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SPECIFIC FEATURES OF NICKEL OXIDES OBTAINED BY THERMAL AND LASER INDUCED DECOMPOSITION OF NICKEL SALTS. A COMPARATIVE STUDY

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ABSTRACT

Following earlier research concerning the decomposition of inorganic salts by a CW CO_2 laser beam (I. Ursu, R. Alexandrescu, I.N. Mihăilescu, I. Morjan, V. Jianu and C. Popescu, J. Phys. B, 19 (1986) L825; C. Popescu, V. Jianu, R. Alexandrescu, I.N. Mihăilescu, I. Morjan and M.L. Pascu, Thermochim. Acta, 129 (1988) 269) the present work describes some results obtained by the processing of four nickel salts, i.e. the hydroxy-carbonate, the nitrate, the sulphate and the chloride of nickel. X-ray investigations of the obtained crystals give evidence for an effect due to the absorptivity properties of the laser radiation by the irradiated salt.

INTRODUCTION

As various authors have already mentioned [1,2], laser induced processes have some specific characteristics which are due mainly to the laser beam features; among these, (i) a strong localized action and (ii) use of the same wavelength quanta, which affords increased spectral absorptivity, are the most important.

During the thermochemical processes induced and driven by CW CO_2 lasers, the substance is thermally decomposed. The kinetics of such decomposition processes, as compared with the usual thermal process, have been studied by us in some earlier work, and we have demonstrated some particular effects in which the absorptivity of the reactants and the reaction

TABLE 1

Absorptivity values of nickel salts at 10.6 μm

Substance	Code	Absorptivity (%)
$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$	K	42
$Ni(NO_3)_2 \cdot 6H_2O$	A	2
$NiCl_2 \cdot 6H_2O$	C	≈ 0
$NiSO_4 \cdot 7H_2O$	S	8

products seems to be involved. The results of X-ray investigations which are presented in this paper give more support to this hypothesis.

EXPERIMENTAL

Substances

Different nickel salts of analytical purity grade were used. Their IR spectral characteristics within the range of CO_2 laser emission (10.6 μm) were investigated and the results are given in Table 1.

Equipment

(a) Laser irradiation experiments were performed by using a CW CO_2 laser of beam intensity 400 W cm^{-2}. The salts, in powdered form, were evenly distributed as a thin layer in a metal reaction cell having a width equal to the diameter of the laser beam. The cell was driven perpendicularly to the beam at various speeds. After each passage through the laser beam, the samples were weighed (accuracy $\pm 5 \times 10^{-5}$ g) until constant weight was achieved. The speeds used were: $v_1 = 0.18$ mm s^{-1}; $v_3 = 0.53$ mm s^{-1}; $v_5 = 1.40$ mm s^{-1}; $v_2 = 0.33$ mm s^{-1}; $v_4 = 0.71$ mm s^{-1}.

(b) A Q 1500 D Derivatograph (MOM Budapest), of Paulik, Paulik and Erdey type, was used for the thermal analysis experiments. Heating rates of 5 and 10 K min^{-1}, alumina as reference, air atmosphere, DTA and DTG sensitivities of 100 mV and a temperature range of 0–1000 °C were used.

(c) The copper $K\alpha$ radiation provided from a Siemens Kristalloflex diffractometer was used for the X-ray diffraction measurements. The diffracted radiation was monochromatized in a monochromator with a curved graphite crystal. A water cooled NaI(Tl) scintillation counter was used to record the radiation. The intensities were determined by counting the number of quanta diffracted within 10 s at every angle of the angular range of the peak by scanning at steps of 0.02° (2θ).

RESULTS AND DISCUSSION

Kinetics of laser induced vs. thermally induced decomposition

The weight losses at a given speed for the four nickel salts were used in order to analyse the kinetics of the decomposition reactions by using the following relationship [3]

$$\ln \mathrm{d}\alpha/\mathrm{d}t = \ln k + n \ln(1 - \alpha) \qquad (1)$$

where α is the degree of conversion, n is the reaction order, k is the rate constant and t is the time.

The weight losses versus time at v_2 are given in Fig. 1(a)–(d) for all four salts. The data were used in eqn. (1), and the values of k and n were calculated from the condition of best correlation coefficient for the straight line [$\ln \mathrm{d}\alpha/\mathrm{d}t$ versus $\ln(1 - \alpha)$].

