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Formation of spinel from hydrotalcite-like minerals and destruction of chromite implanted by inorganic salts

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Abstract

Thermal decomposition of natural hydrotalcites (HT) and the role of hydrotalcite-like materials in the destruction of solid with a spinel-type structure, after grinding with solid phase Na_2CO_3 additives, are investigated by means of infrared (IR) spectroscopy and X-ray powder diffraction (XRD) methods. The thermal treatment of hydrotalcite results in intermediates with contents and structures, which essentially depends on impurities in natural samples, conditions of treatment, as well as the environment. In this study, chromite implanted by inorganic salts is used to illustrate the influence of the mechanical activation of the process to convert spinel to hydrotalcite-like structures. It has been found that the small concentration (4 wt.%) of solid-phase admixture, implanted in the layers near the surface, is favorable for enhancement of the structural changes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: hydrotalcite; spinel; destruction; infrared spectra

1. Introduction

Hydrotalcite (HT), $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ is a hydrated hydroxycarbonate of magnesium and aluminum with a modified brucite-like structure in which the cations occupy the octahedral position (Allman and Jepsen, 1969; Dritz et al., 1987; Arakcheeva et al., 1996). Hydrotalcite-like materials, which can be represented by the general formula:

$$\left[M_{1-x}^{2+} M_x^{3+} (OH)_2 \right]^{x+} A_{x/n}^{n-} mH_2O,$$
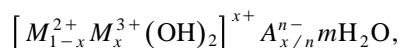
where $M^{2+} = Mg^{2+}$, Ni^{2+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}; $M^{3+} = Al^{3+}$, Fe^{3+}, Cr^{3+}, Ga^{3+}; x is atomic ratio of $M^{3+}/(M^{2+} + M^{3+})$; $A^{n-} = F^-$, Cl^-, ClO_4^-, OH^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, organic or complex anion, form a large group of natural and synthetic clay minerals (Dritz et al., 1987; Aramendia et al., 1999; Hansen and Poulsen, 1999; Hernandes-Moreno et al., 1985; Titulaer, 1993; Bail et al., 1987; Kloprogge and Frost, 1999a,b). A charge deficiency in the positively charged layer of

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di- and trivalent metal hydro-oxides is compensated by hydrated anions in the interlayer region. Hydrotalcites find applications as antacid or antipeptin in pharmaceutical chemistry, as a catalyst support, flame retardant, absorbing agent and anion exchanger, stabilizers for polymers, separator of optical isomers, etc. The catalytic significance of these layered double hydroxides lies in the ease with which the composition of the cations and anions can be controlled.

In recent years, the hydrotalcite–spinel conversion has been widely discussed (Mackenzie et al., 1993; Hibino and Tsunashima, 1997; Valcheva-Traykova et al., 1993; Kloprogge and Frost, 1999a,b). It is known that natural hydrotalcite (as well as phlogopite, pargasite, amesite) is a product of the magnesian skarn transformation, during which spinel and fassaite play a role as a source of Al_2O_3 (Kolesnikova, 1980; Shabinin, 1973; Strubel and Zimmer, 1982). According to the last authors, hydrotalcite is a product of spinel transformation (Strubel and Zimmer, 1982). On the other hand, the hydrotalcite thermal decomposition may result in the spinel formation (Mackenzie et al., 1993; Hibino et al., 1995; Hibino and Tsunashima, 1997, 1998; Valcheva-Traykova et al., 1993; Braithwaite et al., 1994; Kloprogge and Frost, 1999a,b; Aramendia et al., 1999). Such a process was detected by Mackenzie et al. (1993) at 1200°C for hydrotalcite synthesised with a $Al/(Al + Mg)$ ratio of ≈ 0.36. For hydrotalcite with a ratio $Al/(Al + Mg)$ of ≈ 0.33, this temperature was above 800°C (Hibino et al., 1995). Calcination at 800°C leads to samples with powder X-ray diffraction peaks due to ZnO and a spinel (Barriga et al., 1999). Infrared emission spectroscopy indicate spinel, $MgAl_2O_4$, formation at 350–400°C $(Al/(Al + Mg) = 0.25)$, $CoAl_2O_4$ at 300–350°C for $Al/(Co + Al) = 0.25$ (Kloprogge and Frost, 1999a,b). The transformation of reconstructed $Mg–Al–CO_3$ hydrotalcites with only 55–70% of carbonate anions required by stoichiometry to spinel at 400°C is the result of a reaction occurring between the edges of crystallites (Hibino and Tsunashima, 1997, 1998). After thermal decomposition of Mg–Al hydrotalcites, MgO, and Al_2O_3 (various modifications) are also observed depending on the calcination temperature, the initial hydrotalcite content, impurities and by-products in samples (Valcheva-Traykova et al., 1993). "Memory effect" of hydrotalcite, which

allows the original material to reconstitute upon contact with water or water vapor, disappears for $T > 400$°C (Sychev et al., 2001).

