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STUDIES ON INTERACTIONS IN THE $NbBr_5$–Nb SYSTEM

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Abstract

For studying the thermal disproportionation and interaction processes of niobium bromides in the $NbBr_5$–Nb system thermoanalytical and tensimetric methods were employed. The study revealed that the reduction of niobium pentabromide by metallic niobium starts at 257°C and leads to the formation of niobium tetrabromide. The temperature limits of the existence of bromides of niobium in lower oxidation states were determined.

Keywords: interaction, $NbBr_5$–Nb system

Introduction

At present the low niobium bromides attract attention as compounds with a layer structure, that usually possess a number of peculiar physicochemical properties. Hitherto there is no definite technique for synthesizing niobium bromides with known composition. The principal possibility of the synthesis of niobium tetra- and tribromides by reduction of niobium pentabromide with metallic niobium has been described earlier [1–4]. The process is carried out in sealed ampoules with a small temperature difference. In all cases the experiments required a long time (up to several days) and led to the formation of products with a considerable amounts of impurities. Hence, the aim of this work was to study in detail the interaction processes in the niobium pentabromide – metallic niobium system and to determine the temperature limits of the existence of lower niobium bromides by means of thermoanalytical and tensimetric methods.

Experimental

Starting materials: niobium pentabromide was obtained by reaction of metallic niobium with bromine in sealed evacuated ampoules subjected to a gradual

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temperature increase up to 400–450°C. Bromine (All-Union state standard 4109–79 'chemically pure') was purified and dried [5]. The metallic niobium powder used for the reduction of niobium pentabromide was previously held in vacuum (5–10 Hg mm) at 800°C to eliminate adsorbed impurities. Niobium pentabromide was then purified by sublimation in vacuum at 180–200°C. Chemical analysis confirmed the purity of niobium pentabromide:

Obtained: % Nb - 19.03±0.13 % Br - 80.97±0.1

Calculated: % Nb - 18.86 % Br - 81.14

Thermoanalytical studies were carried out in the 20–1000°C range at a heating rate of 10 $deg \cdot min^{-1}$ with a derivatograph Q-1500 D. A mixture with a $NbBr_5$:Nb ratio of 1:4 (sample mass about 0.2 g) was placed in quartz vessels with capillary outlets. The samples were heated twice. At first the temperature was raised to 450°C in a sealed vessel. Then, after cooling to room temperature, the vessel was opened and heated to 1000°C. Thus the substance was held in its own vapour atmosphere or in the atmosphere of disproportionation products at $p=1$ at. Interaction with air was excluded in the first experiment because of excessive gas leakage from the capillary outlet and, in the second one, the vessel itself was held in argon at a constant over pressure of 5–10 Hg mm.

Tensimetric studies were carried out by employing a quartz diaphragm pressure gauge. The initial amount of the mixture was calculated so that the pressure in the working camera of the pressure gauge at the end of the experiment at 850°C did not exceed 1 at. The proportion of the components in the mixture was found experimentally, so that the curve representing the dependence of the pressure in the gas phase on the temperature over the mixture of metallic niobium and niobium pentabromide should truly reflect the processes taking place in the system with changes in composition and amount of the gaseous substance. The heating rate was maintained constant during the experiment.

Discussion

The results of thermoanalytical studies on the $NbBr_5$–Nb system are shown in Fig. 1. The shape of the heating curve shows that the reaction between metallic niobium and niobium pentabromide starts immediately after the niobium pentabromide melting point has been attained which corresponds to an exothermic effect at 257–259°C (Fig. 1A). The most probable reason for the second endothermic effect at 407–410°C is the disproportionation of the niobium tetrabromide obtained. It can be assumed that the disproportionation reaction is reversible and the niobium tetrabromide is formed again upon cooling of the sample in the sealed ampoule. During the second heating of the opened vessel the endothermic effect (T=388°C) which corresponds to the disproportionation of niobium tetrabromide was observed again. The reaction is accompanied by the formation of gaseous products and niobium tribromide (Fig. 1B). A monotonous mass loss occurs in the temperature range 578–700°C which indicates the existence of a phase with variable composition $NbBr_{3.0}$–$NbBr_{2.67}$ [1]. The third endothermic effect apparently due to the decomposition of $NbBr_{2.67}$ starts above 700°C. It should be noted that in some cases the decomposition of $NbBr_{2.67}$ involves two stages through formation of $NbBr_{2.33}$ (as with niobium

