Journal of Thermal Analysis, Vol.40 (1993) 1165-1172

THERMOANALYTICAL AND MICROSCOPIC INVESTIGATIONS OF THE THERMAL DEHYDRATION OF α-NICKEL(II) SULPHATE HEXAHYDRATE

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Thermoanalytical (TA) and hot-stage microscopic techniques were employed to investigate the complicated behaviour of the non-isothermal dehydration of single crystals of α-$NiSO_4 \cdot 6H_2O$. Non-isothermal dehydration to the tetrahydrate proceeds in two stages: (1) surface nucleation and growth of nuclei, followed by advancement of reaction fronts inward; (2) random nucleation and growth near the reaction front as well as in the bulk. Corresponding TA curves were interpreted to represent diffusional removal of evolved water vapour through the surface layer created in stage (1). The dehydration process of the tetrahydrate to the monohydrate is explained on the basis of textural structures produced in the previous step. Crack formation in the surface layer and rapid escape of the water vapour were observed in this step.

Keywords: α-$NiSO_4 \cdot 6H_2O$, hot stage microscopic techniques, polyhydrated crystals, single crystal, TG-DTG, TG-DSC, TG-DTA

Introduction

The thermal dehydration process of the title compound has been one of the targets of thermoanalytical (TA) studies [1–3], in common with other polyhydrated crystals such as $CuSO_4 \cdot 5H_2O$. Earlier thermal dehydration studies of crushed crystals of α-$NiSO_4 \cdot 6H_2O$ revealed that the reaction proceeds via the tetrahydrate and monohydrate to the anhydrate [2, 3], which was confirmed by X-ray diffractometry [3, 4]. Recently, TA studies complemented by optical microscopy were performed by Guarini *et al.* for the cleaved single crystals of α-$NiSO_4 \cdot 6H_2O$ [5, 6]. Observation of the (001) crystallographic surface during the reaction revealed the existence of a fluid phase. The critical role of the surface product layer on the subsequent reaction process was shown by this investigation. Later, a photo-acoustic technique was employed to prove the existence of the surface layer [7].

Such microscopic studies are of great importance for confirming interpretation of the corresponding TA curves [8, 9]. Knowledge of the reaction morphol-

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ogy and/or geometry observed microscopically provides a basis for development of interpretative models for reactions of the type: solid→solid+gas [10, 11]. Such observations may be extended to more detailed microscopic studies [12, 13] and other physicochemical studies concerning reactivity [14, 15], kinetics [9, 13, 16, 17] and crystallographic structure [18]. In the present study, examination of original and internal surfaces during dehydration of single crystals of α-$NiSO_4{\cdot}6H_2O$ were performed and thin section using hot-stage techniques [9, 16, 17, 19, 20]. TA curves for the dehydration process are explained on the basis of the above findings.

Experimental

Single crystals of α-$NiSO_4{\cdot}6H_2O$ were grown from a supersaturated aqueous solution by slow evaporation at ambient temperature. About 25 mg of the well-developed single crystals were stored for TA and microscopic investigations. Samples were identified by the X-ray diffraction, IR spectroscopy and TG.

Single crystals of ca. 25.0 mg were examined by simultaneous TG-DTG, TG-DSC and/or TG-DTA. TA curves were obtained on Shimadzu TGA-50 and Rigaku Thermoflex(8085E1) instruments at various heating rates, Φ, under N_2 at various flow rates. Ignited Al_2O_3 was used as the reference material in the runs complemented by DSC and DTA.

Changes in typical surfaces during linear heating from room temperature to 500°C were observed and photographed, using a reflectance microscope with a programmable hot stage (Linkam TH600). Heating rate and controlled atmosphere were compatible with those used for TA measurements. The temperature distribution in the hot stage was estimated to be within ±5° at 250°C.

Thin sections of single crystals dehydrated in the above TA instruments to different temperatures were prepared employing a technique described earlier [9, 16, 17, 19, 20]. The thin sections were observed microscopically and photo-graphed under polarized light.