In the present work, the hydrotalcite-like mineral–spinel structure transformation has been studied for minerals from Ural, Angara-Ilim and Khabarovsk region (East Siberia, Russia). For reference, the transformation of the spinel-like mineral chromite was included in this study. In addition to calcination, the effects of other factors, such as chemical and mechanochemical treatment are also considered.

2. Experimental

The samples of hydrotalcite-like minerals from different Russian deposits, namely, hydrotalcites, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, from Angaro-Ilim (I), Ural (II); hydrotalcite–serpentine from Khabarovsk region (III); iowaite, $Mg_6Fe_2(OH)_{16}Cl_2 \cdot 4H_2O$, from Talnakh (Norilsk region) (Palchik et al., 1996) and iowaite from the Korshunovsk deposit, Siberian platform; and samples of chromite from Khabarovsk region are studied. To characterize the changes in the crystal structure and phase composition of the samples, the X-ray powder diffraction (XRD), infrared (IR), and Raman spectroscopy methods are used (Moroz and Arkhipenko, 1991, 1993).

XRD patterns were recorded by means of DRON-UM-1 X-ray diffractometer. CuK_α radiation was used as the X-ray source. Recorded diffraction lines were indexed with respect to the JCPDS powder data files. The diffractograms of samples after heat treatment in air were recorded at room temperature.

Infrared spectra were recorded on the Specord 75 IR, Karl Zeiss, Jena and SP3-300, Pye-Unicam spectrophotometers. Samples of 1.8 mg were embedded in spectro-pure KBr in vacuum.

The modeling process of chromite destruction was carried out by laboratory centrifugal mills, which have chemical inactive containers.

Surface areas were measured by the Brunauer–Emmett–Teller (BET) method with argon. After mechanical activation of solid inorganic salts saturated chromite, its particles have been dissolved layer by layer in diluted (1:3) hydrochloric acid. Cr^{3+} and Fe^{3+} ions were determined in the solution by atomic absorption method using a SP-9 device of the firm

Pye-Unicam. The precipitates were characterized by means of X-ray analysis and IR spectroscopy.

The X-ray diffraction patterns indicate the presence of hydrotalcite with chlorite, magnetite (II), and serpentine (III) as the major impurities. Sample III differs considerably from those of I and II in contents of H and C atoms as well as in content of main cations and contains a mixture (50/50) of HT and serpentine (orthochrysotile and lizardite). According to the spectral analysis data, all the samples contain Mn, Ti, and Fe ($< 0.3\%$), i.e. there is a possibility of cationic isomorphous replacement of Mg and Al in the HT structure by Mn, Ti, or Fe. The sample of HT (I) has a $Al^{3+}/(Mg^{2+} + Al^{3+})$ chemical ratio of 0.28. The samples of iowaite from Talnakh and Korshunovsk deposit have a $Fe^{3+}/Mg^{2+} + Fe^{3+}$ chemical ratio of about 0.24 and 0.17, respectively. Microprobe analysis of chromite gives: Cr_2O_3—49.7, FeO—35.04, Al_2O_3—4.97, MgO—3.49, TiO_2—0.69, MnO—0.34, NiO—0.04 wt.%.

Unfortunately, in many cases, the realization of each method is made difficult by specific peculiarities of the materials under study (small amounts, luminescence background, X-ray amorphous phases, etc.).

3. Results and discussion

The hydrotalcite IR spectra demonstrate that the interlayer arrangement can be easily characterized by the molecular vibration of anions CO_3^{2-} and OH^- bonds (Hernandes-Moreno et al., 1985; Moroz and Arkhipenko, 1991). A lowering in the interlayer site symmetry leads to splitting and shifting the characteristic frequencies (Fig. 1, curve 1). The CO_3^{2-} ν_3-band in hydrotalcite is observed at around 1370 cm^{-1} with a shoulder at 1400 cm^{-1}. The 1370 cm^{-1} band intensity allows one to determine the carbonate content (Moroz and Arkhipenko, 1991, 1993).