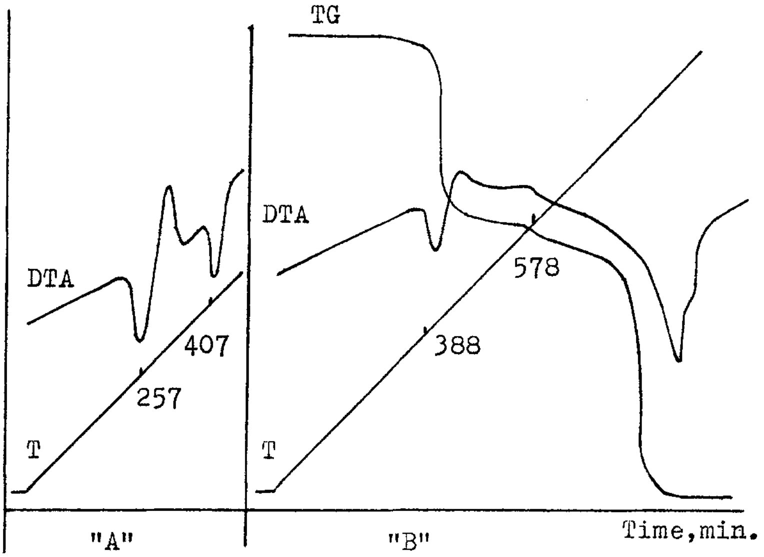

Fig. 1 TG and DTA curves of reduction of $NbBr_5$ by metallic niobium (molar ratio 1:4)

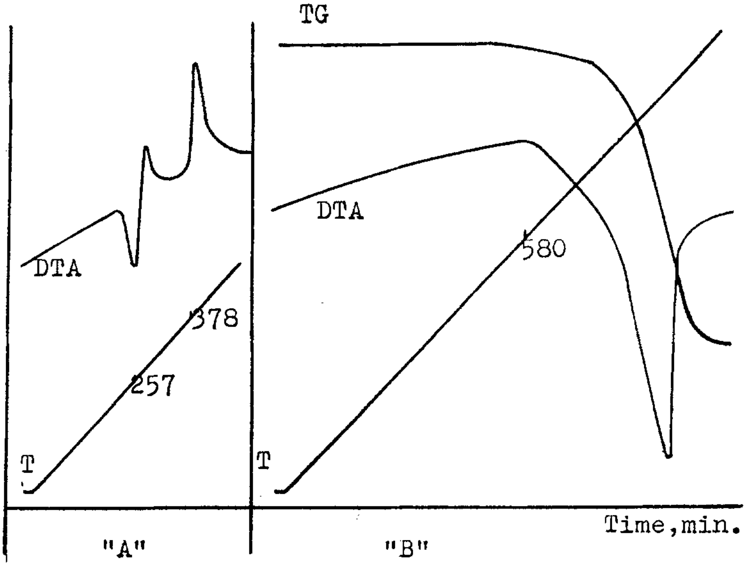

Fig. 2 TG and DTA curves of reduction of $NbBr_5$ by metallic niobium (molar ratio 1:8)

chlorides). If an excessive amount of metallic niobium is used (a $NbBr_5$–Nb molar ratio of 1:8), the niobium pentabromide melts at 257°C, but there is no endothermic effect corresponding to the decomposition of niobium tetrabromide (Fig. 2A). It may be suggested that there is a superposition of two thermal effects with different signs: an endothermic one – corresponding to the decomposition of $NbBr_4$ and an exothermic one – to the formation of niobium tribromide. The exothermic effect prevails because of the excessive amount of metallic niobium. It was confirmed by X-ray studies that, as in the first case, niobium tetrabromide is formed after the melting of niobium pentabromide. The second heating of the opened vessel showed that the product of reaction (supposedly niobium tribromide) is stable up to 580°C and after that a gradual disproportionation starts (Fig. 2B) with a rapid acceleration of the reaction above 700°C.

