****

****

ABSTRACT

****

****

The study of microstructures on crystal surfaces provides useful information about the surfaces and under favourable circumstances can unfold a wealth of information about the history of the growth of the crystals. Dissolution phenomena can yield interesting and useful information about the defect structure in general and line imperfections in particular, in the as-grown crystals. Further plastic deformation is helpful in identifying the line defects and their interaction among themselves and with other defects and also with externally applied forces. In addition to this heat treatment of the crystalline material is likely to throw light on the strengthening mechanism operating in a material. The present work consists of judicious combination of the above study and is centred on growth and microhardness of synthetic single crystals of sodium nitrate and dissolution study of isostructural natural calcite crystals. A large amount of work on topographical study of etched surface and identation-induced plastic deformation of Calcite crystals was carried out by previous workers in this laboratory. In continuation of this work, microhardness of synthetic single crystals of sodium nitrate is carried out. The present work on the chemical and thermal dissolution of calcite cleavages is an extension of the study carried out on these crystals by the previous worker in this laboratory. For lucid presentation the thesis is divided into four parts. The first part is spread over three chapters. The first chapter presents in detail general information about sodium nitrate and calcite crystals. The second chapter reports experimental techniques employed in the present investigation. They are as follows :

(i) High resolution optical microscopy, (ii) Indentation technique using Vickers and Knoop indenters for hardness studies, (iii) Electron microscopy (iv) Etching technique, (v) Electrolytic conductivity, (vi) Silvering technique in high vacuum, (vii) Multiple beam interferometry and (viii) Growth of single crystals of sodium nitrate from melt and solution. Further Chapter III presents methods of graphical analysis of straight line plots.

The second part consists of four chapters presenting in detail the general review of microhardness of crystalline materials (Chapter IV). It is followed by systematic detailed study of the variation of diagonal length of indentation mark with applied load. The relation between load and length of indentation mark is given by Meyer's law, $P = a d^n$, where 'a'&'n' are constants of material. The exponent 'n' is postulated by Meyer to be '2' for all indenters that give geometrically similar shapes (impressions). The value of n is determined from a graph of log P versus log d. Since the relation between log P and log d is linear, the plot is a straight line, the slope of this line gives the value of n. The careful study of these plots shows two clearly recognisable straight lines of different slopes meeting at a kink. The value of n is nearly equal to 2 in high load region, while it is having large value in low load region. This type of behaviour is exhibited by different crystals like Barite, KCl, KBr, Zn, TGS and Calcite studied by previous workers in this laboratory. In view of the limitations of the equipment available in the laboratory, it is not possible to study hardness at high temperatures. Hence crystals of almost identical sizes were slowly and gradually raised to a definite elevated temperature, kept at this temperature for a sufficient time (24 hours in the present work) and were quenched to room temperature by keeping the quenching rate as high as possible. The variation of diagonal length of indentation mark with applied load for sodium nitrate crystals quenched from different high temperatures is also studied. The heat treatment of these crystals produced a change in the slope and intercept of the straight line plots of log P vs. log d and also the shifting of the kink, the meeting point of two distinct plots. Further the effect of quenching on slope of first part corresponding to low load region of the graph is more noticeable. This indicates that the defect structures operate differently in low load and high load regions corresponding to two parts of the graph of log P vs. log d .

The variation of hardness of untreated and thermally treated samples with applied load is systematically presented in chapter (VI). The study indicates that the plot between hardness and load can be qualitatively divided into three portions viz. low load region corresponding to linear part, intermediate load corresponding to non-linear part and high load region corresponding to linear portion of the graph.

The variation of hardness (hardness numbers VHN and KHN) is studied with temperature of quenching. It is found that hardness increases with temperature of quenching. Empirical relations between hardness number (H) and temperature of quenching (T_Q), between (H) and (a) and between (a) and (T_Q) are derived for high load region where hardness is constant and independent of load. They are given by

(i) $H \quad T_Q^{\ k} = \text{Constant}$
(ii) $a_2 \quad H^{\ s} = \text{Constant}$
(iii) $a_2 \quad T_Q^{\ r} = \text{Constant}$

Where k, s and r are constants for a crystal and are numerically less than unity. The sign of these constants decide the nature of crystal. Thus for positive values of k, s and r hardness decreases with increase of quenching temperature and conversely. For the first time a clear physical meaning could be given to a_2, the constant in Meyer's equation in the high load region. a_2 should be considered as hardness coefficient or hardness modulus. It is also shown that for sodium nitrate crystal Knoop hardness number (H_k) and Vickers hardness number (H_v) are almost the same at high loads. Their ratio (H_k/H_v) in high load region is $\simeq 1$. Since the electrical conductivity and hardness are temperature dependent properties for ionic crystals and that physical processes for conduction of electricity through these crystals and their hardness are more or less similar, it is shown that for ionic crystals in general and sodium nitrate crystals in particular, the ratio of electrical conductivity to hardness number is constant at a constant temperature in high load region.

The graphical analysis of straight line plots (chapter-VII) has given interesting and useful information about the weightage of different observations.

