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SOLID-STATE REACTIONS OF TALC TOWARD Ni(II) AT HIGH TEMPERATURES

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ABSTRACT

Solid mixtures within the system talc–$x NiCl_2 \cdot 6H_2O$ in molar ratio 1 : x (x = 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared and fired at temperatures of 1000 and 1200 ° C. Investigation of the rapidly cooled coloured reaction products to room temperature was worked out using X-ray diffraction and ligand-field absorption spectrum techniques. The measured diffractograms showed lines related to forsterite phase and enstatite modifications (proto, ortho and clino). In addition, unreacted NiO and traces of Ni_2SiO_4 phases were detected in reaction products obtained at 1000 ° C, whereas cristoballite appeared in abundance in products obtained at 1200 ° C. Spectra results showed, on the other hand, absorption bands characteristic of an octahedrally coordinated Ni^{2+} in enstatite and forsterite lattices, in agreement with X-ray diffraction data. In general, crystallinity and concentration of some resulting phases were observed to increase on increasing firing temperature as well as Ni concentration.

INTRODUCTION

The nature of solid-state reactions occur on heating layer-lattice minerals such as talc, $Mg_3(Si_2O_5)_2(OH)_2$, is of interest since it helps in interpretation of crystal structure as well as in determination of necessary firing temperatures to develop certain desirable properties. Therefore, the majority of the work reported in literature was done primarily on pure mineral samples [1–4], whereas little information is available on reactions associated with the heating of talc together with transition metal compounds, where possibilities exist for formation of different solid solutions. The probable existence of primary ordering that occurs with the development of such solid solutions on a small scale may be established by the characteristic absorption spectra of the corresponding introduced coloured transition cation. A recent study of talc–Co(II) reactions at relatively high temperatures revealed the presence of (Co, $Mg)_2Si_2O_6$ solid solution, together with other phases according to heat treatment and Co concentration [5]. However, some work will have to continue to be done with the thermal behaviour of talc towards other

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transition metal compounds. It is our aim, therefore, to study in this investigation how talc behaves thermally with Ni(II) under the conditions of firing temperature and Ni-concentration effects.

EXPERIMENTAL

The starting materials were a sample of an early purified and chemically analysed Egyptian talc [5] and the chemical product $NiCl_2 \cdot 6H_2O$ (P.A., Riedel-deHäen). Preparation of the different reacting mixtures, heat treatment and measurements of their spectra (X-ray and ligand-field) were done using the same techniques and apparatus described before [5].

RESULTS AND DISCUSSION

Electronic absorption spectra of the reaction products obtained at 1000 ° C are shown in Fig. 1, whereas Fig. 2 shows those of reaction products obtained at 1200 ° C. Figure 3 illustrates the spectra of some related pure synthesized Ni silicates.

Generally, the results of talc–Ni^{2+} reactions could be expected to be analogous to those previously obtained in talc–Co^{2+} system [5], since the performed experimental conditions were the same in both systems. However, there were some distinguishable differences between the two systems which

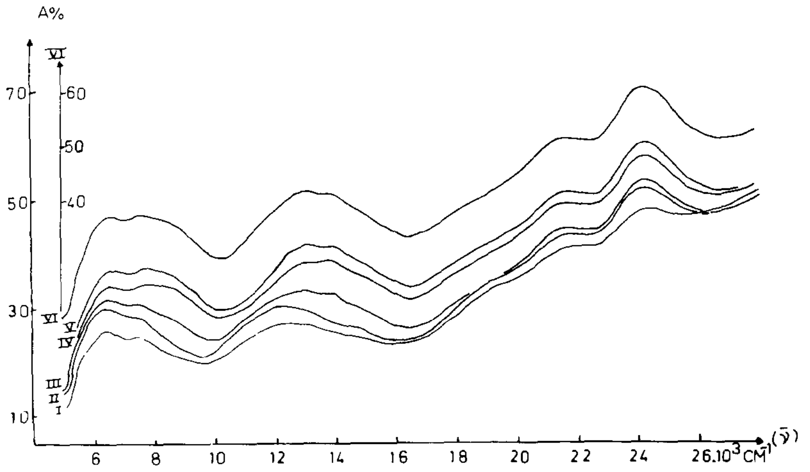

Fig. 1. Electronic absorption spectra of the beige-coloured reaction products in the system talc–$xNiCl_2 \cdot 6H_2O$ treated at 1000 ° C: I, $x = 0.1$; II, $x = 0.2$; III, $x = 0.4$; IV, $x = 0.6$; V, $x = 0.8$; VI, $x = 1.0$.

