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Experimental studies on $NiSO_4$ by thermal analysis and calorimetry

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ABSTRACT

This work includes very new experimental studies on pure $NiSO_4$ with Differential Thermal Analysis (DTA), simultaneous Thermo Gravimetry (TG), and Dynamic Scanning Calorimetry (DSC). Literature only describes the decomposition of $NiSO_4$, and all related multi-nary phase diagrams with nickel sulfate as a compound show a lack in data in the $NiSO_4$-rich region. Indeed, our experiments demonstrate that $NiSO_4$ is stable in equilibrium state and melts at 1483 ± 3 K with an enthalpy of melting of, $\Delta_{fus}H_{1483\ K} = 44 \pm 2$ kJ mol^{-1}. Prior to this, it undergoes a never before observed structure change at 1243 ± 3 K (nominated as 'dkostruct') with the transformation energy $\Delta_{tr}H_{1243\ K} = 3.9 \pm 0.2$ kJ mol^{-1}. The change from this high to low temperature structure (orthorhombic) is probably connected with a volume expansion. The standard heat capacity $C^0_{p\ (298\ K)} = 93 \pm 7$ J mol^{-1} K^{-1}, and from the polynomial for $C^0_{p\ (T)}$, derived quantities for the enthalpy increment and the entropy could be deduced for the temperature range from 298 to 950 K. From empirical analysis the heat of formation for $NiSO_4$(c) is $\Delta_f H_{298\ K} = -880 \pm 10$ kJ mol^{-1}.

1. Introduction

Economic and environmental considerations require an increase of the efficiency of coal-fired power plants. Coal-fired steam power plants can achieve efficiencies in excess of 50% by increasing the steam parameters to 700–750 °C and 350 bar. These conditions require nickel-base alloys with long term creep rupture strength and low oxidation rate, which are therefore already in use in gas turbines with gas temperatures beyond 1200 °C.

Hot corrosion on nickel-base alloys is initiated by the deposition or the condensation of corrosive species like alkali sulfates and dependent on the concentration of alkalis in the hot flue gas. $NiSO_4$ itself is formed by the reaction of the oxide scale of Ni-base alloys with SO_3, and its stability is dependent on the SO_3 partial pressure in the hot flue gas. $NiSO_4$ and alkali sulfates form low melting eutectics causing severe corrosion.

The motivation to study nickel sulfate is the controversial information about the substance in the literature [1–29]. Most of the studies are related to $NiSO_4$ hydrates and only a few of them were dedicated to the anhydrous form [6,14,15,18,21–25]. Measurements of all authors result in a decomposition although the compound could be stable at high temperature as depicted by Roslik et al. [6], Ingraham [21], Rapp [25]. All phase diagrams with nickel sulfate as one of the compounds have a data gap in the $NiSO_4$ rich part [1,4,13] that makes it difficult to understand the aforementioned alkali sulfate related processes under applied conditions and accrued phases.

This work includes the experimental studies of $NiSO_4$(c) with Differential Thermal Analysis (DTA) coupled with simultaneous Thermo Gravimetry (TG) to determine transition temperatures and enthalpy of fusion. From the polynomial function of the heat capacity $C^0_{p(T)}$ measurements with the Dynamic Scanning Calorimeter (DSC), the enthalpy H^0_T and the entropy S^0_T could be deduced.

2. Experimental

The thermo-analytical studies on $NiSO_4$(c) have been carried out at Forschungszentrum Jülich, GmbH by means of three complementary methods, that were Differential Thermal Analysis (DTA) simultaneously coupled with Thermo Gravimetry (TG) to deduce enthalpies and transition temperatures, and for the heat capacity measurements, the Dynamic Scanning Calorimetry (DSC).

2.1. Differential Thermal Analysis and Gravimetry (DTA/TG)

Anhydrous pure $NiSO_4$ (nominal purity 99.99 mass%, Sigma-Aldrich, Saint Louis, USA) was first measured in open Al_2O_3, quartz, and platinum crucibles. The stability of sulfate systems is sensitive to variation in the equilibrium state. Since the pressure equilibrium constant is dependent on the partial pressures of SO_2 and O_2, a change in partial pressures can force a decomposition process. To accomplish an equilibrium state, the quartz (Fig. 1)

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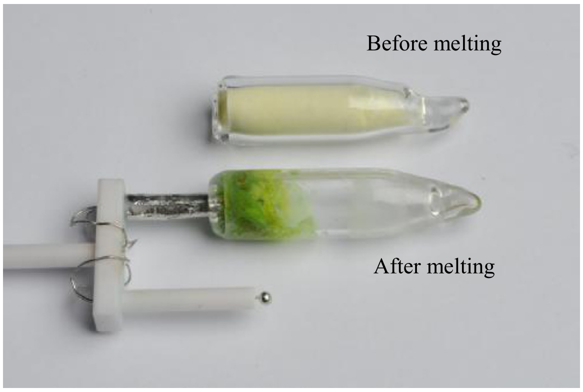

Fig. 1. $NiSO_4$ in DTA quartz crucible before and after melting.

and platinum crucible were sealed in a hydrogen/oxygen flame. The quartz container had a valve adapter to evacuate the system down to 100 Pa. Traces of possible moisture were removed by heating the sample up to 500 °C before sealing the crucible. The platinum crucible was squeezed at the end after filling the sample under dry argon in a glove box and then welded outside the box in a flame.

