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TOPOCHEMISTRY OF THERMAL SOLID STATE TRANSFORMATIONS IN Ni(II)-COMPLEXES

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ABSTRACT

Solid state transformations in complex compounds of nickel: $Nien_2(NO_2)_2$, $Nien_2(NCS)_2$ (en-ethylenediamine) were investigated by DTA and DSC methods, thermomicroscopy and X-ray. Structural transformations were shown to proceed via the growth of new phase nuclei. An interface advance is of anisotropic character and accompanied by crystal cracking. Rate of the transformation depends upon crystal thickness. This fact is of particular importance for thermoanalytical experiments.

INTRODUCTION

The energetics and kinetics data on the solid state transformations obtained by thermoanalytical techniques are not enough to clear up a detailed mechanism of the reactions. It is necessary to study reagent structure, morphology of the reaction products, topochemical features of the process by X-ray methods, optical and electron microscopy[1].

The present paper deals with the results of investigation of the product morphology and the kinetics of structural transformations of complex compounds of nickel: $Nien_2(NO_2)_2$ and $Nien_2(NCS)_2$. The change of NO_2-groups coordination is responsible for the linkage isomerization of $Nien_2(NO_2)_2$[2], while in $Nien_2(NCS)_2$ solid state transformation we did not observe spectroscopically any change of NCS coordination.

RESULTS AND DISCUSSION

I. Linkage isomerization in $Nien_2(NO_2)_2$.

The DTA curve of $Nien_2(NO_2)_2$ shows an endothermic peak at 383-423 K obviously due to the isomerization of the complex. The ΔH for the transformation determined by DSC method (Setaram DSC 111, heating rate 1°/min) is 8,4 kJ/mol. The DSC curves taken from single crystals differ greatly from those of powder samples (fig.1,a).

The reaction in single crystals begins at 353-358 K after the 10 min. induction period with the formation of new phase nuclei at

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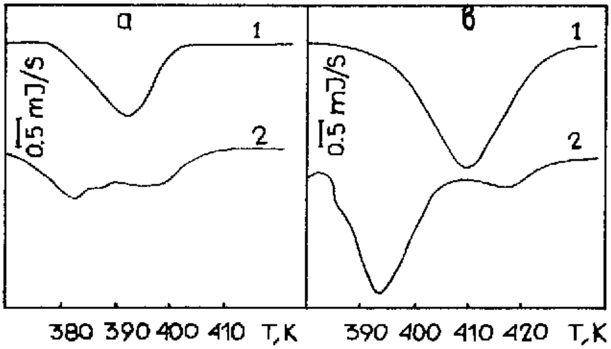

Fig.1. DSC-curves of the complexes: a) Nien$_2$(NO$_2$)$_2$ 1 - powder, 23,9mg; 2 - single crystal, 25,5mg. b) Nien$_2$(NCS)$_2$ 1 - powder, m=85mg; 2 - single crystal,105mg.Heating rate: 1 deg/min

the edges or defects on the crystal surface.A reactionary boundary motion is parallel to crystal edges and is accompanied by cracking of the initial crystal in the same directions.But in thin(30-50mkm) plates of crystals,cracking was not observed.A detailed analysis of kinetics of the interafce advance by filming proved it to be of interrupted jump-like character(fig.3,a),and thin crystals (less than 50mkm)to react slower than crystals with the thickness 100-200 mkm.

2. Phase transition in Nien$_2$(NCS)$_2$.

The DTA curve of Nien$_2$(NCS)$_2$ reveals an endothermic peak at 403-453 K due to the phase transition.DSC curves of single crystal and powder of Nien$_2$(NCS)$_2$ had different froms, and the values of ΔH of the transformation were 4,8 kJ/mol and 7,1 kJ/mol,respectively (fig.1,b).

Microscopically we observed two different morphological types of transformation (1 and 2),depending on the reaction conditions (fig.2,b).

1) Slow growth of single crystal nuclei with a non-coherent interface.Rate of nuclei growth does not depend on crystal thickness and is 10^{-7}cm/sec at T-397 K.