The thermally induced reactions were recorded by derivatograms, as shown in Figs. 2(a)–(d). The thermogravimetric data were processed by use of the integral equation [4]

$$\ln F(1 - \alpha) = -E/RT + \ln A/b \qquad (2)$$

where $F(1 - \alpha)$ stands for the conversion integral,

$$F(1 - \alpha) = \int_0^\alpha \frac{\mathrm{d}x}{(1 - x)^n}$$

E is the activation energy, T is the temperature, R is the gas constant, A denotes the pre-exponential factor and b is the heating rate. From the plot of $\ln F(1 - \alpha)$ versus $-1/RT$ and the condition of best correlation coefficient, the parameters n, A and E have been calculated.

The final products obtained by both methods were investigated by means of X-ray diffraction, and NiO_x, $x \leqslant 1$, was detected as the major phase.

The results of calculations according to eqns. (1) and (2), together with the proposed reactions, are given in Table 2.

It may be noted that none of the laser induced decomposition processes follows the thermally induced decomposition paths. The first (and major) difference consists in the number of decomposition steps: only one for the laser induced reactions and at least two for those induced thermally. The unique stage which is recorded for the laser induced processes is probably a rapid development of the observed thermal stages, with superimposed kinetics due, probably, to a slow physical process (diffusion of the evolved gases, or growth of the crystals).

Since all the studied decomposition reactions are heterogeneous, the kinetic parameters so calculated can have limited physical significance [5], and we have considered them more as fitting parameters. However, the results presented below seem to indicate that their values are related to some