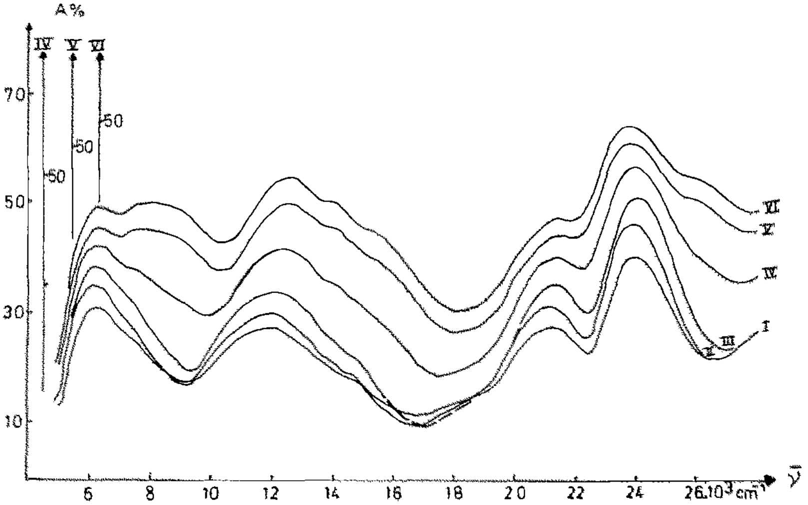

Fig. 2. Electronic absorption spectra of the yellowish, yellowish-green and greenish coloured reaction products in the system talc–xNiCl$_2$·6H$_2$O treated at 1200 °C: I, $x=0.1$; II, $x=0.2$; III, $x=0.4$; IV, $x=0.6$; V, $x=0.8$; VI, $x=1.0$.

appeared: (a) nature of characterized phases in reaction products; (b) saturation limit of Ni^{2+} ions in enstatite; (c) crystallinity and concentration of some resulting phases.

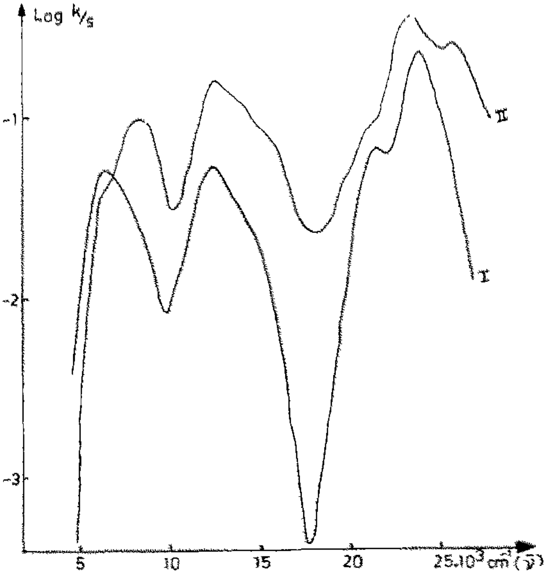

Fig. 3. Electronic absorption spectra of synthesized $Ni_{0.2}Mg_{1.8}Si_2O_6$ (I) and $Ni_{0.6}Mg_{1.4}Si_2O_6$ (II).

From the result of identification processes it seems likely that three phases other than Ni–enstatite are present in reaction products. These additional phases differ obviously in nature according to firing temperature. Whereas NiO, traces of Ni_2SiO_4 and amorphous SiO_2 phases were detected in reaction products treated at 1000 °C, the crystalline phases Ni–forsterite $(Ni, Mg)_2SiO_4$, Ni_2SiO_4 and cristoballite SiO_2 were formed on further heating the reaction products at 1200 °C.