For some natural hydrotalcites, the thermal decomposition was studied. As follows from IR spectra, the structure of the obtained product depends on the heating regime (Figs. 1 and 2). After heating at 250°C, the ν_3 band splits into the two lines at around 1355 and 1526 cm^{-1} (Fig. 2, curve 2), which have been previously found for a bridged bidentate CO_3^{2-}
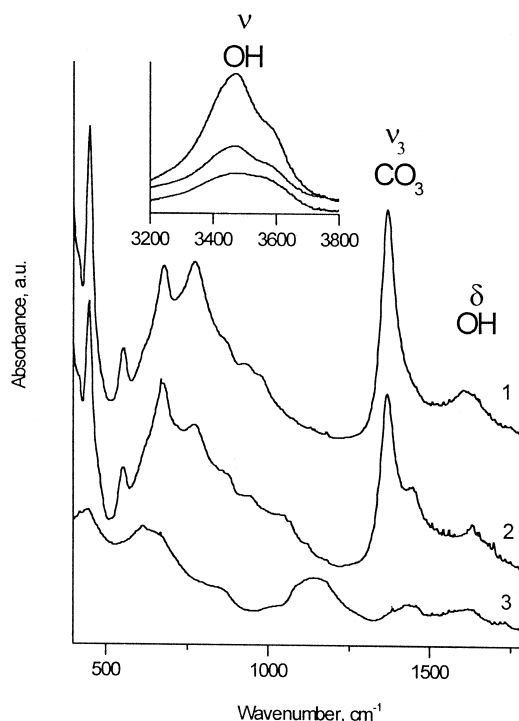

Fig. 1. IR spectrum of hydrotalcite from Angara-Ilim (East Siberia, Russia) (1) after heating at 250°C in KBr pellet (2) and heating at 600°C in air for 14 h (3).

complex (Hibino et al., 1995). This band splits into the three lines at 1360, 1418 and 1518 cm^{-1} after heating at 250°C for 5 h (Fig. 2, curve 3). After heating at 250°C in KBr pellet, the CO_3^{2-} ν_3 two bands are recorded at 1368 and 1448 cm^{-1} for the Angara-Ilim hydrotalcite (Fig. 1, curve 2). After heating at 600°C for 14 h, the bands of MgO and spinel appear (Fig. 1, curve 3).

X-ray diffraction patterns show the dynamics of change in the CO_3^{2-}–H_2O interlayer space of the hydrotalcite in the hydrotalcite–serpentine sample (Fig. 3). After heating on air, the d_{003} and d_{006} reflections decrease from 7.71 and 3.84 to 6.60 and 3.64 Å (Fig. 3, curve 2), but these reflections increase to 8.60 and 4.31Å (Fig. 3, curve 3) after heating in an autoclave in H_2O ($T = 300°C$, 24 h). After autoclaving for 48 h, gibbsite (g) is detected (Fig. 3, curve 4). The 6.60 and 5.52 Å reflections are observed for the Ural hydrotalcite after heating ($T = 250°C$, 5 h), the 5.52 Å reflection being absent in hydrotalcite–serpentine sample. The loss of the in-
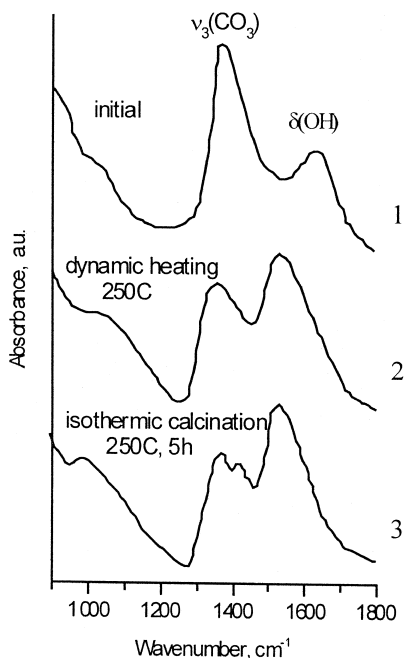
Fig. 2. IR spectra of hydrotalcite from Ural (Russia) obtained after heat treatment of the samples (1) original, (2) 250°C for 1 min and (3) 250°C for 5 h.

