

HOW THERMAL TREATMENT INFLUENCES THE PHASE TRANSITION OF NiMoO_4

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ABSTRACT

Thermal treatment raises the temperature of the $\alpha \rightarrow \beta$ NiMoO_4 transition and lowers the temperature of the $\beta \rightarrow \alpha$ return transition. This effect is attributed to a temperature-induced relaxation of strain.

INTRODUCTION

The main industrial application of NiMoO_4 is the preparation of Ni-Mo catalysts for hydrodesulfurization reactions. Recent studies showed that NiMoO_4 presents catalytic interest in oxidation reactions (ref. 1). Especially it was pointed out that the β phase of NiMoO_4 presents higher catalytic activity than the α phase in the oxidation of propylene to acrylic acid. Others members of the family of isostructural compounds to which NiMoO_4 belongs, CoMoO_4 and MnMoO_4 , present best catalytic behaviour in the phase which is isostructural to β - NiMoO_4 (ref. 2).

Hence the definition of the stability field of the phases of NiMoO_4 is of a practical interest. Both phases are monoclinic and mainly differ in the coordination of molybdenum, pseudo-octahedral in the β phase and tetrahedral in the α phase (ref. 3).

All literature data show the wide hysteresis loop of the transition, but the transition temperature data are widely scattered (ref. 4). This scattering is evidence of the strong influence of the conditions of the sample preparation on the transition temperature, as Saito and coworkers (ref. 5) found out about CoMoO_4 . Nevertheless the phase transitions of CoMoO_4 occur at lower temperatures than the NiMoO_4 transitions, and quenching of the β phase is possible in CoMoO_4 only (ref. 3). Hence Saito devoted his attention mainly to the study of the metastability of the β phase, while our main interest concerns the effects of high-temperature strain relaxation on the phase transitions.

METHODS

NiMoO_4 was prepared by precipitation from 0.25 aqueous solution of $\text{Ni}(\text{NO}_3)_2$ and H_2MoO_4 . By precipitation at pH 5.2 and 90°C hydrated nickel molybdate precursor with characteristic lattice pattern was formed. Small shifting from the chosen conditions brought to the co-precipitation of molybdenum poly-anions or

nickel hydroxide, strongly modifying the properties of the precipitate (ref. 6).

The precursor was submitted to the thermal analysis directly after two hours drying at 110°C, or after the required thermal treatment in air. NiMoO₄ obtained by thermal activation of the precursor was characterized by X-ray diffractometry, Raman spectroscopy, and atomic absorption spectroscopy.

Thermoanalytical tests were carried out using a Mettler TA2000C thermoanalyzer. Test conditions were: 25 mg of sample, heating rate 25 K/min, cooling rate 15 K/min, maximum temperature 800°C if not otherwise stated, air atmosphere. Tests under oxygen or nitrogen showed no significant changes compared to the tests under air.

X-ray diffraction tests were performed using Cu K α radiation and a Ni filter. The strain was evaluated using the Langford single-line method (ref. 7). The method parts the contributions of the crystallite size and strain to the X-ray diffraction line profile. The Cauchy contribution to the line width is attributed to the crystallite size, and the Gauss contribution to the strain. Both contributions can be derived from the ratio between the line width at half maximum intensity and the integral width. The crystallite-size is calculated by the Scherrer formula

$$D = \frac{\lambda}{\beta_c \cos\theta}$$

where β_c is the integral width of the Cauchy profile, purged of the contribution of a reference infinite not-distorted crystal. Strain is calculated as

$$e = \frac{\beta_g}{4 \operatorname{tg}\theta}$$

where β_g is the integral width of the Gauss profile, modified in a similar way. We used NiMoO₄ annealed one week at 550°C as reference crystal. We obtained the same line profile by heating NiMoO₄ at 750°C and we assumed that a steady state was attained. However we cannot exclude that the sample presented residual strain, hence our strain data must be considered as relaxable strain data. Strain data were calculated using the 220 reflection.

RESULTS AND DISCUSSION

$\alpha \rightarrow \beta$ transition

The endothermal DTA peak of the $\alpha \rightarrow \beta$ transition is reported in figure 1. No transition peak was detected when the thermal treatment before DTA test was carried out below 550°C, although the transition occurs, as shown by the presence of the return $\beta \rightarrow \alpha$ peak.