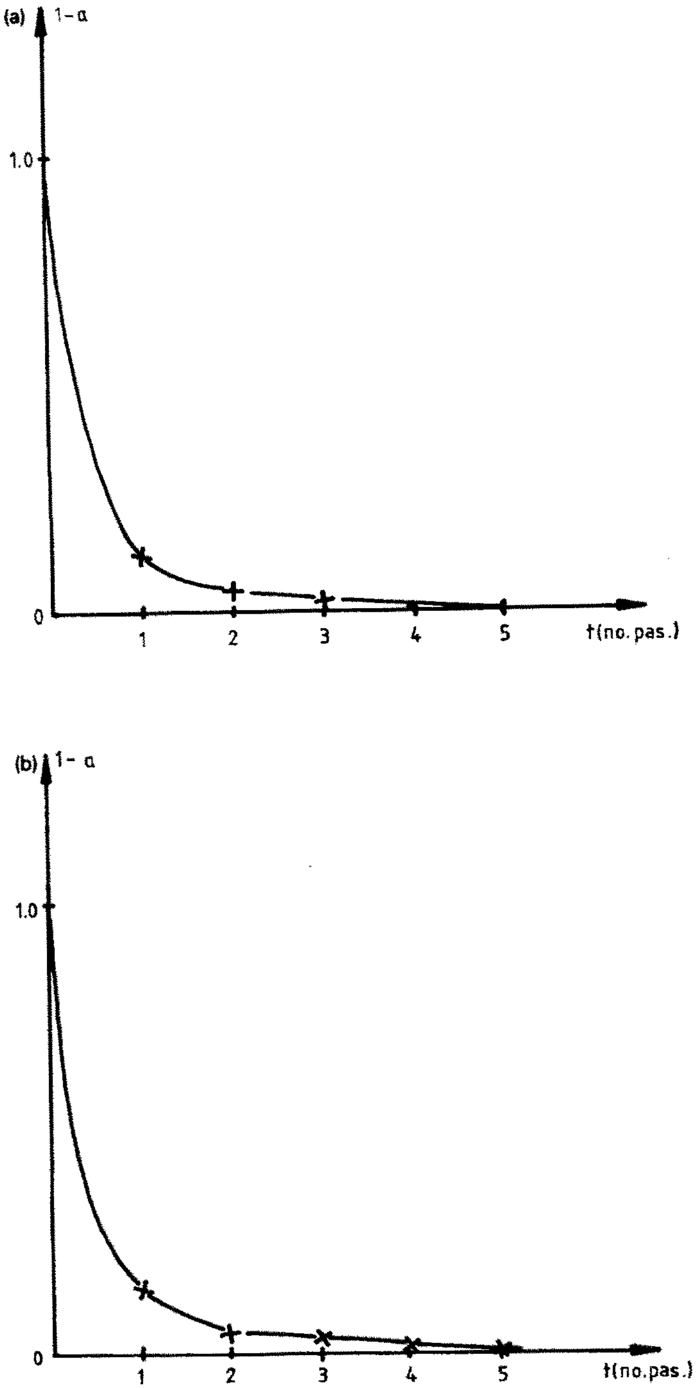

Fig. 1. Plots of changes with time of the degree of conversion of nickel salts by laser decomposition: a, nickel hydroxycarbonate; b, nickel nitrate; c, nickel sulphate; d, nickel chloride.

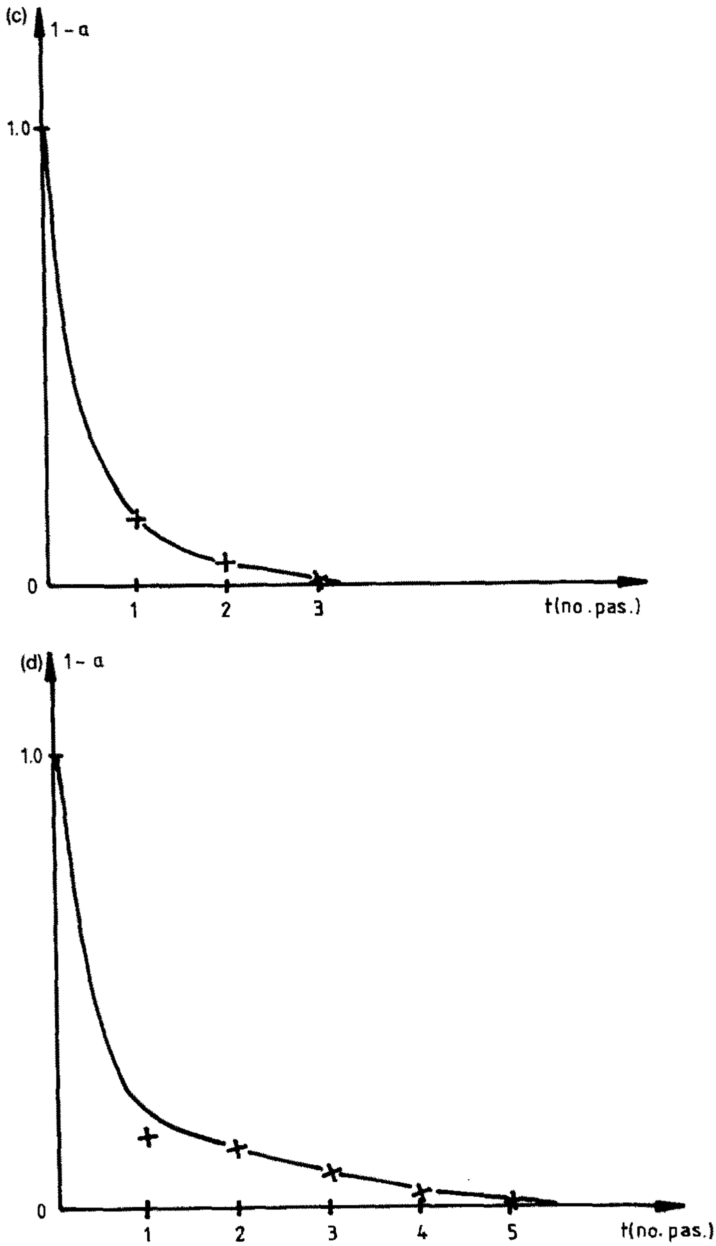

Fig. 1 (continued).

process characteristics, and it is therefore probable that the activation energy parameter E, at least, is not simply a fitting number.

Crystallographic investigations

The temperature measured in the impact region by means of an optical pyrometer was ca. 1000 ° C. In order to compare the oxides obtained by laser irradiation with those obtained by thermal treatment, a short passage (about 1 min) through a 1000 ° C region was made. The treated samples, with NiO_x as major phase, were investigated by X-ray diffraction techniques in order to obtain (a) the mean size of the crystallites (Fig. 3), and (b) the lattice parameter *a* along the [200] and [111] crystallographic directions (Fig. 4).

