Thermochimica Acta, 85 (1985) 47–50
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYTICAL, STRUCTURAL AND MORPHOLOGICAL STUDIES ON THE MECHANISM OF THE DECOMPOSITION OF $ME(SCN)_2$ TO MES_2 ($ME = CO/NI$)

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ABSTRACT

The course of the thermal decomposition of the metal(II) thiocyanates $Co(SCN)_2$ and $Ni(SCN)_2$ has been studied as function of pressure and ambient atmosphere. In nitrogen as well as under vacuum conditions these two compounds decompose in the temperature range of 600 - 650 K under formation of the respective metal disulfides CoS_2 (cattierite) and NiS_2 (vaesite). In spite of the structural analogies between the initial materials as well as between the solid products, different macroscopic mechanisms for the decomposition processes are established by morphological investigations.

INTRODUCTION

The preparation of transition metal sulfides is usually performed by heating mixtures of the elements in sealed quartz tubes at relatively high temperatures (above 900 K). Quite often, however, the product is formed as mixture of several phases or as a single phase with ill-defined stoichiometry. Obviously preparative methods which can be performed under less arduous experimental conditions and which, moreover, lead to stoichiometric monophasic products are of interest.

We therefore set out to study the mechanistic course of the thermal decomposition of the transition metal thiocyanates $Co(SCN)_2$ and $Ni(SCN)_2$ as function of pressure and ambient atmosphere by means of structural, thermoanalytical and morphological investigations.

0040-6031/85/$03.30

RESULTS

Cobalt(II) thiocyanate as well as nickel(II) thiocyanate can be prepared as single crystalline material (ref. 1, 2). They adopt similar structures (table 1) characterized by $[Me(SCN)_2]_n$ layers (001), within which the distorted octahedral coordination of the metal atoms are made up of four sulfur atoms in a square-planar arrangement and two nitrogen atoms in trans position. Thus the metal atoms are linked by four Me-SCN-Me and two Me-S-Me bridges.

Table 1: Crystallographic data of $Co(SCN)_2$ and $Ni(SCN)_2$

	$Co(SCN)_2$	$Ni(SCN)_2$
space group	monoclinic, C2/m	monoclinic, C2/m
a	10.590 Å	10.476 Å
b	3.719 Å	3.628 Å
c	6.161 Å	6.165 Å
β	106.0°	106.9°
Z	4	4

Combined thermogravimetric / mass spectrometric measurements reveal that these thiocyanates undergo decomposition processes in the temperature range of 600 - 650 K. The formation of the solid products, however, is strongly dependent on the pressure and the ambient atmosphere, under which the experiments are carried out: Mixtures of metal oxides and metal sulfides are obtained in air, whereas metal oxides only are formed as solid products in oxygen. Under these experimental conditions, obviously, not only metal - nitrogen bonds and sulfur - carbon bonds within the thiocyanate ligands, but also metal - sulfur bonds are broken.

Under vacuum conditions or in inert gas atmosphere, however, the metal disulfides CoS_2 – which corresponds to the mineral cattierite (ref. 3) – and NiS_2 – which corresponds to the mineral vaesite (ref. 3) – are obtained as pure phases. These disulfides adopt analogous structures again, i.e. they are isostructural to FeS_2, the mineral pyrite (table 2), (ref. 4).

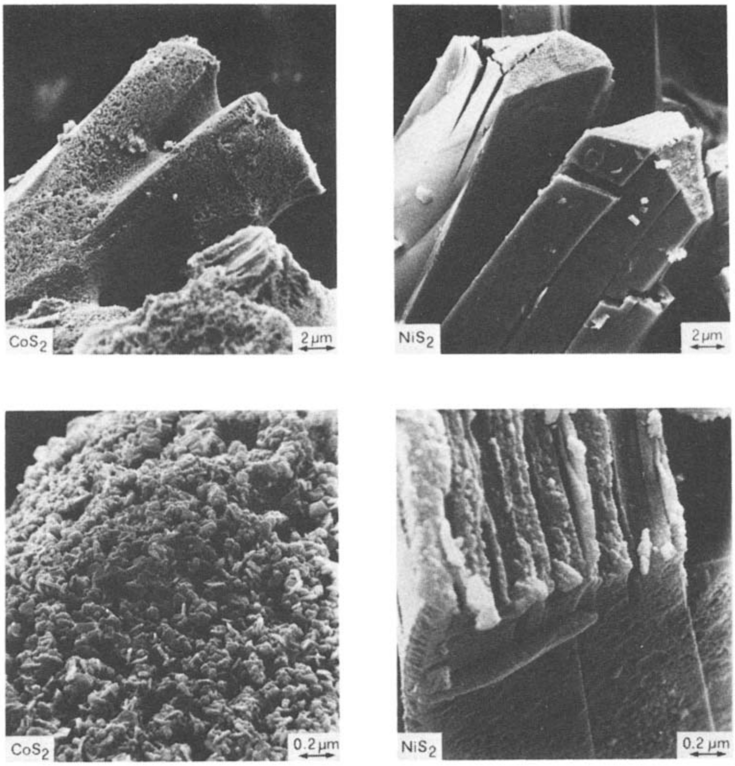

Fig. 1: Scanning electron micrographs of the decomposition products CoS_2 and NiS_2 obtained from the respective thiocyanate precursors.

Table 2: Crystallographic data of FeS_2, CoS_2 and NiS_2

	FeS_2	CoS_2	NiS_2
crystal system	cubic	cubic	cubic
a	5.417 Å	5.523 Å	5.670 Å
Z	4	4	4

Under the aforementioned experimental conditions bonds between metal atoms and nitrogen atoms as well as bonds between sulfur and carbon are broken. The stoichiometric ratio between metal and sulfur, however, is fully preserved.

In spite of the obvious analogies between the mechanistic courses of the decompositions of $Co(SCN)_2$ and $Ni(SCN)_2$ on a microscopic, first coordination sphere level, considerable differences in the concomitant macroscopic changes are observed by scanning electron microscopy; the solid products exhibit basically different morphologies: Whereas NiS_2 is formed as pseudomorphous phase, i.e. under preservation of the shape of the initial nickel thiocyanate single crystal, the decomposition of $Co(SCN)_2$ is characterized by the formation of very small, unorientated CoS_2 crystallites (fig. 1).

Attempts to prepare the pure disulfide phases at even lower temperatures in hydrogen atmosphere failed: Under formation of H_2S and HCN as volatile products, mixtures of MeS_x phases (where $x < 2$) are obtained.

CONCLUSIONS

Metal sulfides, in particular phases with high sulfur content, can be prepared at comparatively low temperatures as monophasic products by decomposing selected precursors. Detailed investigations on the mechanistic course of the decompositions as function of pressure and ambient atmosphere lead to the establishment of defined experimental conditions under which the desired phases can be obtained. Metal thiocyanates represent well suited precursors for such kind of preparations, since well defined thiocyanate compounds of most of the transition metals can be synthesized and, moreover, their decomposition to sulfides can be well controlled.

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