

PRECIPITATION OF NICKEL DIHALIDE IN THERMALLY PRETREATED NaCl : Ni²⁺ CRYSTALS

T. MORAWSKA-KOWAL, D. NOWAK-WOŹNY AND M. SUSZYŃSKA

W. Trzebiatowski Institute of Low Temperature and Structure Research
Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland

(Received May 17, 1994; revised version July 5, 1994)

Optical absorption and the yield stress value of NaCl : Ni²⁺ crystals were measured as functions of the annealing temperature. Morphology and possible structure types of the NiCl₂ particles formed under different annealing conditions have been shortly discussed.

PACS numbers: 61.72.-y, 78.20.-e, 78.50.-w

1. Introductory information

It was evidenced previously [1-5] that the absorption spectra of nickel-doped NaCl crystals are sensitive to both the concentration and the dispersion form of the dopant. In order to obtain more details about the aggregation- and/or precipitation-related phenomena Bridgman-grown NaCl : Ni²⁺ crystals were solution-treated, i.e. air-quenched after 30 minutes of annealing at 873 K, and additionally annealed at temperatures ranging between room temperature (RT) and the solution treatment temperature (ST). For aim of comparison, as-received (AR) samples were also tested. The dopant concentration, equal to 160 ppm, was determined from the absorption coefficient of the main absorption band (α_C) according to the method described elsewhere [6]; the ppm is expressed as the number of NiCl₂ moles per 10⁶ moles of NaCl. For these samples the yield stress value was critically compared with some data obtained from the optical absorption spectra. The stress/strain curves were taken at RT by using the 1112 INSTRON machine working at the strain rate of $3 \times 10^{-4} \text{ s}^{-1}$; the yield stress value (σ_0) was determined at 0.1% of plastic strain. Optical absorption spectra were measured in the spectral range from 50×10^3 to $11 \times 10^3 \text{ cm}^{-1}$ by employing the SPECORD M-40 (Zeiss) spectrophotometer.

2. Results and discussion

2.1. Optical absorption

Spectral characteristics of the detected absorption bands have been collected in Table I for as-received, solution-treated and samples additionally annealed (AA) after the solution treatment. The oscillator strength values f_i were calculated according to the Smakula equation for Gaussian bands with the refractive index-value taken for RT [7].

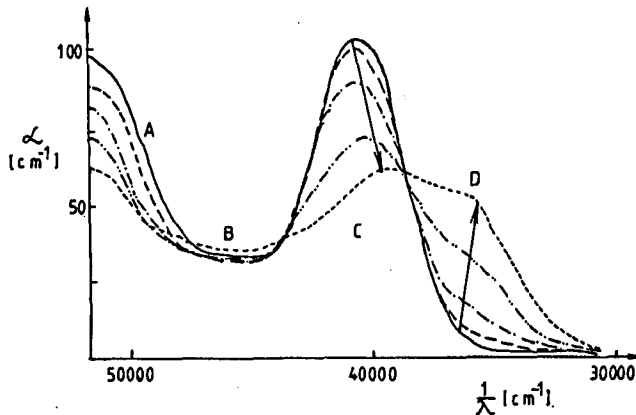


Fig. 1. Changes of the optical absorption spectra during isochronal (50 h) annealing at temperatures 323–623 K; the arrow marks the direction of the increasing temperature.

TABLE I
Some characteristics of the optical absorption bands.

Samples Quantity	AR	ST	323 K	473 K
λ (A) [nm]	193	200	197	200
α (A) [cm^{-1}]	80	82	82	35
f (A)	0.12	0.14	0.13	0.16
λ (B) [nm]	216	—	216	216
α (B) [cm^{-1}]	29	—	30	28
f (B)	0.02	—	0.02	0.01
λ (C) [nm]	242	248	242	252
α (C) [cm^{-1}]	116	100	108	50
f (C)	0.15	0.14	0.15	0.03
λ (D) [nm]	—	—	—	276
α (D) [cm^{-1}]	—	—	—	49
f (D)	—	—	—	0.07

Figure 1 presents the absorption spectra of ST-samples isochronally annealed (50 h) at temperatures between 323 and 623 K. Especially interesting are the results obtained for ST-samples additionally annealed at temperatures above 473 K. While the AR- and ST-spectra consist of three (A, B, C) and two (A, C) strong bands, respectively, the AA-spectra exhibit the presence of an additional band (D) located at about 276 nm. The absorption coefficient of this band (α_D) increases during the annealing and this increase is accompanied by the decrease in α_C characteristic of band C. It seems reasonable to assume that the centres related to D-type optical transitions appear at the expenses of centres related to the characteristic C-type absorption.