Several factors such as shape, size and eccentricity of etch pits, etching time, etching temperature, concentration and composition of dislocation etchant associated with the controlled chemical dissolution of Calcite were studied by previous workers in this laboratory. In continuation of this work chemical kinetics and dissolution of a cleavage face of calcite at different etching temperatures and for different concentrations of strong alkali (aqueous solution of sodium hydroxide) is presented in part III, which consists four chapters. General survey of literature available on etching of crystals is given in Chapter-VIII. Chapter-IX presents detailed study of the effect of time of etching, concentration of etchant and temperature of etching on formation and widening of etch pits. The quantitative study of the variation of etch rates (V) with concentration (C) keeping temperature constant show a maximum at a particular concentration and is independent of temperature of etching. The factors responsible for appearance of maxima in V-C plots are analysed by considering PH value, electrolytic conductivity σ_c and viscosity (μ) of the etchant (aqueous solution of sodium hydroxide). It is observed that the maximum values of etch rates (V_{tm} and V_{sm}) and electrolytic condustivity σ_m in the V-C plots and σ-C plot respectively are different. Detailed analysis has revealed that the ratio of maximum rate of etching of tangential dissolution to the maximum surface dissolution rate, viz. V_{tm}/V_{sm} and not the absolute values, V_{tm} and V_{sm}, should be considered while studying the salient features of dislocation etchant. Thus V_{tm} / V_{sm}, σ_m and etchant concentration are found to be important factors in the chemical dissolution of Calcite by aquenous solution of sodium hydroxide at different etching temperatures. Comparative study of the properties of the present etchant with those of Lactic and Formic acids reported earlier has disclosed that the relation between (V_{tm} / V_{sm}) and C and also between σ_m and C are linear and independent of etching temperature. The study of viscosity of the aqueous solution of sodium hydroxide has clearly shown that high viscosity and the formation of thin film of reaction product calcium oxide on a cleavage surface of calcite are responsible for different values of etchant concentration at which V_t, V_s and σ attain maximum values. The thickness of the oxide film is found to be a function of etchant concentration and etching time.

The study of the Arrhenius plots of log V versus reciprocal of temperature has yielded useful information about the activation energy of the reacting species at a certain concentration of the etchant. Just as the ration (V_{tm} / V_{sm}) is more important in the analysis of the properties of the etchant, the ratio of the activation enefgy (E_t) of tangential dissolution of ledges to the activation energy (E_s) of surface dissolution, viz. (E_t/E_s) is important in deciding the quality of chemical etch pits. The ratios (V_t/V_s) and (E_t/E_s) determine the visibility and quality of etch pits on calcite cleavages. It is now well-established that they must be greater than ten and one respectively. A chemical reaction can be diffusion-controlled or kinetically-controlled or a mixture of the two processes. This nature can be decided by comparing the activation energies of chemical dissolution (E_s or E_t) and viscosity (E_μ). It is observed that for a chemical reaction to be kinetically controlled (E_s / E_μ) and (E_t / E_μ) should be greater than one. This is indeed found to be the case in the present work of chemical dissolution of calcite in aqueous solutions of sodium hydroxide.

In continuation of work on thermal dissolution of calcite cleavage faces carried out in this laboratory, quantitative study of the effect of time and temperature of etching on widening of thermal etch pits with plane shape of rhombus on a cleavage surface is presented (chapter-X). The Thermal etch rates (V_t) of tangential dissolution along directions $[1\bar{1}0]$ and $[1\ 10]$ and surface dissolution V_s were determined in the range of etching temperatures 540 to 605°C. The Arrhenius plots of log V vs. 1 / T determined the activation energies $E_{t\ th}$ and $E_{s\ th}$. These activations energies are found much larger than those of chemical dissolution of calcite cleavage faces using different dislocation etchants. This suggests origin of thermal etch pits to be at dislocation-free sites such as kinks, steps and impurity centres etc. The ratio $E_{t\ th}/ E_{s\ th}$ is found to be greater than one, supporting the earlier observations on chemical dissolution regarding the visibility and quality of thermal etch pits.

Multiple beam interferometry (MBI) and Scanning electronmicroscopy (SEM) are sophisticated techniques for studying fine features on treated and untreated surfaces of materials. In the present work MBI is used to determine depth of chemical etch pits on calcite cleavages. The plots of etch pit dimensions along three directions namely length, breadth and depth against temperature are curvilinear and are having almost identical form. This indicates that initial preferential dissolution of ledges along these three directions are proportional and do not depend on the crystallographic symmetry of the crystal in general and face under observation in particular. Dissolution process is considered to be the reverse of natural growth of a crystal. SEM is used to carry out the measurement of dissolution edges of the etch patterns, consisting of blocks and etch pits, on the etched surface. However the correlation between the dimensions of the etched ledges of the block pattern in a direction normal to the cleavage surface and lattice parameter along this direction is not excellent. Systematic detailed study of fine features of etched ledges and their orientations with respect to the normal characteristic features of chemical and thermal etch pits and also of indented etched and unetched surfaces could not be carried out due to frequent non-functioning of SEM extending over a considerably large time period.

The microhardness of thermally untreated and treated synthetic single crystal of indium antimonide, a compound belonging to III-V group of periodic table, is optically studied and is reported in the appendix alongwith the graphical analysis. The experimental work was carried in a manner identical with that reported for single crystals of sodium nitrate. A surprising result has emerged, namely in the high load region the empirical relations derived for sodium nitrate crystals are also found to be true for indium antimonide cleavages. It is thus clear from the work on alkali halides (KCl, KBr), Barite, TGS, Zinc, Calcite and the present work on sodium nitrate and indium antimonide that the empirical hardness formulae derived in a phenomenalogical manner describe the quench hardness of these crystals. This suggests that the physical processes responsible for quench hardness must be more or less similar.

The part four consists of Chapter XII which presents in brief the conclusions obtained from the present study and the future plan of work.