(a) The mean size of the nickel oxide crystallites was determined along the [111] and [200] crystallographical directions using the Debye–Scherrer formula with corrections calculated as indicated by Kaelbe [6]. The results are given in Fig. 3.

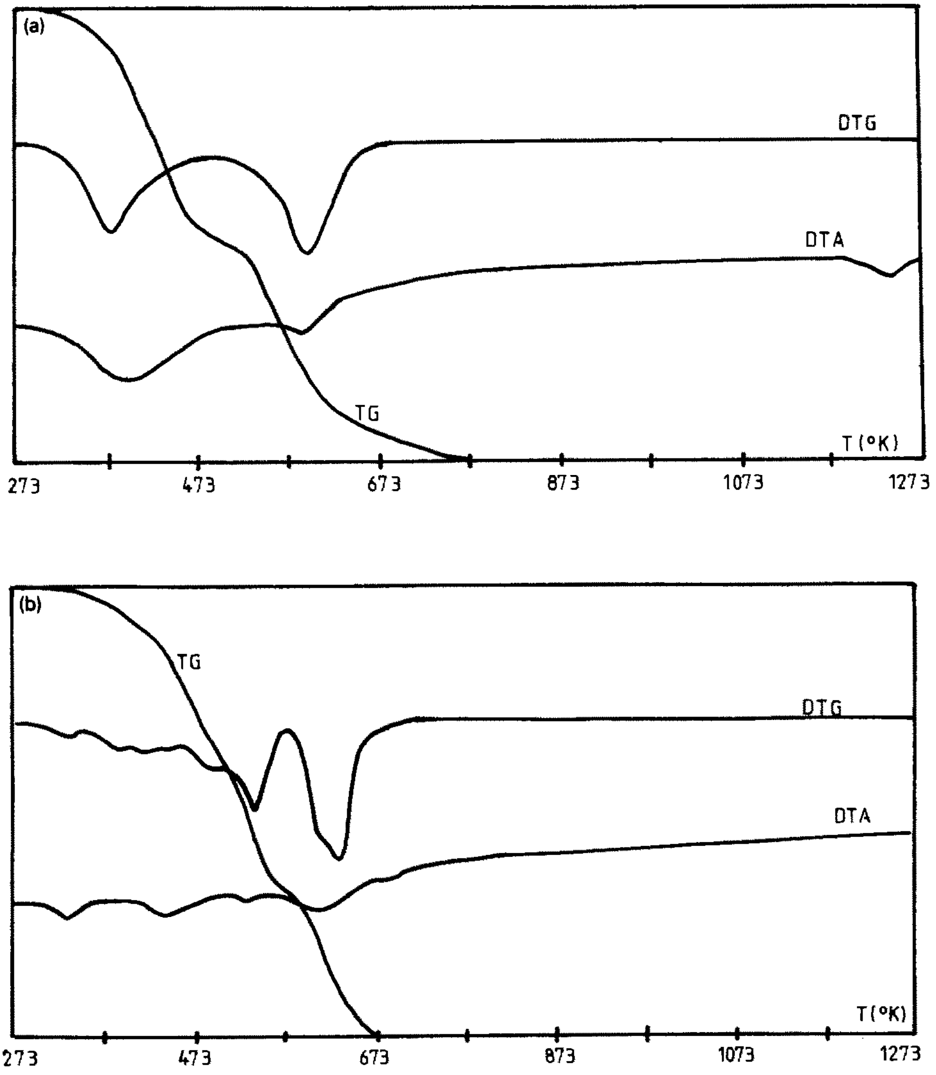

Fig. 2. Derivatographic curves of a, nickel hydroxycarbonate; b, nickel nitrate; c, nickel sulphate; d, nickel chloride.