2.2. 0.1% proof stress

Figure 2 shows the effect of annealing time at different annealing temperatures upon the yield stress value of AA-crystals ($\sigma_0(t)$) with respect to the ST-ones ($\sigma_0(\text{ST})$); the annealing temperature was chosen from the range between RT and 673 K. It has been stated that the value of $\Delta\sigma_0 = \sigma_0(t) - \sigma_0(\text{ST})$ is positive for AA-samples annealed at temperatures between RT and 473 K; for higher annealing temperatures $\Delta\sigma_0 = 0$.

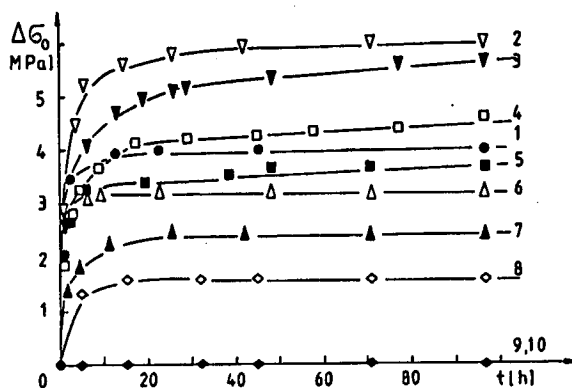


Fig. 2. Yield stress changes ($\Delta\sigma_0(t) = \sigma_0(t) - \sigma_0(\text{ST})$) induced by annealing at 323 (1), 333 (2), 343 (3), 353 (4), 373 (5), 403 (6), 433 (7), 463 (8), 473 (9) and 523 K (10).

The optical (α_C , α_D) and mechanical ($\Delta\sigma_0$) characteristics of isochronally annealed samples have been compared in Fig. 3. Although the yield stress value of samples annealed at high temperatures (at and above 473 K) is equal to the value characteristic of ST specimens ($\Delta\sigma_0 = 0$), the absorption spectra of both kinds of crystals differ from each other. Thus, the relative softening of AA-samples cannot be related to thermal decomposition of the obstacles effective after annealing at low temperatures; these obstacles are related to NiCl_2 particles formed in NaCl crystals at about 323 K [2]. The effect of the high temperature annealing is explainable in terms of a $\text{NiCl}_2 \Rightarrow \text{NiCl}_2^*$ transformation, where the NiCl_2^* particles could be considered as the "vacancy-rich" NiCl_2 phase suggested by Andreev et al. [8].

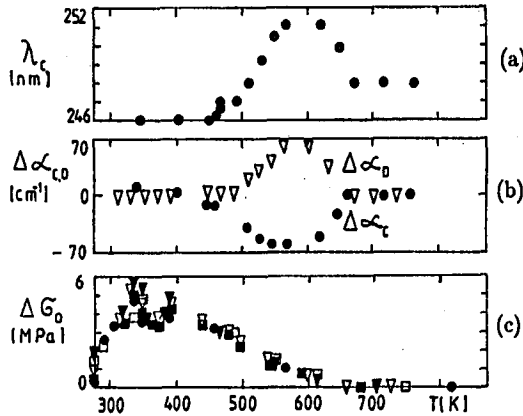


Fig. 3. The isochronal (50 h) dependences of the C-band position (a), of the changes of absorption coefficients of bands C and D (b), and of the yield stress changes (c).

2.3. Precipitation-related phenomena

Some aspects of the precipitation of nickel dihalide phases were investigated by using an Avrami-type equation in which the fraction of the dopant transformed into precipitated particles (p) was determined in the way previously proposed for NaCl:Eu²⁺ crystals [9].

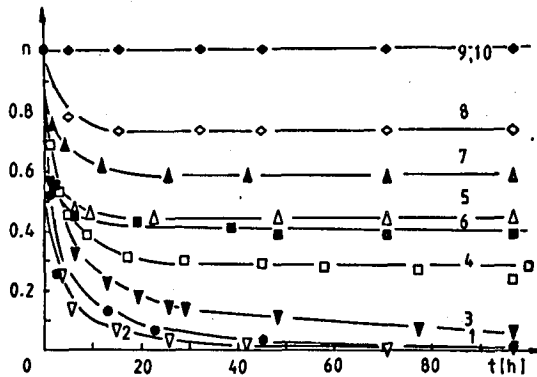


Fig. 4. Time dependences of the unprecipitated fraction of the dopant (n) during annealing at 323 (1), 333 (2), 343 (3), 353 (4), 373 (5), 403 (6), 433 (7), 463 (8), 473 (9) and 523 K (10); the data are representative of the absorption coefficient of the main absorption band.

