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THE STRONTIUM-STRONTIUM HYDRIDE PHASE SYSTEM

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Abstract

The Sr-SrH₂ phase diagram was studied by thermal analysis, chemical analysis of equilibrated phases and X-ray diffraction. The maximum solubility of SrH₂ in strontium metal is 38 mole % at the peritectic temperature of 880°C. Strontium metal undergoes an allotropic transformation at 555°C and melts at 768°C. A second transformation was found, at about 240°C, in samples containing hydrogen. Strontium hydride was found to have an allotropic transformation at 855°C.

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Introduction

The strontium-hydrogen system has not been investigated very extensively. Strontium was shown by Zintl and Harder² to form SrH₂ which is a saltlike hydride with an orthorhombic lattice and a structure which has a slightly distorted hexagonal closest packing of the metal atoms. The enthalpy of formation of strontium hydride has been reported by Guntz and Benoit³ to be 42.2 kcal./mole. Strontium metal

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has been reported to exist in three allotropic forms. The stable phase at room temperature is face centered cubic. Sheldon and King,⁴ Hirst, et al.⁵ and Schottmiller⁶ report that at about 215°C the face centered cubic phase transforms to a hexagonal closest packed phase and that this phase transforms at about 605°C to a body centered cubic phase which is stable to the melting point. These results were obtained by high temperature X-ray diffraction investigation of finely divided strontium metal. Rinck reported a phase transition at 540°C on the basis of thermal arrests in cooling curves and a transition at 235°C on the basis of slight changes in the electrical resistance and thermal expansion coefficients.

In view of the pronounced effect of hydrogen on the phase transitions of calcium metal reported by Peterson and Fattore⁷ and the large solubility of hydrogen in barium metal reported by Peterson and Indig,⁸ this investigation of the strontium-strontium hydride system was undertaken. Thermal analysis and analysis of equilibrated phases were used to establish the phase relationships and X-ray diffraction was used to a limited extent to confirm the results.

Experimental Procedures

Materials. — Strontium metal obtained from King Laboratories, Syracuse, New York, was purified by distillation at 825°C under 8 mm. argon pressure. Semiquantitative spectrochemical analysis indicated the principal metallic impurities as: less than 1000 ppm barium, less than 1000 ppm calcium, less than 500 ppm magnesium. A typical chemical analysis showed 60 ppm N₂, 200 ppm C, 15 ppm Fe, 50 ppm Mn, 20 ppm Ni, and 10 ppm Cr. The average hydrogen content of the material was 350 ppm of hydrogen or 1.5 mole % SrH₂ as determined

by a vacuum fusion. In order to obtain strontium with a lower hydrogen content, a quantity of the distilled material was placed in a sealed tantalum capsule and held under dynamic vacuum at 800°C for 48 hours. This procedure reduced the hydrogen content to 0.4 mole % strontium hydride. The oxygen content was not determined due to the lack of a suitable analytical method. The strontium metal was handled in a glove box under a helium atmosphere reported to be 99.99 % pure.

Differential Thermal Analysis. — Thermal analysis capsules 6 cm. long and 2 cm. in diameter were made from type 304 stainless steel. The capsules had a 1.5 mm. wall thickness. A thermocouple well was welded into the base of the capsule. The chromel-alumel thermocouples used in this investigation were periodically calibrated at the melting points of a National Bureau of Standards aluminum sample and a sample of electrolytic silver. The thermal analysis samples were prepared by weighing out approximately 10 gm. of the metal in a helium-filled glove box into a partially closed thermal analysis capsule. The capsule was placed in a quartz tube which was closed at one end and sealed with Apiezon W wax to a stopper with a stopcock at the other end. This closed tube was transferred from the dry box to the hydrogen charging apparatus which was then evacuated and closed off. In this apparatus, the sample was heated to 450°C and allowed to react with a measured quantity of hydrogen. Very pure hydrogen was obtained from the thermal disassociation of uranium hydride. Following the charging of the sample to a known hydride composition, the capsule was welded shut and the sealed capsules were transferred to the differential thermal analysis apparatus. The loss of hydrogen by diffusion through the capsule walls during thermal

analysis was measured by observing the pressure in the closed thermal analysis apparatus. This loss was found to be negligible in all cases. A differential thermocouple located in an empty stainless steel capsule immediately above the sample was used to give greater sensitivity in observing the thermal arrests. Even at heating and cooling rates up to 10°C per min., excellent agreement between the temperatures of thermal arrests upon heating and cooling was obtained.