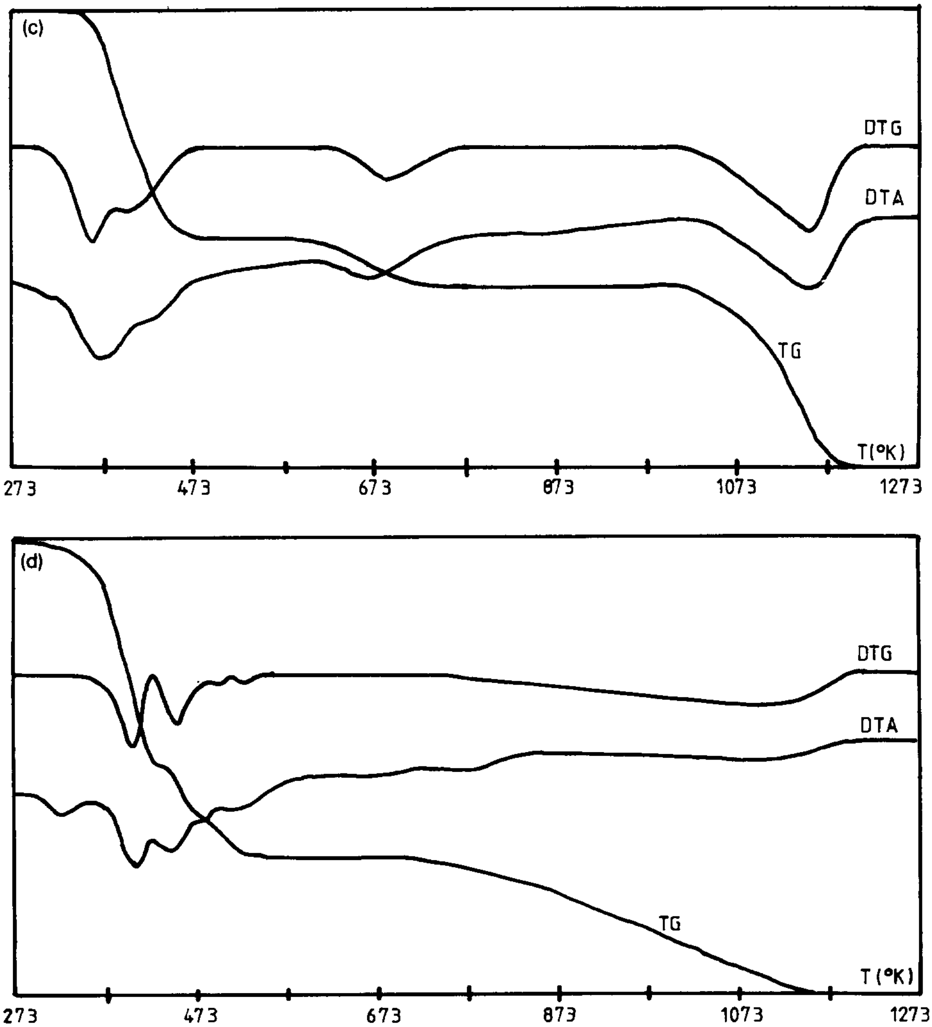

Fig. 2 (continued).

One may note that thermally treated samples have small crystallites of roughly equal lengths along both crystallographic directions, whilst the laser treated crystallites are larger, with different lengths along the two directions. An increase of the dimension along the [200] direction is observed. The biggest difference for the two preparative methods is recorded for sample K, which also has the greatest difference between the dimensions along the two directions for the laser crystallites. It may be emphasized that more isotropically grown thermal crystallites exhibit a more difficult growing stage.

By comparing the absorptivity data (see Table 1) with the results from Fig. 3, it may be noted that salts with higher absorptivity lead to nickel oxides with an increased anisotropy of shape. The most anisotropic oxides are, it follows, those obtained from nickel hydroxycarbonate and nickel

TABLE 2

Comparative reaction routes and kinetic data on laser and thermal decomposition of nickel salts

