Thermodynamics of the Solid Ni-S System

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Published measurements of sulfur vapor pressure were used to determine thermodynamic properties of the solid Ni-S system above 800 K. They were Gibbs–Duhem integrated to estimate the formation properties of stoichiometric Ni$_3$S$_2$, NiS, and NiS$_2$. Statistical thermodynamics was applied to find partition functions, interaction energies, and free energies to find possible atom arrangements in Ni$_{1-x}$S$_2$ and Ni$_{1-x}$S$_2$. Theoretical calculations indicated that nickel vacancies may exist in quasi-chemical order in the former phase and randomly in the latter phase. A strong indication was that Ni$_{1-x}$S$_2$ should have a sulfur bcc structure with nickel atoms distributed in octahedral sites having a Ni$_3$S$_4$ configuration. The possible existence of sulfur vacancies was theoretically investigated.

I. INTRODUCTION

There are three nickel sulfides (Ni$_{3-x}$S$_2$, Ni$_{1-x}$S, and NiS$_2$) known to exist above 800 K. The compositional range of nonstoichiometry is relatively wide in Ni$_{3-x}$S$_2$ and Ni$_{1-x}$S. As for the former phase, Lin et al. measured the chemical potential of sulfur, concluding that two phases should exist. Yagi and Wagner supported such a phase separation by measuring the chemical diffusivity and electrical conductivity besides the chemical potential. Stølen et al. measured the heat capacity of the low- and high-temperature phases of Ni$_3$S$_2$, giving no definite conclusion about the existence of two phases. Fjellvåg and Andersen conducted numerous high-temperature diffraction experiments to determine the lattice constant of Ni$_{1-x}$S$_2$ between $x = -0.4$ to $+0.4$ in a temperature range from 800 to 1100 K. They confirmed no possible indication of phase separation. Cemic and Kleppa made a calorimetric study of low-temperature Ni$_3$S$_2$, low-temperature NiS, high-temperature NiS, and NiS$_2$ to estimate the formation heats, which were close to those calculated from the equilibrium sulfur pressure measurements by Lin et al., Rosenqvist, Rosenqvist, and Rau. Schifflman and Miller applied the Knudsen effusion technique to calculate the S vapor pressure and the heat of formation for the three phases, which differed substantially from the preceding measurements and calculations. The primary objective of the present work is to find how atoms should be arranged and how vacancies should be distributed in high-temperature compounds of Ni$_{3-x}$S$_2$ and Ni$_{1-x}$S by applying statistical thermodynamics to published chemical potential measurements. This was possible owing to the strong dependence of thermodynamic properties on the crystallographic arrangement of atoms.

II. THERMODYNAMIC ACTIVITY OF Ni AND ENTHALPY OF FORMATION OF Ni$_3$S$_2$

Figure 1 shows a phase diagram of the Ni-S system between $X_S = 0.3$ and 0.7 in a temperature range from 473 to 1333 K. It is a part of the diagram given by Okamoto, except that the regions of $\beta$ (or high-$T$ Ni$_3$S$_2$) and Ni$_{1-x}$S$_2$ agree in shape with those by Kullerud and Yund and except that the transition temperatures are in accordance with those given by Rau. The two broken lines in the $\beta$ phase were originally suggested as phase separation by Lin et al. In the embedded figure as an enlarged view of a lower portion of the $\beta$ phase, the shaded area represents a path of Gibbs–Duhem integration to calculate the activity of Ni at three temperatures. To integrate the measured activity of S, we need to know the activity of Ni at one or more points of composition. In the Ni-S system, the only known value exists as the definition of one for pure Ni. Rau measured the equilibrium pressure of disulfide gas through the entire region of Ni$_{3-x}$S$_2$. According to the phase diagram of Figure 1, the temperature range of his measurements between 853 and 907 K is suitable for such integration. Beyond the compositional range of high-$T$ Ni$_3$S$_2$, He measured the S activity in the Ni$_{1-x}$S phase above 914 K. Thus, in the latter phase, we need theoretical extrapolation to lower temperatures for the purpose of such integration, as will be described later.

