczek ten został uzyskany w procesie siarkowania czystego metalu. Stwierdzono, że proces redukcji zachodzi zgodnie z prawem liniowym, a jego energia aktywacji wynosi 103 kJ/mol. Należy podkreślić, że w wyniku siarkowania niklu oraz redukcji siarczku, otrzymany został materiał charakteryzujący się bardzo rozwiniętą powierzchnią właściwą, co stwarza potencjalne możliwości jego wykorzystania do celów katalitycznych.

1. Introduction

Kinetics and mechanism of sulphide reduction in contrast to oxides were not, as yet, extensively studied [1-6]. On the other hand, detailed explanation of these problems is important of both: theoretical and industrial point of view. From theoretical point of view, it is interesting to explain the details of the reduction mechanism not only of the sulphide directly to metal, but also the course of intermediate steps of this process, showing the formation of transient sulphide (reduction of higher to lower sulphides). It should be noted that up to now, the reduction mechanism of sulphides down to metal had only been studied, without any reports concerning the reduction mechanism and kinetics of higher sulphide to lower sulphide. On the other hand, all these information are very important in industrial applications, because they offer new possibilities for the optimization of metals production in the reduction process of sulphides. However, most important potential possibilities of utilization of metallic materials obtained in reduction of sulphides, constitutes heterogeneous catalysis. It is well known already that nickel may play an important role as a catalyst in a number of chemical reactions, for example in production process of hydrogen from glycerine [7]. Most important problem in this area of research is highly developed surface of catalyst. This is not easy problem to be realized in particular in the case of metals. Preliminary investigations have demonstrated that during sulphidation of nickel under appropriate thermodynamic conditions, the NiS

reaction product is porous and show highly developed surface area, as shown in Fig. 1. During reduction of this form of NiS specimen to pure nickel, the highly developed surface area remains virtually unchanged. Thus, this rather simple method could be used in obtaining suitable catalysts for a number of chemical processes. The optimisation of this process needs detailed information on the kinetics and mechanism of NiS reduction.

Thus, the present paper is an attempt to get new information on the kinetics of NiS sulphide reduction as a function of temperature.

2. Materials and Experimental Procedure

The kinetics and mechanism of nickel sulphide reduction have been investigated, using NiS developed in this laboratory as a starting material. Thus, in the first stage thin foil of high purity nickel has been cut into rectangular specimens (0.125 mm×20 mm×10 mm) and sulphidized completely in the helium-sulphur vapors gas mixture. The sulphidation process of nickel has been carried out at 873 K and sulphur vapor pressure of 130 Pa. Under these conditions the only reaction product was NiS sulphide. Reduction process of NiS sulphide has been carried out under isothermal conditions at the constant rate of the flowing gas through the reaction chamber equal to 50 cm³/min. Reaction gas mixture constituted argon with 1% of hydrogen. Figure 1 illustrates typical surface

*   AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND
♯   Corresponding author: smola@agh.edu.pl

area of the morphology of the nickel sample after completely its sulphidation. As can be seen, the sulphidation product constitutes the ground together large NiS crystals, physical dimensions of which did not virtually change with reaction time.
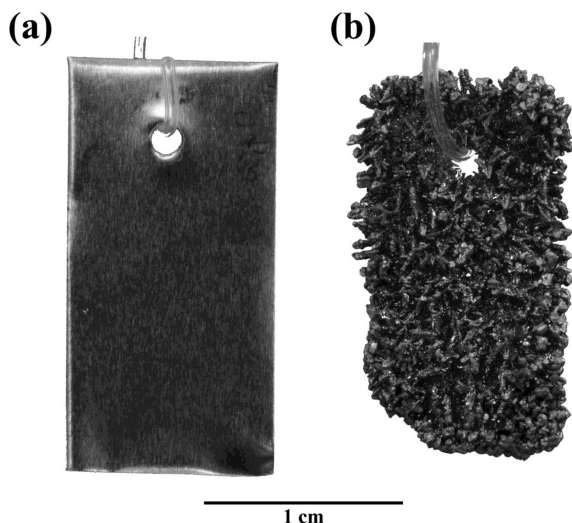

Fig. 1. Morphology of investigated samples: a) Ni foil before sulphidation and b) after complete sulphidation to NiS carried out in 873 K, under sulphur pressure of 130 Pa

The reduction kinetics of NiS sulphide has been studied in microthermogravimetric equipment, enabling the mass changes of a given sample to be followed continuously under isothermal conditions with the accuracy of the order of 10^{-6} g. The details of the apparatus and the experimental procedure have been described elsewhere [8].

3. Results and discussion

The results of reaction rate measurements are summarized in Fig. 2. It follows from this graph that the reduction process of NiS sulphide follows linear rate law, which implies that the rate determining step of the overall reduction rate is one of chemical reactions and not diffusion process.
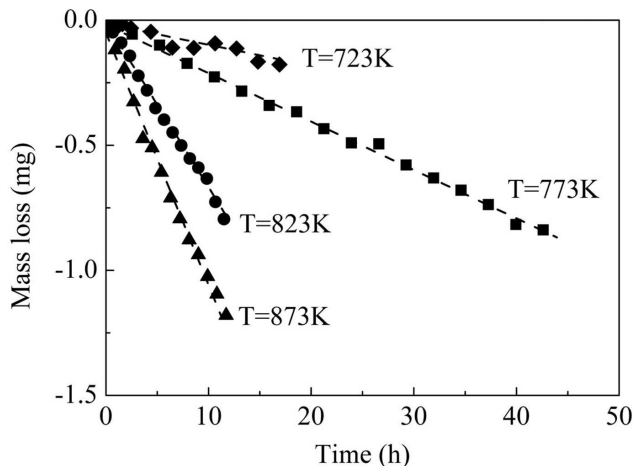

Fig. 2. Results of the NiS sample mass changes during reduction under isothermal conditions, obtained for several temperatures

Such a conclusion is reasonable if one considers the fact that the surface area of the reaction does not virtually change with reaction time and thereby, the only variable is the mass of the sulphide sample as a function of time. Consequently, it may be written:

$$\Delta m = kt + C$$

where Δm is the mass change of the sample (during reduction), k is the linear rate constant, being the direct measure of the reduction rate, t is reduction time and C is a constant.