The mechanism of formation of $(Ni, Mg)_2Si_2O_6$ solid solution appears to proceed in similar way to that of $(Co, Mg)_2Si_2O_6$ [5]. However, the saturation limit of $MgSiO_3$ with $NiSiO_3$ (found at about 0.2 mol% Ni^{2+} per mol talc) is lower than that in the case of the talc–Co^{2+} system [5]. This apparent difference in saturation limit may be related to a different distribution of Co^{2+} and Ni^{2+} ions over the two available lattice positions Mg(I) and Mg(II) in enstatite $Mg_2Si_2O_6$ as well as to the effect of such ions on metasilicate formation. Previous spectra results of pure synthesized $Ni_xMg_{2-x}Si_2O_6$ [6] and $Co_xMg_{2-x}Si_2O_6$ [7] systems showed that Ni^{2+} ions prefer to occupy the larger lattice positions M(I) rather than the others, whereas Co^{2+} ions are distributed over the two lattice positions. On the other hand, it was reported that the presence of Ni^{2+} ions lowered the formation of metasilicate but highly increased the stability of orthoenstatite phase [8]. The present low estimated saturation limit seems accordingly to agree with the behaviour of Ni^{2+} ions in prefering to occupy only one lattice position and also in lowering metasilicate formation.

Moreover, the orthophase in the resulting $(Ni, Mg)_2Si_2O_6$ enstatite was observed to increase in comparison with the analogous phase in $(Co, Mg)_2Si_2O_6$ enstatite [5]. Such a result is in agreement with previous investigation [8] studying the effect of Ni^{2+} and Co^{2+} ions on the stability of orthoenstatite phase, where Ni^{2+} ions appeared to be more effective than Co^{2+} ions.

Apart from the phase $(Ni, Mg)_2Si_2O_6$ which is formed and identified along the whole series of reaction mixtures at the two firing temperatures, additional phases appeared on increasing Ni concentration (x mol%), which were promoted to go into further reactions, markedly at a temperature of 1200 °C.

At a firing temperature of 1000 °C and in the concentration range of $x = 0.4$–1.0, two additional phases NiO (increased on increasing x) and Ni_2SiO_4 (in trace according to the reaction: $2NiO + SiO_2 \rightarrow Ni_2SiO_4$) were identified. At a firing temperature of 1200 °C the additional phases were identified as cristoballite SiO_2, in all reaction products, Ni_2SiO_4 (at $x = 0.4$) and Ni forsterite $(Ni, Mg)_2SiO_4$ (at $x = 0.6$–1.0), but in varying concentrations according to variation in Ni concentration. As a result of the formation of the phases Ni_2SiO_4 (in trace) and $(Ni, Mg)_2SiO_4$ (increased on increasing Ni concentration), one would expect a change in SiO_2 concentration. Actually, a decrease and an increase in SiO_2 concentration were observed at the formation of the Ni_2SiO_4 and $(Ni, Mg)_2SiO_4$ phases, respectively. This observation is understandable if one assumes the following occurring reactions:

$$2NiO + SiO_2 \rightarrow Ni_2SiO_4 \tag{1}$$

$$(Ni, Mg)_2Si_2O_6 + Ni_2SiO_4 + 2MgSiO_3 + SiO_2 \rightarrow 3(Ni, Mg)_2SiO_4 + 3SiO_2 \tag{2}$$

The second reaction seems to take place after a probable increase in the concentration of the $(Ni, Mg)_2Si_2O_6$ and Ni_2SiO_4 phases in the range of $x = 0.6–1.0$. Thus, accordingly, disappearance of this probable increase of these two phases accompanied by an increase of both the phases Ni forsterite and cristoballite could be observed. In fact, results of identification processes confirmed such expected concentration changes of reactants and products.

It was reported, however, that on increasing Ni concentration during synthesis of Ni enstatite of composition $Ni_{0.6}Mg_{1.4}Si_2O_6$, within the pure oxidic system $xNiO \cdot 2 - xMgO \cdot 2SiO_2$, two phases, Ni forsterite $(Ni, Mg)_2SiO_4$ and cristoballite SiO_2, were identified [6]. Investigation of spectra of the resulting Ni^{2+}-containing reaction products (Figs. 1 and 2), on the other hand, showed, generally, three main absorption bands characteristic of an octahedrally coordinated Ni^{2+} ion which could be assigned to:

$$\left.\begin{array}{lll} \mathrm{I} & {}^3A_{2g}\,(F) \rightarrow & {}^3T_{2g}\,(F) \\ \mathrm{II} & \rightarrow & {}^3T_{1g}\,(F) \\ \mathrm{III} & \rightarrow & {}^3T_{1g}\,(P) \end{array}\right\downarrow \quad \bar{\nu}\mathrm{cm}^{-1}$$

According to such an assignment [9], a comparison between band position of known related Ni^{2+}-containing host lattices such as $Ni_{0.2}Mg_{1.8}Si_2O_6$ (Fig. 3 [6]), $Ni_xMg_{2-x}SiO_4$ [10], Ni_2SiO_4 [11], NiO [12] and that of the present talc–Ni^{2+} system products could be achieved.