Isothermal Equilibration. — The distilled strontium was cast into rods and machined to specimens 3 cm. long and 1.25 cm. in diameter in a glove box. These rods were heated to the desired temperature and allowed to react with hydrogen to form a coating of strontium hydride. The specimens equilibrated below 450°C were first heated to 600°C under vacuum and cooled to the desired temperature before adding hydrogen. This was done to destroy a layer of surface contamination, probably strontium hydroxide as indicated by the work of Svec and Staley,⁹ which prevented reaction of the metal with hydrogen below 450°C. Enough hydrogen was added so that at equilibrium the core of the rod was saturated and completely covered by the hydride phase. The samples were held at the temperature of interest until equilibrium was reached. Then the two phases were separated and the hydrogen content determined by the vacuum fusion technique described by Peterson and Fattore.⁹

X-ray Diffraction. — This method was used in the temperature range from 25 to 400°C where only limited data were available from the isothermal equilibration and differential thermal analysis investigations. The differential thermal analysis data did not show a thermal arrest in this temperature range although several authors using X-ray powder

methods have reported a transformation in pure strontium metal in the temperature range from 213 to 235°C.^{6, 4, 5, 11} Diffraction of an X-ray beam incident at a small angle to the surface of a solid sample was used in this investigation in preference to the more conventional powder sample methods because of the possibility of serious contamination of the sample in the latter method. The massive sample was placed in a Vycor tube which had a thin hemispherical Vycor window at the end. The sample was positioned so that a collimated X-ray beam penetrated the window and impinged on the sample surface at a small angle. The diffraction patterns were recorded on a flat photographic plate. Experimental difficulties made accurate measurement of the diffraction angles impossible, but changes in the patterns corresponding to the reported f. c. c. to h. c. p. transition could be clearly recognized. The samples were loaded into the Vycor tube in a helium-filled glove box. After removal from the dry box, the tube was evacuated for the remainder of the experiment. Electrical resistance windings around the Vycor tube allowed the sample to be heated up to 400°C. The sample temperature was measured by a thermocouple inserted in a hole in the specimen and located approximately one mm. beneath the diffracting surface.

Results

The strontium-strontium hydride phase diagram is shown in Fig. 1. This system is quite similar to the calcium-calcium hydride system and the barium-barium hydride system. A sample containing 0.4 mole % strontium hydride had a melting point of 768°C which is in good agreement with the current values reported for pure strontium in the literature. Schottmiller⁶ reported the melting point to be 774°C, Hirst, et al.⁵

reported 768°C and Rinck¹¹ reported 770°C. The correction for the increased melting point of this sample based on the 0.4 mole % strontium hydride content and the slope of the melting temperature vs. composition curve would be only 1.1°C and this is less than the probable error in the melting point measurement. With increasing hydrogen content the melting point of metallic strontium slowly increased to a peritectic at 880°C where the maximum solubility of strontium hydride in solid strontium metal was 38 mole %.

An allotropic transformation at 557° was indicated by a thermal arrest on heating in the 0.4 mole % strontium sample. The correction for the residual hydrogen content of this specimen would give a transformation temperature of 555°. The thermal arrest of the slowest cooling rates was found at 540° which is in excellent agreement with the transformation temperature reported by Rinck on the basis of cooling curves. The temperature of the allotropic transformation increased with increasing hydrogen content until a peritectoid was reached at 620°C with a maximum solubility of 14 mole % strontium hydride in the lower temperature metal phase. This peritectoid temperature is very close to the temperature reported by Schottmiller,⁶ Hirst, et al.,⁵ Sheldon, et al.⁴ for the allotropic transformation of h. c. p. strontium to b. c. c. strontium.