Figures 4 and 5 show the isothermal n -values ($n = 1 - p$) determined from the optical and mechanical data, respectively, and Table II collects values of the Avrami parameter m [10]. According to the precipitation models [11, 12], the precipitation rate below 403 K, where $m < 1$, should be driven by a dislocation-aided

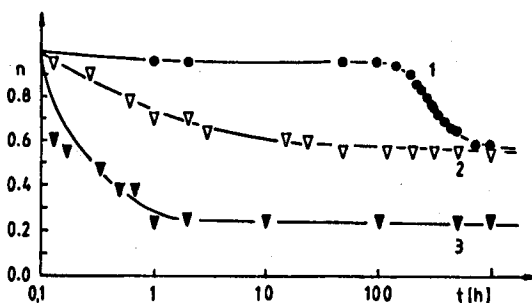


Fig. 5. Time dependences of n during annealing at 473 (1), 573 (2) and 623 K (3); these data are representative of the yield stress measurements.

TABLE II
Values of the Avrami parameter m .

T [K]	m
283	0.1
323	0.1
333	0.3
353	0.4
363	0.7
373	0.8
433	1.5
474	2.0
573	1.5
623	1.5

process, whereas above this temperature bulk diffusion and processes at the particle/matrix interface should be dominant ($m = 1.5 \div 2.0$). This means that the strengthening effect is characteristic of this annealing temperature range for which $m < 1$, whereas $m > 1$ correlates with $\Delta\sigma_0 = 0$.

2.4. Structure of the $NiCl_2^*$ phase

In order to explain the correlations between precipitation and strengthening phenomena let us assume that both nickel dihalide particles formed under different annealing conditions are of the same geometrical shape. In terms of the considered precipitation models [11, 12], they should be rods oriented along (110) direction. In fact, this shape was confirmed experimentally by some microscopic observations [13, 14].

If so, the high temperature phase should have the same crystallographic structure as the low temperature one, i.e. the hexagonal unit cell of the $CdCl_2$ -type.

Because of some differences in the density of NaCl crystals containing either NiCl₂ or NiCl₂^{*}, considered as equivalent to the "vacancy-rich" NiCl₂ phase [8], one has to expect that the lattice parameter h^* of the high temperature phase is slightly larger than h characteristic of the low temperature NiCl₂.

In order to estimate the h^* -value, the elementary cell of NiCl₂ was matched with that of NaCl. It was assumed that the sixfold rotation axis of the NiCl₂ elementary cell is parallel to the shortest slip vector of the matrix, $d_{(110)}$. A matching parameter was estimated on the basis of the following relation:

$$\varepsilon = (n^* - n)/d_{(110)},$$

where $n^* = hn_{\text{hex}}/d_{(110)}$, n is the entire part of n^* and n_{hex} is the number of hexagonal NiCl₂ cells along the $\langle 110 \rangle$ direction. This parameter described the misfit parameter for a group of n_{hex} NiCl₂ elementary cells.

The smallest value of ε (0.04) was obtained for a group of 7 NiCl₂ cells. On assuming that the ε parameter for 7 cells of the high temperature phase is equal to zero, the new parameter of h^* equals 17.38 Å.

3. Summary

In additionally annealed solution-treated NaCl:Ni²⁺ crystals the dopant is precipitated in two forms of the nickel dihalide. Both phases are hexagonal with a slightly different lattice parameter " h ". The transformation occurs at temperatures equal and higher than 473 K and involves the decrease in crystal density.

This work has been done in frames of the project No. 2 P302 178 04 of the Committee for Scientific Research.

References

- [1] K. Polak, *Z. Phys.* **223**, 338 (1969).
- [2] D. Nowak-Woźny, M. Suszyńska, *Acta Phys. Pol. A* **81**, 419 (1992).
- [3] M. Suszyńska, *Science Forum* **126-128**, 419 (1993).
- [4] M. Suszyńska, R. Capelletti, *Mater. Chem. Phys.* **34**, 228 (1993).
- [5] D. Nowak-Woźny, M. Suszyńska, M. Szmida, R. Capelletti, *J. Mater. Sci.* **28**, 645 (1993).
- [6] D. Nowak-Woźny, PhD Thesis, Inst. of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław 1994.
- [7] *The Physicochemical Handbook*, Eds. J. Gajewska, S. Pietras, J. Rudzińska, A. Schellenberg, PWN, Warszawa 1974 (in Polish).
- [8] A. Andreev, M. Hartmanova, V.A. Klimov, *Phys. Status Solidi A* **41**, 697 (1977).
- [9] D. Nowak-Woźny, *Cryst. Res. Technol.* **24**, 979 (1989).
- [10] M. Avrami, *J. Chem. Phys.* **9**, 177 (1941).
- [11] C. Zener, *Trans. A.I.M.E.* **167**, 550 (1946).
- [12] C. Wert, *J. Appl. Phys.* **20**, 943 (1949).
- [13] A. Andreev, M. Hartmanova, V.A. Klimov, *Phys. Status Solidi A* **62**, 35 (1980).
- [14] M. Szmida, private communications.