The Gibbs–Duhem relation under constant temperature and total pressure may be rearranged to yield

$$\ln a_{Ni} = -f_{S_2} X_S d \ln f_{S_2} \quad \frac{1}{2(1 - X_S)}$$

where $X_S$ is the mole fraction of S, $a_{Ni}$ is the thermodynamic activity of Ni, and $f_{S_2}$ is the fugacity of diatomic gas, $S_2$. Rau’s measured pressure for Ni$_{3-x}$S$_2$ was below 10 atm and is considered to equal the fugacity, while he directly gave the fugacity for Ni$_{1-x}$S. No measured solubility of S in Ni exceeded 480 wt ppm (equivalent to $X_S = 9 \times 10^{-5}$), which is virtually null. Thus, the integration may start at the Ni-coexistent composition of the Ni$_{3-x}$S$_2$ phase by setting $a_{Ni} = 1$ there in Eq. [1]. The standard free energy of formation of the binary Ni-S system at the absolute temperature $T$ is defined and modified via Eq. [1] to

$$\Delta_G^o = RT \left\{ (X_S/2) \ln f_{S_2} + X_{Ni} \ln a_{Ni} \right\}$$

$$= RT \left\{ (X_S/2) \ln f_{S_2} - (1 - X_S) \int_0^{f_{S_2}} \frac{X_S d \ln f_{S_2}}{2(1 - X_S)} \right\}$$

where $R$ is the gas constant. The standard state pressure here is set at 1 atm, which is slightly different from the definition ($= 0.1$ MPa $= 0.9872$ atm) in the NIST-JANAF.

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Manuscript submitted December 9, 2005.
and high Ni$_3$S$_2$ are thermodynamically more stable below 882.117 K, at which S$_2$ exerts 1 bar (=0.9869 atm) as a gas component, the standard state of S is liquid. Broken lines and the specific volume is not affected by the number of Ni vacancies. (4) The term $E$ consists of interaction energies between nearest neighboring atoms, $e_{NiS}$, $e_{NiNi}$, and $e_{NiS}$, where $(i)$ stands for the $i$th nearest neighbor. (5) The interaction energies are independent of temperature and composition.

A. Atom Arrangement as Ni$_{5+x}$S$_4$ and Quasi-Chemical Equilibrium in High-Temperature Ni$_3$S$_2$

Kullerud and Yund$^{[1]}$ reported that high-$T$ Ni$_3$S$_2$ (Ni$_{3+z}$S$_2$) is nonquenchable. This strongly indicates that its crystal structure should be different but closely related to that of low-temperature Ni$_3$S$_2$. The latter phase, called heazlewoodite, is known as a rhombohedral phase belonging to the space group $R32$.$^{[15,16]}$ Stoklosa and Stringer$^{[17]}$ proposed that the high-$T$ phase should be defected in both anion and cation sublattices, which seems questionable because they used quenched samples. Fjellvåg and Andersen$^{[11]}$ explained that S atoms in the low-$T$ phase build a nearly bcc arrangement, of which a subset of tetrahedral holes is occupied by Ni atoms. They also conducted a high-temperature X-ray diffraction study to find that the high-$T$ phase is cubic with Ni atoms not in fcc arrangement. From the preceding facts, we may conclude that the high-$T$ phase must have S atoms in bcc arrangement and Ni atoms in octahedral holes (rather than tetrahedral holes) with no fcc arrangement. Although no researcher mentioned such bcc arrangement of S atoms, the following thermodynamic analysis will confirm the preceding proposed conclusion.

Figure 3 shows Rau’s measurements of $P_{S_2}$ (equated to $f_{S_2}$) over Ni$_{5+z}$S$_4$ at temperatures of 853, 907, 949, 992, and 1044 K.$^{[11]}$ Other studies$^{[4,5]}$ gave $P_{H_2S}/P_{H_2}$ ratios, which were here converted to $P_{S_2}$ via the JANAF Tables$^{[14]}$ by noting the change in standard state at 882.117 K, where liquid S exerts 1 bar of $P_{S_2}$. An inflection point exists between the mole fractions $X_S = 0.41$ and 0.42 below 992 K. This phenomenon has been confirmed in other studies.$^{[4,5]}$ It strongly indicates that a base phase should exist above this point, particularly beyond the range of measurements. This is because the preceding inflection is for an