Results and discussion

Figure 1 shows typical TG-DTG curves for non-isothermal dehydration of the single crystals at various Φ under N_2 at 30 $ml{\cdot}min^{-1}$. A complicated reaction behaviour of the dehydration processes from the hexahydrate to the monohydrate via the tetrahydrate would be expected from Fig. 1. For dehydration of the monohydrate, two separate DTG peaks are observed at lower Φ, whereas a single peak appears at $\Phi = 10$ $deg{\cdot}min^{-1}$. Typical simultaneous TG-DSC curves are shown in Fig. 2. DSC endotherms correspond in complexity to the TG-DTG curves.

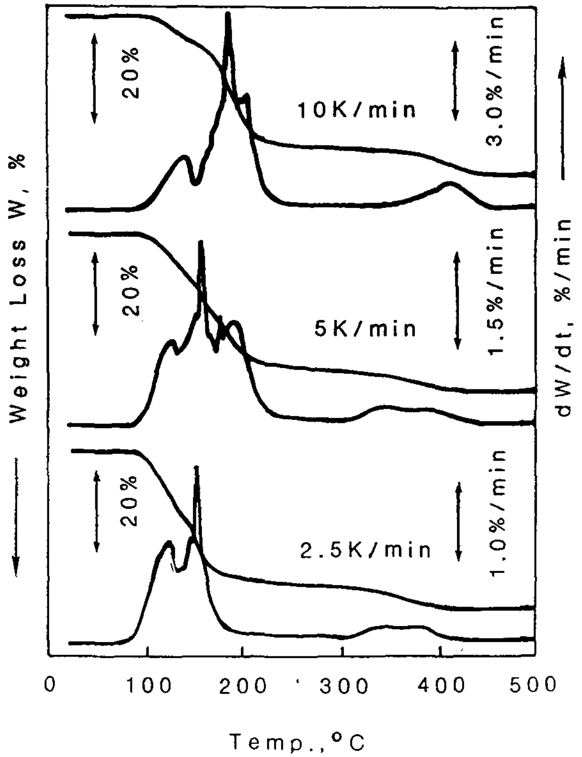

Fig. 1 Typical TG and DTG curves for non-isothermal dehydration of single crystals of α-$NiSO_4 \cdot 6H_2O$ at different heating rates under nitrogen flowing at 30 ml·min^{-1}

Figure 3 shows microscopic views of the nucleation and growth processes on the (001) original surface during linear heating under N_2 at 30 ml·min^{-1}. The surface was almost covered with the product layer of the tetrahydrate at about 90°C at $\Phi = 5.0$ deg·min^{-1}. This implies that the reaction begins with rapid nucleation and growth on the surface, yielding a product surface layer termed 'orange peel [5]'. Polarizing microscopic views of a (001) internal surface of the partially dehydrated crystal are shown in Fig. 4. It is evident that the early dehydration stage of the hexahydrate to the tetrahydrate proceeds through advancement of reaction front into the crystal (Fig. 4(a)). The reaction front is not uniformly flat, as has been observed for several dehydration reactions of other salt hydrates [9, 16, 17, 19, 20]. This suggests that there is a possibility of applying a 'fractal-like' description to physico-geometrical models of the advance of the reaction front [21–23]. Another important finding is related to the existence of a strain zone of appreciable thickness within the reactant adjacent to the reaction front [10, 11]. Recently, such a strain zone has been demonstrated based on physicochemical and/or microscopic evidence [13, 17, 23]. The reaction interface is not a single sharp reactant–product discontinuity but extends as a recognizable layer within which there is a systematic variation in lattice dimension in the direction of interface advance [24]. The existence of a strain zone is expected for the present salts because of the intricate shape of the reaction front. More detailed examination of the interphasal zone of the present reaction would be useful for formulating the dehydration mechanism.