Substance	Laser irradiation	Thermal heating in the derivatograph
$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$	$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O \rightarrow 2NiO + CO_2 + 2H_2O$ $n = 3$; $k = 7.776\ s^{-1}$	(i) $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O \rightarrow NiCO_3 \cdot NiO + 2H_2O$ $n = 1$; $E = 8.5$ kcal mol^{-1}; $A = 10^2\ s^{-1}$ (ii) $NiCO_3 \cdot NiO \rightarrow 2NiO + CO_2$ $n = 1$, $E = 30.9$ kcal mol^{-1}; $A = 10^9\ s^{-1}$
$Ni(NO_3)_2 \cdot 6H_2O$	$Ni(NO_3)_2 \cdot 6H_2O \rightarrow NiO + 2NO_2 + 1/2\ O_2 + 6H_2O$ $n = 1.27$; $k = 3.609 \times 10^{-2}\ s^{-1}$	(i) $Ni(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{continuous}} Ni(NO_3)_2 + 6H_2O$ (ii) $Ni(NO_3)_2 \rightarrow NiO + 2NO_2 + 1/2\ O_2$ $n = 3/2$; $E = 62.9$ kcal mol^{-1}; $A = 8.7 \times 10^{21}\ s^{-1}$
$NiCl_2 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O \rightarrow NiO + 2HCl + 5H_2O$ $n = 1$; $k = 6.969 \times 10^{-3}\ s^{-1}$	(i) $NiCl_2 \cdot 6H_2O \rightarrow NiCl_2 \cdot 2H_2O + 4H_2O$ $n = 0.4$; $E = 12.3$ kcal mol^{-1}; $A = 3 \times 10^4\ s^{-1}$ (ii) $NiCl_2 \cdot 2H_2O \rightarrow NiCl_2 \cdot H_2O + H_2O$ $n = 2$; $E = 71.2$ kcal mol^{-1}; $A = 10^{35}\ s^{-1}$ (iii) $NiCl_2 \cdot H_2O \xrightarrow{\text{continuous}} NiO + 2HCl$
$NiSO_4 \cdot 7H_2O$	$NiSO_4 \cdot 7H_2O \rightarrow NiO + SO_3 + 7H_2O$ $n = 3/2$; $k = 0.125$ s	(i) $NiSO_4 \cdot 7H_2O \rightarrow NiSO_4 \cdot 3/2\,H_2O + 11/2\,H_2O$ $n = 2$; $E = 20.4$ kcal mol^{-1}; $A = 10^8\ s^{-1}$ (ii) $NiSO_4 \cdot 3/2\,H_2O \rightarrow NiSO_4 + 3/2\ H_2O$ $n = 3/2$; $E = 46.3$ kcal mol^{-1}; $A = 2.4 \times 10^{13}\ s^{-1}$ (iii) $NiSO_4 \rightarrow NiO + SO_3$ $n = 1/3$; $E = 59.4$ kcal mol^{-1}; $A = 7.5 \times 10^8\ s^{-1}$

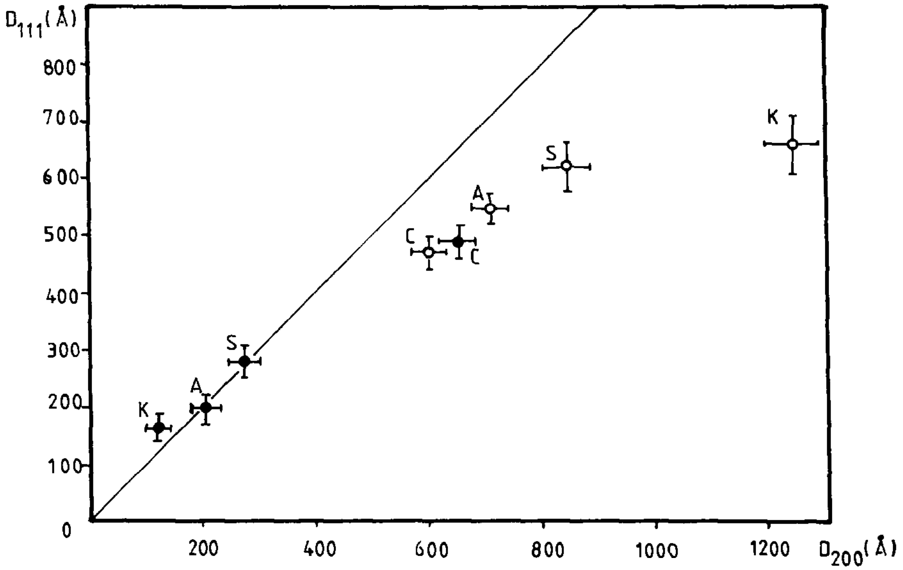

Fig. 3. The mean size of NiO_x crystallites: ●, thermally obtained crystallites; ○, laser produced crystallites.