Tensimetric data confirm the results of thermoanalytical experiments. Changes in vapour pressure with temperature over mixtures with different proportions of the components were studied. Curve 1 (Fig. 3) was obtained during heating of a $NbBr_5$–Nb mixture with a $NbBr_5$:Nb molar ratio of 1.8:1. The relatively large excess of niobium pentabromide led to the coincidence of the obtained curve with the one reflecting the dependence of the vapour pressure of pure niobium pentabromide on the temperature [6]. In this case the reaction between niobium pentabromide and metallic niobium was not observed. During triple heating of one sample with a $NbBr_5$:Nb molar ratio of 1.1:1 curves 11–1Y were obtained. Their differences can be explained in the following way: portions AK, AK', AK'' of curves 11-1Y correspond to two competitive processes with changes in the amount of gas. The first process – evaporation of niobium pentabromide – leads to an increase in pressure over the system. The second process, which leads to a reduction in pressure with increasing temperature, corresponds to the reaction between niobium pentabromide and metallic niobium. The probably scheme of reaction is as follows:

$$NbBr_{5(g)}+Nb_{(s)} \rightarrow NbBr_{4(g)}$$

Portions KL, K'L', K''L'' of the curves correspond to the thermal expansion of vapours in the ideal gas approximation. During temperature increase when the $NbBr_4$ formed in the system starts to disproportionate with the formation of niobium pentabromide, the dependence of the vapour pressure of niobium pentabromide over solid niobium tetrabromide on temperature becomes logarithmic (portions LF', L'F', L''F'' of the curve). As proposed in [7], this process can be described by the following equation:

$$\log p\ (NbBr_5 \text{ over } NbBr_4 \text{ and } NbBr_x) = 15.02\pm0.38-(8.25\pm0.03)\times10^3/T.$$