How the starting temperature of the peak depends on the thermal treatment of the sample is shown in table 1. Crystallite size and strain of the sample are also reported in table 1.

The transition temperature increases as the previous thermal treatment of the

TABLE 1

$\alpha \rightarrow \beta$ transition temperature and samples characterization.

Pre-treatment	T_b (°C)	D (Å)	$e \cdot 10^3$
1) 2hrs 480°C	-	288	2.9
2) 30min 550°C	572	616	2.3
3) 2hrs 550°C	588	657	1.7
4) 30min 750°C	641	837	-
5) 7d 550°C	668	864	-

sample becomes more severe. The thermal treatment likely relaxes the strain induced by the crystallization of NiMoO_4 from the precursor. Transition temperature and strain data are in good agreement with the hypothesis of easier nucleation of the new phase at lattice defects.

Similar results were obtained by Auffrédic et al. (ref. 8) studying a different system. They observed a decrease in the transition temperature as the strain was increased by grinding. They explained this result by supposing that residual strain reduced the activation energy of the transition. This hypothesis can account for the increase of the activation energy of the $\alpha \rightarrow \beta$ NiMoO_4 transition, which was observed as the activation temperature of the sample was raised (ref. 9).

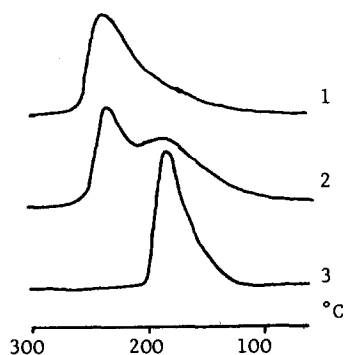


Fig. 2. $\beta \rightarrow \alpha$ transition. DTA of NiMoO_4 after heating at (1) 700, (2) 800, (3) 900°C.

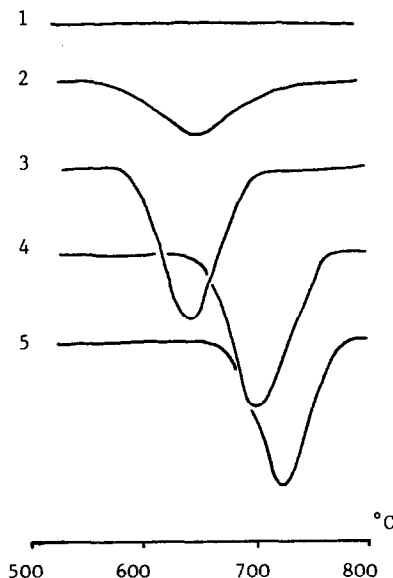


Fig. 1. $\alpha \rightarrow \beta$ transition. DTA of NiMoO_4 after thermal treatment; numbers refer to table 1.

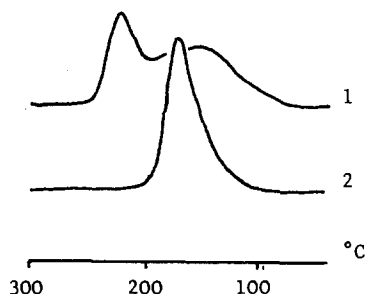


Fig. 3. $\beta \rightarrow \alpha$ transition. DTA of NiMoO_4 after 2hrs heating at (1) 700, (2) 800°C.

$\beta \rightarrow \alpha$ transition

The exothermal DTA peak of the return transition is given in fig. 2. The kinetics of the transition is affected by the temperature at which NiMoO_4 has been heated in the thermoanalyzer before the cooling analysis.

The transition peak split in two when the maximum temperature is raised from 700 to 800°C, and only the second peak remains when the maximum temperature is 900°C. The starting temperature of the peak is 257, 256 and 200°C respectively.

It is possible to account for this behaviour by supposing that the higher temperature peak arises from another strain-controlled kinetics. Thermal treatment at high temperature can relax the strain, so destroying the centers over which the new phase can form with the faster kinetics of the first peak.

The effects of a two hours treatment at high temperature are shown in fig. 3. A longer treatment at a given temperature has the same effect as a further rise of the temperature. This result is in agreement with the hypothesis of defect-controlled kinetics.

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