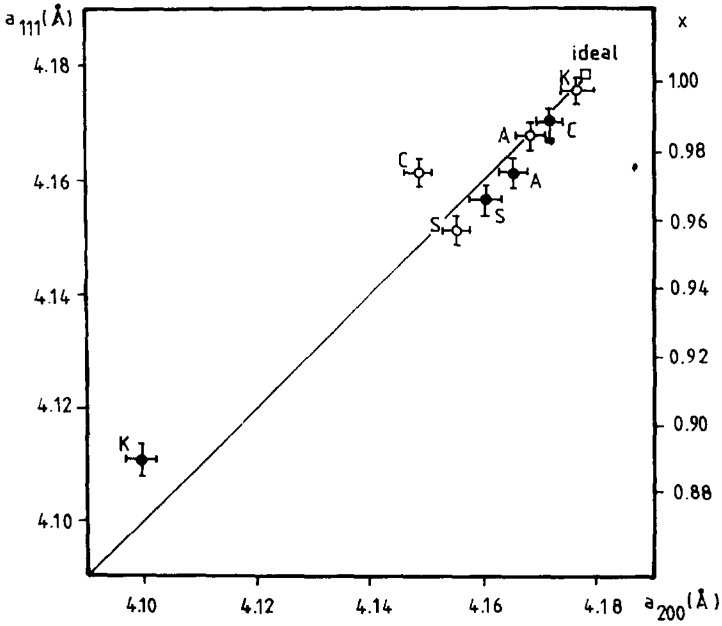

Fig. 4. The lattice parameter a and the values of the stoichiometric coefficient x of NiO_x crystallites: ●, thermally obtained crystallites; ○, laser prepared crystallites.

sulphate; nickel nitrate and chloride give oxides with a lattice close to isotropic. The crystallite sizes may be arranged in the same order.

On the other hand, the size of thermal crystallites follows a different hierarchy, which seems to be dictated by the maximum value of E, the activation energy, of the decomposition steps as calculated in Table 2. Their sizes increase in the order $K < A < S < C$.

It may be supposed that the absorption of the incident quanta by the nickel salt is correlated with the growth of the crystallites in a specified direction (the face of the cube in this case). If the absorptivity is very low (salts A and C) the laser action seems to be purely thermal and the crystallite sizes follow the order imposed by the parameter E.

(b) The lattice parameter, a, and the stoichiometric coefficient, x, are given in Fig. 4. The shift of a from the ideal value is probably due to the different losses of oxygen during the treatment. Nonstoichiometry of the oxides was detected for all the samples by this method. The highest difference between the laser prepared crystals as compared with the thermally obtained ones may be noted for those obtained from nickel hydroxycarbonate, salt K. In this case the laser prepared crystallites are almost ideal, whereas those obtained by the thermal procedure are the most nonstoichiometric. A smaller difference is recorded for the oxides obtained from nickel chloride, C. The oxides S and A obtained by both methods are very similar. Arranging the laser crystallites according to their decreasing stoichiometry, the following order is obtained: $K \rightarrow A \rightarrow C \rightarrow S$. Although it does not seem to be a causal relationship, the same hierarchy may be obtained by adding the values of E (from Table 2) of the thermal decomposition steps and arranging the sums in increasing order.

It seems, also, that the absorptivity of the salt does not have a significant effect on the final crystal stoichiometry, since the decreasing order of the absorptivity values (see Table 1) is $K \rightarrow S \rightarrow A \rightarrow C$, obviously different from the order above.

Effect of speed of passage through the laser beam

In order to study the effect of the speed of passage through the laser beam, two salts with widely different absorptivity values have been investigated, namely nickel hydroxycarbonate and nickel nitrate (K and A). The results, given as the mean size of crystallites in the direction D_{200}, are shown in Fig. 5.

Once more the influence of the absorptivity on the laser effect should be pointed out. The dimensions of oxides K decrease as the speed increases, and appear to reach a limiting value (ca. 500 Å) for speeds higher than 1 mm s^{-1}. On the other hand the crystallite mean size of oxide A seems to be unaffected by changing the speed of passage.