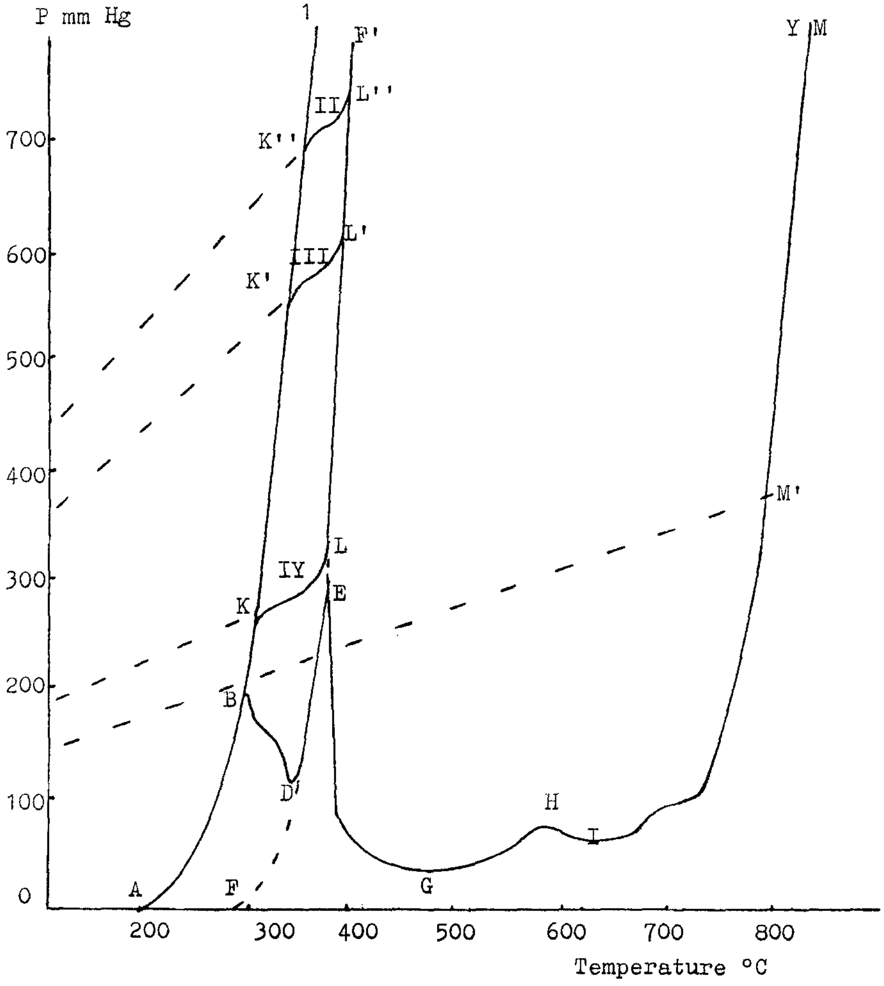

Fig. 3 Dependence of vapour pressure on temperature in the $NbBr_5$–Nb system

Curve Y in Fig. 3 corresponds to the mixture with a $NbBr_5$:Nb molar ratio of 1:4.3. The processes taking place in the system during heating up to 387°C (point E) can be explained as stated above, but larger amounts of metallic niobium in the system promote formation of larger amounts of niobium tetrabromide (section BD of the curve), however, heating of the sample over 387°C leads to a sharp decrease in pressure over the system. In further discussion of P-T curves one must take into consideration that an excessive amount of metallic niobium powder is constantly present in the system. The heterogeneous processes of its interaction with the gas phase can occur only on the surface of metallic particles, but they are inhibited by the solid products of the reaction ($NbBr_4$ in particular). The destruction of $NbBr_4$ layer leads to the opening of the metal surface which is highly reactive and interacts with gaseous niobium pentabromide with the formation of a solid niobium tribromide phase. This process is accompanied by a sharp pressure drop in the system (section EG of the curve). Minor pressure oscillations in the system (section GHI of the curve) can be explained by changes in the composition of the niobium tribromide phase, and the increase in pressure above 645°C (section IM of the curve) can be ascribed with certainty to the disproportionation of the $NbBr_{2.67}$ phase. The results of tensimetric and thermoanalytical experiments are in good agreement. At the beginning of the discussion it was assumed that the interaction between metallic niobium and niobium pentabromide started already at 203–308°C (section AB of the tensimetric curve in Fig. 3). This assumption was confirmed by the fact that the pressure in the system in the final section IM of the curve increased over point M. The quantity of the gaseous molecules of niobium halide formed (section MM' of the curve) is proportional to the quantity of gaseous molecules which enter the reaction in section AB of the curve.

Conclusions

It was ascertained that:

1) a fast reaction of niobium pentabromide with metallic niobium is observed at temperatures higher than 257°C with the formation of niobium tetrabromide;

2) niobium tetrabromide is stable up to 388°C at $p=1$ at;

3) niobium tribromide is stable up to 578°C; in monotonously changes its composition to $NbBr_{2.67}$ above this temperature;

4) The $NbBr_{2.67}$ phase is decomposed above 700°C.

The obtained data were used for developing a sufficiently effective technique for the synthesis of niobium bromides in lower oxidation levels. On the other hand, this study defines a series of problems which have to be solved. The most important of them are connected with the exact chemical composition of gaseous and solid products of disproportionation of lower niobium bromides with a bromine content index lower than 2.67.

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