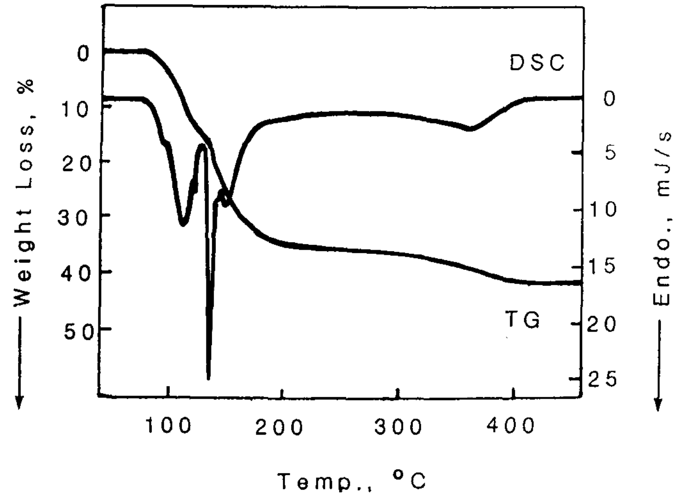

Fig. 2 Typical TG and DSC curves for non-isothermal dehydration of a single crystal of α-$NiSO_4 \cdot 6H_2O$ under nitrogen flowing at 30 ml·min^{-1} (Φ = 5.0 deg·min^{-1})

Shoulders detected in the accelerating part of the first DTG and DSC peaks (Figs 1 and 2) can be interpreted as due to 'arrest [9, 25]' of the advance (Fig. 4(b)). The thickness of the layer changes depending on heating rate and gaseous atmosphere. In the light of Figs 4(b) and (c), the subsequent process is characterized by a nucleation and growth mechanism in the bulk. More developed product crystallites are observed in the bulk than in the surface layer created during the previous stage. This may be due to a higher pressure of evolved water vapour and a slow change in pressure at reaction sites, being controlled by diffusion of water vapour through the surface layer. On the original surface, wet spots could be recognized, enabling identification of the end of possible diffusion pathways. Such diffusion appears responsible for the corresponding parts of the TG-DTG curves shown in Fig. 1.

Guarini *et al.* assumed that the surface product layer resulted from direct formation of the monohydrate at the very beginning of dehydration and not via the tetrahydrate [5–7], this being different from the subsequent reaction in the bulk. This is not in accordance with quantitative dehydration to the tetrahydrate for the crushed crystals [25]. Another interpretation of the change in dehydration mechanism is possible in relation to increase in pressure of evolved water vapour at the reaction interface, caused by 'impedance [9, 26]'. Similar behaviour was observed for the dehydration of single crystals of $K_2CuCl_4{\cdot}2H_2O$ to the anhydrate, which did not produce any hydrated intermediate. Further crystallographic and/or spectroscopic investigation of the surface product layer produced at the very beginning of the process is required.