The hygroscopic nature of nickel sulfate [3] requires a process of preparation and handling in a glove-box under Argon. For a sufficient sample to crucible mass ratio, about 300–400 mg $NiSO_4$ were prepared in the container. Studies by the high temperature Simultaneous Thermal Analyzer (STA 429, Netzsch, Selb, Germany) method followed well defined temperature programs with a standard rate of 5 K/min. Different heating and cooling rates of both, 2 and 10 K/min supported the analysis of super-cooling behavior and the scrutiny of DTA response. Simultaneously, a balance recorded the mass and allowed to find out the beginning of possible weight loss due to decomposition.

The characteristic inception temperatures of the DTA curves, representing phase transitions, were evaluated by the determination of the intersection of the extrapolated baseline and the tangent at the point of greatest slope on the leading edge of the peak (onset determination).

Transition temperatures were measured with a thermocouple type S (Pt/(Pt 10%Rh)). An easy way to calibrate the thermocouple is done with certified reference samples and their transition temperatures. The calibration runs with SiO_2 (571 °C, $\alpha \rightarrow \beta$-quartz), Ag (961 °C, M.P.) and Au (1064 °C, M.P.) under the same condition like the studies on $NiSO_4$ yielded within an estimated accuracy of the observed thermal effects of ± 3 K.

The ambiance during the measurements in open cells was dynamic with 100 ml/min in both, argon and dry air. In terms of contrastable results, the dynamic flow rate was the same also on the studies with a sealed crucible.

2.2. Dynamic Scanning Calorimetry (DSC)

The heat capacity ($C^0_{p(T)}$) determination was conducted in the same lab as the studies with DTA/TG with a commercially available instrument Netzsch GmbH, Selb/Bavaria of type DSC 404C and a special sample holder purpose-built for $C^0_{p(T)}$.

Regarding the thermal analysis, DTA and DSC measurements are quite similar. The difference of the temperature ΔT between the reference and sample side of the sample holder is recorded in DTA versus the time t or the temperature T, ($\partial H \propto \Delta T/\partial t$ or $\Delta T/\partial T$) to find transition temperatures and enthalpies in one run and with heating/cooling rates close to the equilibrium temperature (<5 K/min).

In DSC (commonly called ‘differential scanning calorimetry’) the heat-flux $\dot{Q}$ is dynamically calculated by integration of the difference ($\Delta T - T_{\text{ref}}$) versus the time t, ($\dot{Q} = \int (\Delta T - T_{\text{ref}})\,dt$). For heating/cooling rates close to the equilibrium temperature, the differential scanning calorimetry is similar to DTA. In contrast to this, a heating rate of 20 K/min is standard for the determination of $C^0_{p(T)}$ and this rate is far from the equilibrium temperature. To distinguish between the two modes on DSC, we want to name the method to determine the heat capacity ‘dynamic scanning calorimetry’, which is used in this article.

The determination of the heat capacity requires a base line-, a reference-, and a sample-experiment under identical measurement conditions. Hence, the heat dissipation of both, the empty crucible and the sample holder set-up, was determined as the base-line background $DSC_{\text{bgr}(T)}$. Since this background was also part in the reference and the sample measurement, respectively, it had to be subtracted from those. As the reference, we have used a sapphire sample with a comparable mass like that of nickel sulfate. With the known heat capacity of sapphire (reference), $C^0_{p(T)}$ (ref), the following equation (Eq. (1) was used to calculate the heat capacity $C^0_{p(T)}$ (sam) of the sample.

$$C^0_{p\,(T)}\ (\text{sam}) = \frac{m_{\text{ref}}}{m_{\text{sam}}} \frac{(DSC_{\text{sam}} - DSC_{\text{bgr}})_{(T)}}{(DSC_{\text{ref}} - DSC_{\text{bgr}})_{(T)}} C^0_{p(T)}\ (\text{ref}) \tag{1}$$

where m is the mass, ref is the reference, sam is the sample, and bgr is the base (background).

Three samples with five runs on each were carried out, and the last two were selected for the $C^0_{p(T)}$ determination. Since the DSC measurements had to be executed under open system conditions, the highest temperature did not exceed 950 K to avoid sample mass loss.

3. Results and discussion

3.1. DTA and TG

The aim in the first package of the studies was to analyze the behavior of $NiSO_4$ under free vaporization conditions in open crucibles. $NiSO_4$ decomposes stoichiometrically in all cases, but at different temperatures, following Eq. (2).

$$NiSO_4(c) \leftrightarrow NiO(s) + SO_2(g) + \frac{1}{2}O_2(g) \tag{2}$$

The equilibrium constant of Eq. (2) only depends on the partial pressures of SO_2 and O_2.

$$K_{\text{p}} = p(SO_2) \times \sqrt{p(O_2)} \tag{3}$$

The highest measured decomposition temperature was at 890 °C. Different temperatures of destruction provide evidence of an occasional interference and not of a singular decomposition point. Stochastic events triggered by impurities, seed crystals, catalytic reactions and so on, might initiate a disturbance of the metastable state of the open system that conducts the decomposition of $NiSO_4$. Once the reaction started, the loss of non-condensable gases and with it the change in the equilibrium constant (Eq. (3)), continues the decomposition process.

Equilibrium measurements are only possible in a closed system. However, tests with sealed platinum tubes with $NiSO_4$ showed unanticipated weight loss at temperatures about 900 °C, although there was no leak found after cooling down. The reason for this is a permeability of platinum for SO_3 at high temperature and high pressure. A decomposition of nickel sulfate in this permeable ‘open’ system started at ~900 °C and could not be avoided, even with thicker crucible walls.