2) Rapid advance of a semi-coherent interface leads to the formation of a textured product.An interface advance is of aniso-

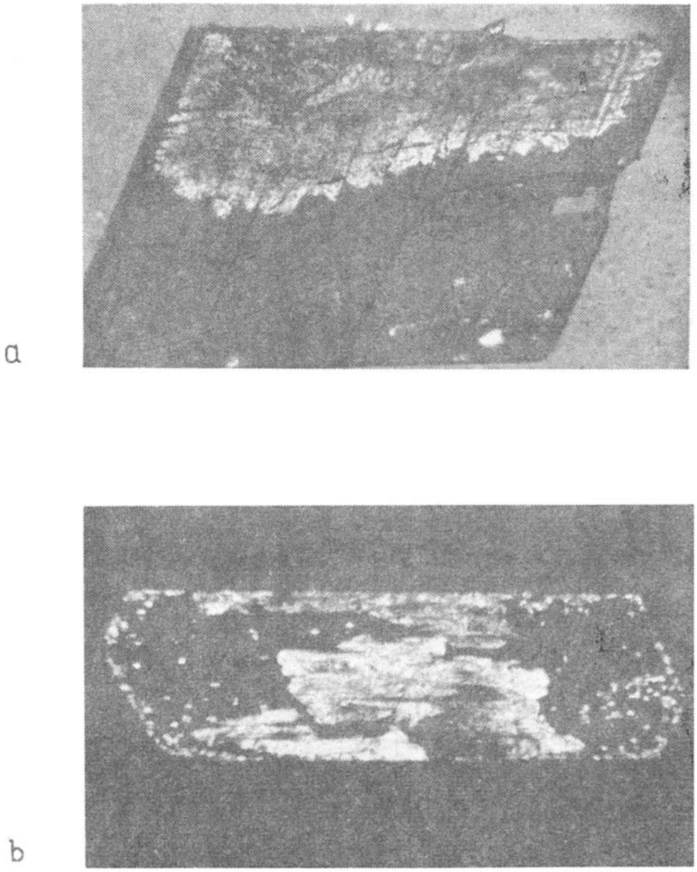

Fig.2. Micrographs of phase transitions in single crystals of $Nien_2(NO_2)_2$ (a) and $Nien_2(NCS)_2$ (b).Polarized light; x 50.

tropic character,the rate is maximal along the crystal edges.Crystal cracking occured in the same directions and not in crystals with 30-50 mkm thickness.The process rate depends on the crystal thickness (fig.3,b): 10^{-4}cm/s in crystals with 100-200 mkm thickness and 10^{-3}cm/s in thin crystals with 30-50 mkm thickness($T=397K$).

It should be noted that in thin crystals the process proceeds mainly according to the 1st mechanism,i.e. via a slow growth of the single crystal nuclei.

Relaxation processes of elastic stresses existing at the interface should be taken into account to explain kinetic-morphological

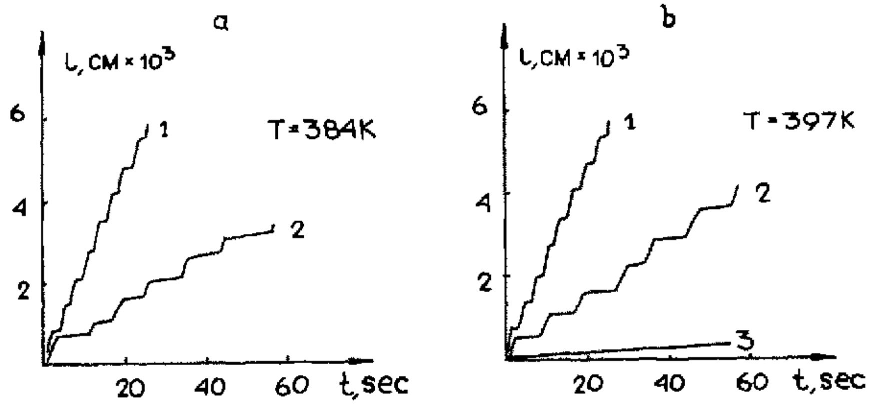

Fig.3. Kinetic curves of interface advance in single crystals of $Nien_2(NO_2)_2$ (a) and $Nien_2(NCS)_2$(b): 1-crystal thickness 100-200 mkm; 2 - crystal thickness 30-50 mkm; 3 - growth of single crystal nuclei in $Nien_2(NCS)_2$.

features of the process investigated.The stress relaxation causes crystal cracking in the slip planes as well as the formation of new defects due to plastic deformation.The latter is believed to be responsible for interrupted interface motion.Stress relaxation along slip planes leads to interface advance anisotropy.A slow interface advance in thin crystals,which do not undergo the cracking,can be connected with a slow rate of relaxation process.

Thus,the results obtained by means of microscopic observations, concerning products morphology and process kinetics expand greatly information obtained by thermoanalytical experiments,they make possible to discuss reliability of kinetic data evaluated by thermal analysis.

REFERENCES

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