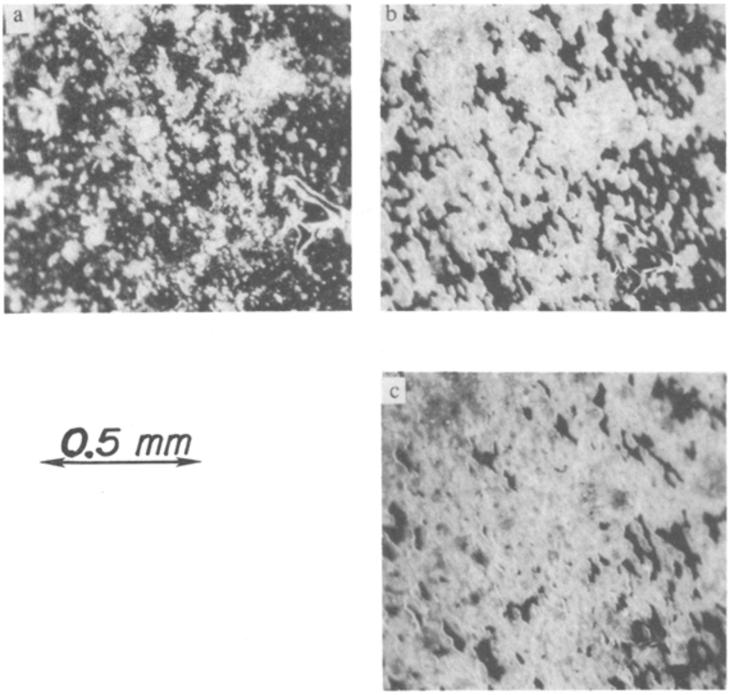

Fig. 3 Microscopic views of the original (001) surfaces of α-$NiSO_4{\cdot}6H_2O$ heated under nitrogen at 30 $ml{\cdot}min^{-1}$ to various temperatures: (a) 80°C, (b) 85°C and (c) 90°C ($\Phi = 5.0$ $deg{\cdot}min^{-1}$)

The dehydration behaviour of the tetrahydrate to the monohydrate seems to depend on the structural configuration produced in the above reaction. Grain boundaries among the crystallites as well as outer surface of the crystallite assembly would be expected to be some of the most reactive sites, which may be subjected to reaction more or less simultaneously. Water vapour diffusion through the surface layer is again important in this reaction geometry. Figure 5(a) shows microscopic views of the outer surface obtained at about 150°C, in which crack formation in the surface layer is observed. Rapid escape of water vapour through the cracks was accompanied by increase in the crack width during a certain time

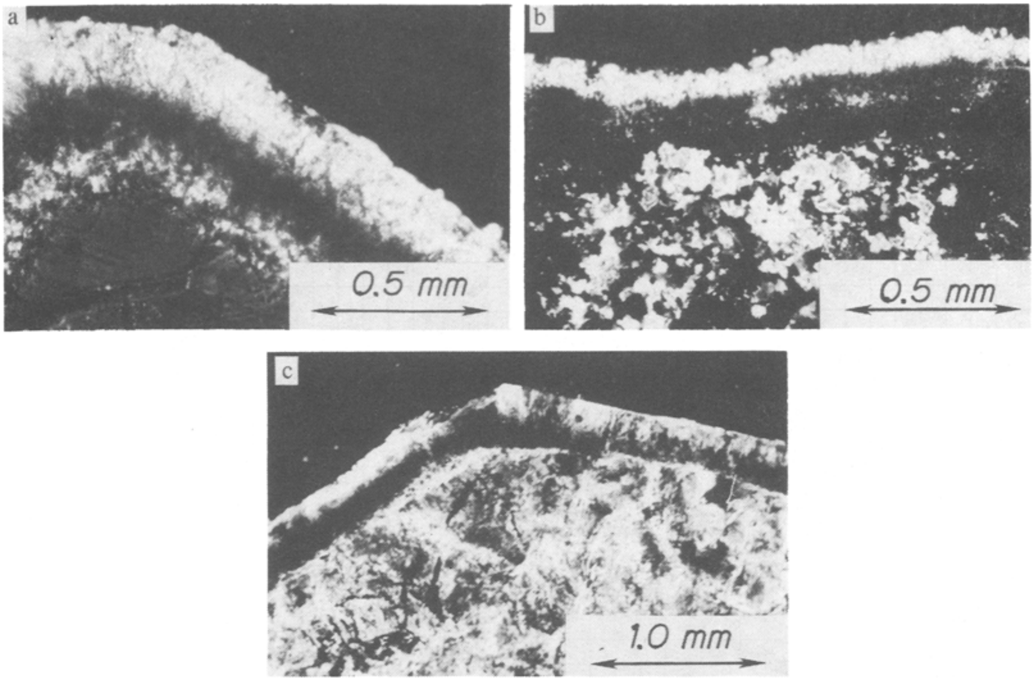

Fig. 4 Polarizing microscopic views of internal (001) surfaces of single crystals of α-$NiSO_4 \cdot 6H_2O$ dehydrated under nitrogen at 30 ml·min^{-1} to various dehydration fractions (Φ = 5.0 deg·min^{-1}): (a) 4.8 wt%-loss (-0.7H_2O), (b) 6.8 wt%-loss (-1.0H_2O) and (c) 10.3 wt%-loss (-1.5H_2O)