Differential thermal analysis also revealed a thermal arrest at 855°C in samples containing more than 38 mole % strontium hydride. This thermal effect was attributed to an allotropic transformation in strontium hydride. This interpretation was supported by the increasing intensity of this thermal arrest, relative to the thermal arrest at the peritectic temperature, with increasing hydrogen content. Similar allotropic transformations occur in barium hydride at 600°C⁸ and calcium hydride

at 780°C.⁷ The melting point of strontium hydride was not determined because of the high dissociation pressure of this material above 1000°C.

The solubility of strontium hydride in solid strontium metal at various temperatures was determined by isothermal equilibration studies. This was done to confirm the interpretation of the thermal analysis data and to provide data on the solubility of strontium hydride in the lower temperature phases of strontium metal where no thermal analysis data were obtained. Excellent agreement between solubilities indicated by the thermal analysis data and the isothermal equilibration data was obtained in those regions of the system where both methods could be employed. This study was also useful in giving the composition of the hydride phase. The hydride phase had almost exactly the composition SrH_2 when equilibrated with strontium metal at temperatures below 500°C. At higher temperatures, analysis of the hydride phase showed a slightly lower hydrogen content. The data for the solubility limit of strontium hydride in the lower temperature metal phases gave a smooth curve from 12.8 mole % strontium hydride at 597°C to 2.45 mole % strontium hydride at 212°C.

A plot of the maximum solubility of strontium hydride in strontium metal vs. the reciprocal of the absolute temperature is shown in Fig. 2. An abrupt change in slope was found to occur in the region of the γ to β transformation temperature. The data for the solubility of a strontium hydride in β strontium metal indicate an enthalpy of solution of +10,600 calories per mole of strontium hydride. The data for the solubility of a strontium hydride in the γ phase indicate an enthalpy of solution of +3,400 calories per mole of strontium hydride. No evidence was obtained

from either thermal analysis or solid solubility of the phase change reported at about 215°C. Two samples were studied by X-ray diffraction from room temperature up to 286°C. The first sample contained 3.27 mole % strontium hydride, which is above the solid solubility limit in this temperature range. A reversible crystallographic transformation was observed between 236 and 244°C in this specimen. The second sample contained 0.40 mole % strontium hydride. This sample was examined from room temperature to 286°C, the highest temperature that could be obtained with the present apparatus, and no crystallographic transformation was observed.

Discussion

The question of the allotropy of strontium has not been completely clarified by this investigation. The transition to the b. c. c. structure in pure strontium at about 555°C is quite well established by the concordance of the results of this investigation and those of Rinck. The raising of this transformation by hydrogen in solution to a peritectoid at about 620° would explain the transformation reported at about 605° if the powdered X-ray specimens contained hydrogen as an impurity. The lower transition is not well established, although it certainly occurs at about 215 to 235° in specimens containing sufficient hydrogen, and additional investigations with very low hydrogen content strontium should be made.

As in the barium-barium hydride system and the calcium-calcium hydride system, hydrogen has a greater solubility in the solid metal phase than in the liquid phase and increasing the concentration of hydrogen increases the melting temperatures of these metals. Also characteristic

of the calcium-calcium hydride, strontium-strontium hydride and barium-barium hydride system is the extensive endothermic solubility of the hydride in the metal phase. The maximum solubility increases from calcium to strontium to barium respectively. Thus it is seen that the position of strontium between calcium and barium in the alkaline earth family of metals is clearly reflected in the character of its metal-hydride phase system.

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Figure Captions

Fig. 1. The strontium-strontium hydride phase system.

Fig. 2. Solubility of SrH_2 in strontium vs. reciprocal temperature.

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Fig. 2. Solubility of SrH_2 in strontium vs. reciprocal temperature.

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