Fig. 3, in turn, illustrates the temperature dependence of the NiS reduction rate, presented in Arrhenius plot of coordinates. The calculated apparent activation energy of this process equals 103 kJ/mol. It should be noted that virtually the same values of activation energy of Ni_3S_2 reduction have been found by Tan and Ford (101.9 kJ/mol) [3] and Cech and Tiemann (104.6 kJ/mol) [4]. This agreement clearly indicates that the surface reaction is the slowest step in the overall reduction rate mechanism of nickel sulphide.
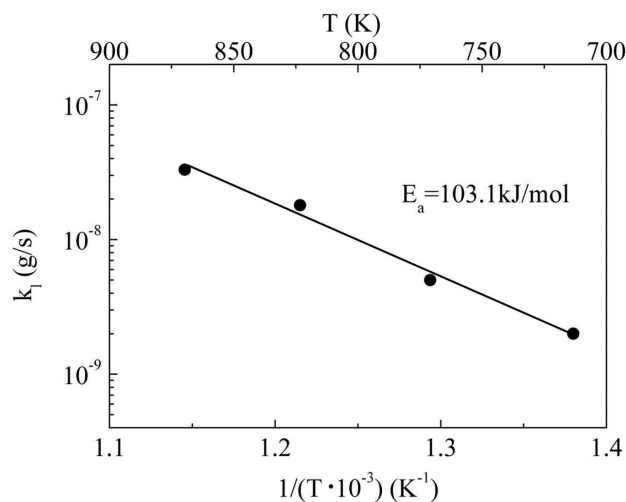

Fig. 3. Temperature dependence of the NiS reduction rate, presented in Arrhenius plot of coordinates

Microscopic observations of the cross-sections of nickel sulphide samples have shown that the reduction process proceeds not only on the surface of NiS specimens, but also in the interior of the samples, as shown in Fig. 4.
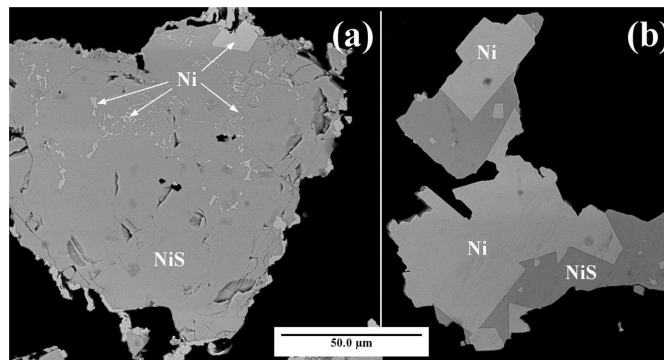

Fig. 4. Microphotographs of cross-sections of the NiS samples: a) after 140 hours of reduction at 823 K, and b) after 400 hours of reduction at 823 K

During the NiS reduction process, the formation of wiskers on the specimen surface may often be observed, as

illustrated in Fig. 5. Oxides and sulphides of transition metals are known to show catalytic activities. One of the fundamental problem in this area of research is to get as high as possible surface area. The results obtained during this work strongly suggest that reduction of nickel sulphide follows to highly developed nickel surface, because the reduction process of nickel sulphide results in the formation of a number of nickel crystals and not in the formation of compact area. This phenomenon is clearly visible in Fig. 5, showing the surface of nickel sulphide sample after its reduction to nickel.
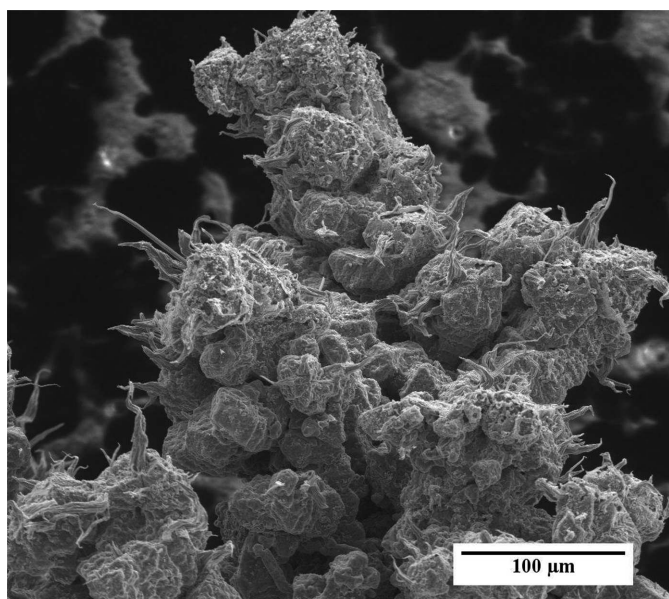

Fig. 5. Microphotograph of the wiskers formed on the top of NiS grains during isothermal reduction at 823K

4. Conclusions

The results described in the present paper allow the following conclusions to be formulated. Nickel sulphide undergoes at moderate temperatures ($\approx$873 K) rather slow reduction rate, being of the orders of magnitude lower than the rate of nickel sulphidation. The reduction process of NiS proceeds not only on the specimen surface but also in the interior of NiS sample. Such a mechanism of reduction process leads to large development of surface area of nickel product, which is particularly important in application in heterogeneous catalysis.

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