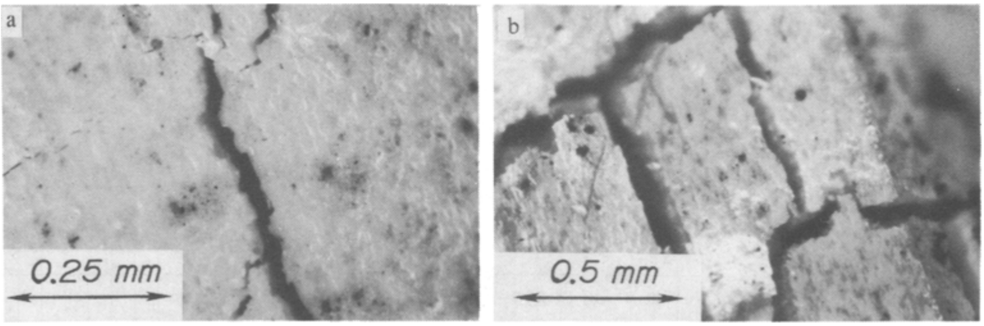

Fig. 5 Microscopic views of original (001) surfaces of α-$NiSO_4 \cdot 6H_2O$ heated under nitrogen at 30 ml·min^{-1} to temperatures: (a) 150°, (b) 300°C (Φ = 5.0 deg·min^{-1})

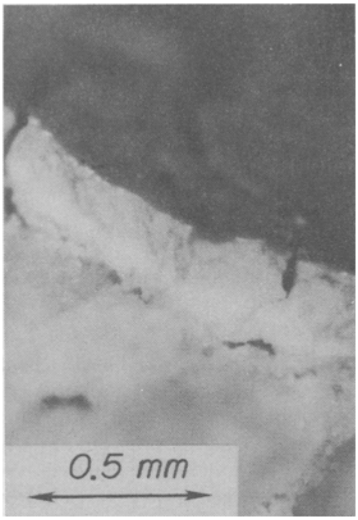

Fig. 6 Microscopic view of cross-section of the monohydrate produced

interval. The complex features on DTG and DSC peaks for dehydration of the tetrahydrate to the monohydrate correspond to water loss behaviour, termed 'bubbling [5]'. The crack system developed during reaction is shown in Fig. 5(b). The monohydrate product has the texture shown in Fig. 6. Separate DTG peaks for dehydration of the monohydrate observed at lower heating rates seem to be due to structural differences between surface layer and internal product.

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Zusammenfassung — Mittels thermoanalytischen und heiztischmikroskopischen Methoden wurde das komplizierte Verhalten der nichtisothermen Dehydratation von α-$NiSO_4 \cdot 6H_2O$-Einkristallen untersucht.Die nichtisotherme Dehydratation zu Tetrahydrat erfolgt in zwei Etappen: (1) Keimbildung an der Oberfläche und Keimwachstum, gefolgt von einer Fortsetzung der Reaktionsfront zum Inneren hin; (2) Random-Keimbildung und Wachstum in der Nähe der Reaktionsfront und im Innern. Die entsprechenden TA-Kurven zeigen ein diffusives Entfernen des freigesetzten Wasserdampfes durch die in Etappe (1) entstandenen Oberflächenschicht hindurch. Der Dehydratationsprozeß von Tetrahydrat zu Monohydrat wird auf der Grundlage der im voran- gehenden Schritt entstandenen Gefügestrukturen erklärt. In diesem Schritt wird eine Rißbildung in der Oberflächenschicht und ein schnelles Ausströmen des Wasserdampfes beobachtet.