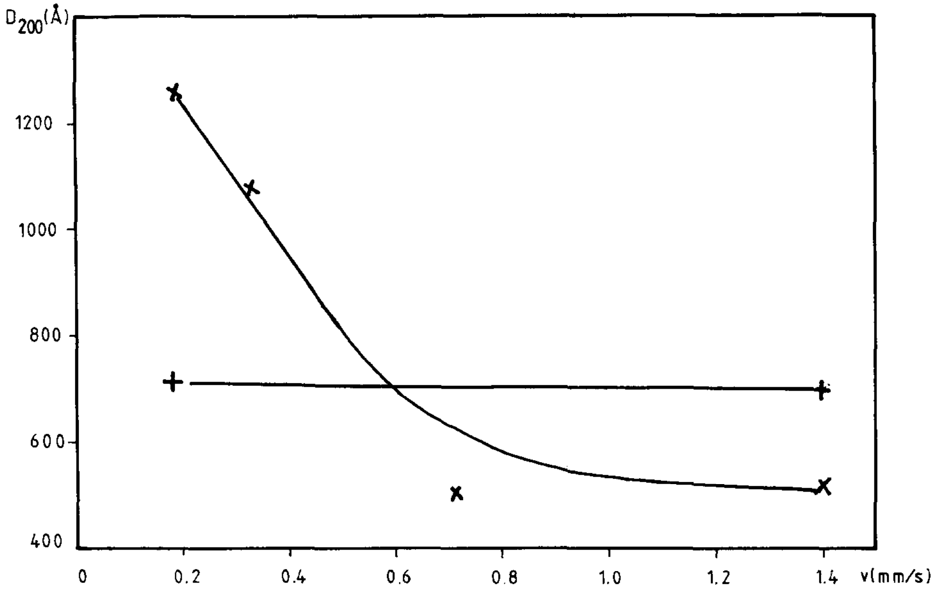

Fig. 5. Dependence of mean size of obtained NiO_x crystallites on the speed of passage through the laser beam: ×, nickel oxide from nickel hydroxycarbonate; +, nickel oxide from nickel nitrate.

The above fact suggests that salts with appreciable initial absorptivity for the laser radiation follow a different decomposition path to those with low (or zero) absorptivity when they are irradiated. In this last case the effect of the laser beam seems to be a purely thermal one.

CONCLUSIONS

Summing up the discussions, we consider that the following points should be underlined.

(i) There are some physical characteristics of the obtained nickel oxide crystallites (shape, dimensions) which are probably influenced by the absorptivity of the beam of laser quanta. A salt of higher absorptivity gives crystallites which are more anisotropic than those obtained by the thermal procedure. A low absorptivity salt gives crystallites which are similar to those obtained by the thermal procedure.

The laser action may be considered, then, as comprising two parts: a thermal effect, which acts when the salt has low (nil) absorptivity for the quanta; and a characteristic laser effect which occurs when the salt absorbs the quanta.

(ii) The decomposition of the laser irradiated salt probably follows the same course as for the thermally decomposed salt. This conclusion we consider to be supported by the relationship which seems to exist between the stoichiometry of the laser produced crystallites and the sum of the values of E for the observed thermal reactions. The kinetics followed by the salt during decomposition by each of the methods are different. A subsequent paper will deal further with this topic.

(iii) Although the parameters calculated with eqns. (1) and (2) have been considered essentially as fitting parameters, the activation energy parameter E, at least, seems to have some physical meaning, since its value is closely related to the energies which are involved in the experiments described above.

REFERENCES

1 V.I. Konov, in I. Ursu and A.M. Prokhorov (Eds.), Lasers and Applications, Central Institute of Physics Press, Bucharest, Vol. 1, 1982.
2 D. Bauerle (Ed.), Laser Processing and Diagnostics, Springer-Verlag, Berlin, 1985.
3 I.G. Murgulescu, T. Oncescu and E. Segal, Introduction to Physical Chemistry, Ed. Academiei, Bucharest, 1981 (in Romanian).
4 E. Segal and D. Fătu, Introduction to Non-isothermal Kinetics, Ed. Academiei, Bucharest, 1981 (in Romanian).
5 J. Šesták, J. Therm. Anal., 16 (1979) 503.
6 D. Negoiu, Treatise of Inorganic Chemistry, Ed. Tehnica, Bucharest, 1972 (in Romanian).