tercalated water molecules is accompanied by a decrease in the (003) repeat distance from 7.59 to 6.60 Å for a synthetic hydrotalcite-like material up to 240°C (Pesic et al., 1992). In the temperature range 300–600°C, hydrotalcites are X-ray amorphous. In this region, the structural transformation is controlled by IR spectroscopy. The hydrotalcite–serpentine sample heated up to 1000°C transform into a product containing forsterite (f), enstatite (e), spinel (s), and corundum (c) (Fig. 3, curve 5). Thus, only traces of spinel are detected for this sample after 1000°C treatment.

Thermal treatment induces the transformation of iowaite, $Mg_6Fe_2(OH)_{16}Cl_2 \cdot 4H_2O$, into a product containing periclase and minerals with spinel structure: magnetite at 570°C and magnesioferrite at 1000°C for iowaite with a ratio $Fe/(Fe + Mg)$ of about 0.24 (Mazurov et al, 2000); periclase and magnetite above 400°C ($Fe/(Fe + Mg) \approx 0.215$) (Kohls and Rodda, 1967); MgO and magnesioferrite, $MgFe_2O_4$, at 400°C ($Fe/(Fe + Mg) \approx 0.26$) (Braithwaite et al., 1994). The infrared spectrum of iowaite from Talnakh with a ratio $Fe/(Fe + Mg)$ of

≈ 0.2 shows the OH-stretching absorption band with a maximum near 3400 cm^{-1} and H–O–H deformation band with a maximum near 1630 cm^{-1} (Fig. 4, curve 1). At 500°C, this bands disappear (Fig. 4, curve 2, 3). New bands are observed around 430 and 585 cm^{-1}, which indicate magnesioferrite, $MgFe_2O_4$, formation.

In order to shed some light on the origin of hydrotalcite materials encountered in nature in the vicinity of spinel, where it is believed to protect the spinel phase from tectonic deformations, a sample of chromite was subjected to treatment with inorganic salts in a planetary mill.

Mechanical explosion on solids causes their structure to be significantly changed. These changes are characterized by arising new inner interfaces as well as dislocations and various modes of point defects. The small concentrations of inorganic salt implanted in the layers near the surface are favourable for enhancement of structural changes (Rebinder et al., 1944, 1948; Rebinder, 1966). In the present work,
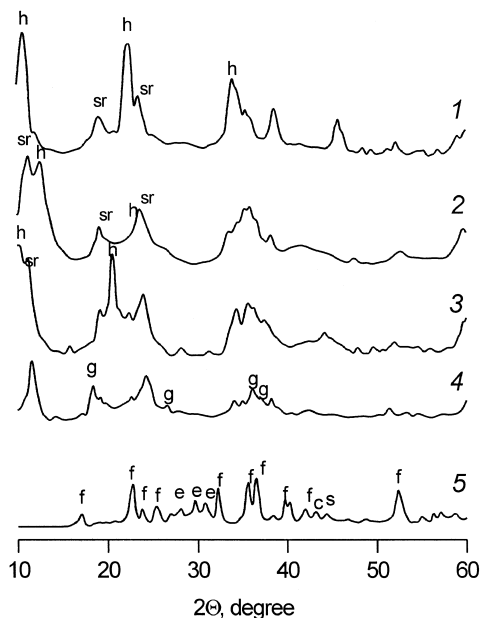

Fig. 3. Powder X-ray diffraction patterns of hydrotalcite–serpentine from Khabarovsk region (East Siberia, Russia) obtained after heat treatment of the samples (1) original; (2) at 260°C for 5 h, after heating at 300°C in an autoclave in H_2O; (3) 24 h; (4) 48 h; (5) 1000°C; h—hydrotalcite, sr—serpentine, f—forsterite, e—enstatite, s—spinel, c—corund, g—gibbsite.
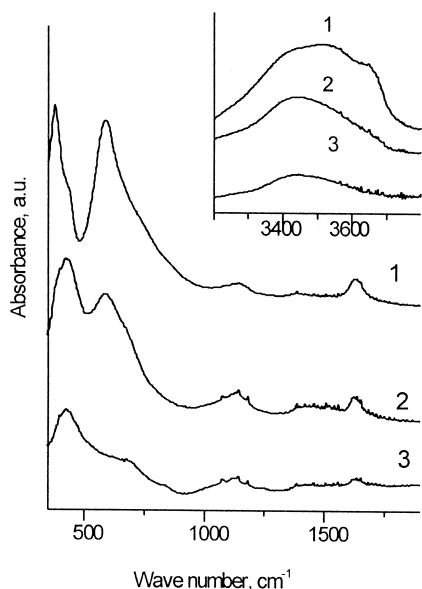
Fig. 4. IR spectra of iowaite from Talnakh (Russia) obtained after heat treatment of the samples (1) original, (2) 500°C for 1 min and (3) 500°C 2 h.