The spectra obtained after firing at 1000 °C (Fig. 1) showed the formation of:

(a) Ni enstatite $(Ni, Mg)_2Si_2O_6$ (main maxima: I, 6500–7500 cm^{-1}; II, 12750 cm^{-1}; III, 24250 cm^{-1} and a shoulder (21600 cm^{-1}) (Fig. 1 and Fig. 3, curve I);

(b) olivine phase Ni_2SiO_4 in trace (main maxima: I, 7500 cm^{-1}; II, 12400 cm^{-1}; III, 24000 cm^{-1} and a shoulder (21000 cm^{-1}) [11] and

(c) appearance of NiO at 0.4–1.0 mol% Ni^{2+} (main maxima: I, 7500 cm^{-1}; II, wide maximum with middle point at 14000 cm^{-1} and III, 24000 cm^{-1} [12]).

It is obvious that absorption bands of Ni enstatite at 0.1–0.2 mol% Ni^{2+} began to change their general shape and maxima positions due to high density of NiO and probably due to the olivine phase. An increase of intensity of absorption bands of Ni enstatite and NiO was also observed in the ranges 0.1–0.2 and 0.4–1.0 mol% Ni^{2+}, respectively. The constant minima positions at 16500 cm^{-1} (Fig. 1) are in accordance with the remaining unchanged beige colour of all reaction products.

The spectra measured after further firing the reaction mixtures at 1200 ° C (Fig. 2) are well defined and showed higher intensity than those obtained at 1000 ° C. In general, the three characteristic absorption bands and a shoulder of Ni^{2+} in the enstatite phase $(Ni, Mg)_2Si_2O_6$ could be located at all Ni concentrations (Figs. 1, 2 and 3, curve I). However, appearance of new absorption bands, difference in band structure and a slight shift of maxima and minima position towards IR or UV regions could be clearly seen at 0.6–1.0 mol% Ni^{2+} (Fig. 2). The appearance of three other maxima at about 8000 (broad) 12250–12500 and 23800–24000 cm^{-1}, together with a shoulder at 26200 cm^{-1} indicated the formation of an additional coloured phase which could be safely identified as Ni forsterite $(Ni, Mg)_2SiO_4$. This identification is based simply on a comparison between the obtained spectra and those of pure synthesized Ni forsterite $(Ni, Mg)_2SiO_4$ (maxima: 8500, 12600 and 23500 cm^{-1} and a shoulder at 26000 cm^{-1} [10] and $Ni_{06}Mg_{1.4}Si_2O_6$ [6], where two phases, Ni forsterite and cristoballite, were formed and characterized (Fig. 3, curve II). The presence of Ni_2SiO_4 in trace at 0.4 mol% Ni^{2+}—as estimated by X-ray analysis—seems not to affect the spectra considerably (Fig. 2, curve III).

The colour of the reaction products changed from yellowsih, yellowish green to greenish which may be correlated to an increase of Ni forsterite concentration. This gradual change in colour agrees well with the observed shift of the minimum at 16800 cm^{-1} towards the UV region at 18200 cm^{-1}. It is evident that the experimental results of both absorption spectra and X-ray analysis methods confirm each other.

In conclusion, the most significant results of the present work which differ from those of talc–Co system [5] are:

(1) NiO seems to promote crystallization process at increasing temperature and Ni concentration since the crystallinity of the characterized phases (in the sense of an increase of their corresponding diffracted lines) increased.

(2) Unreacted NiO in reaction products at $x = 0.4$–1.0 mol% Ni^{2+} and 1000 ° C was detected.

(3) Low saturation limit of $MgSiO_3$ with $NiSiO_3$ (at about 0.2 mol% Ni^{2+}), within the solid solution $(Ni, Mg)_2Si_2O_6$, where the orthophase is more stable.

(4) Olivine phase, Ni_2SiO_4, which was detected in trace, appeared not to react further with free SiO_2 to give $2NiSiO_3$ even at 1200 ° C.

(5) High concentrations of cristoballite SiO_2 and Ni forsterite $(Ni, Mg)_2SiO_4$ were estimated in reaction products on increasing Ni concentration and at 1200 ° C.

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