the structural changes of chromite, as the most stable mineral to mechanical and chemical explosions, were investigated. A planetary mill was used. When dissolving the mineral particles layer by layer, the relationship between the sizes of coherent dispersion blocks (CDB) as well as microdistortions (MD) and the depth of the layer near the surface has been established (Fig. 5). The size of the coherent dispersion blocks depends on the type of inorganic salt added. Among salts used ($(NH_4)_2HPO_4$, NaCl, NH_4Cl, Na_2CO_3), a destruction maximum was found for Na_2CO_3 at 4% concentration for 5–10 min grinding. The dependence of chromite solubility in HCl after grinding with water and different ammonium salts (chloride, carbonate and hydrophosphate) on the grinding time is given in Kornev and Razvorotneva (1998). Excepting $NH_4H_2PO_4$, the other salts intensify the fracture process.

For the mechanically treated chromite, the appearance of additional vibrational frequencies in the IR spectra indicated the formation of new complexes "surface addition" (Fig. 6). The stretching internal modes of carbonate ions were recorded at 1375 and 1510 cm^{-1}. The first of these bands is inherent to the hydrotalcite-like compounds (Hashi et al., 1983;

Gadsden, 1975; Hernandes-Moreno et al., 1985; Moroz and Arkhipenko, 1991; White, 1974). The observed bands differ from IR ν_3 CO_3^{2-} bands of iron (Fe^{2+}) carbonate or chromium (Cr^{3+}) carbonate, which have maximum at 1460 or 1466 cm^{-1}, respectively (Ross and Goldshmith, 1964; White, 1974), and 1438 cm^{-1} (siderite) (Gadsden, 1975). IR bands of HT-like compounds have maximum at 1370 (strong), 1515(medium) (stichtite) and 1360 cm^{-1} (pyroaurite). At the same time, the coexistence of these two modes is usually associated with bridged bidentate CO_3 complexes, which formation is typical of the hydrotalcite decomposition products (see above). At mechanical treatment, the maximum of the chromite solubility was observed for 4% of Na_2CO_3 (Fig. 7). That correlates closely with the data of the IR measurements, which detected the maximal changes in the chromite structure for such a solid-phase admixture concentration (Fig. 6b). Fig. 7 (curve (○)) shows that increase in the concentration of the additive leads to a strong reduction of the chromite specific surface, which adequately influences the efficiency of the solution. As can be seen, the BET surface areas grow from 2.3 m^2/g for 5 min grinding chromite without salt to 15.8 m^2/g for 5 min grinding chromite with 4 wt.% Na_2CO_3. Post-grinding powder particles have cracks (Kornev
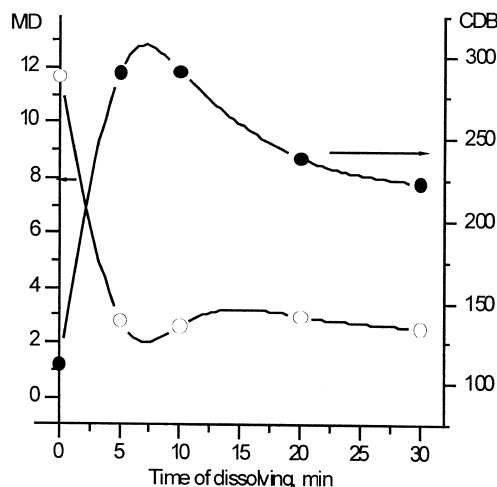

Fig. 5. The relationship between the sizes of coherent dispersion blocks (CDB) (●) and microdistortion (MD) (○) with time of dissolving the mineral particles layer by layer near surface for chromite with 4 wt.% Na_2CO_3 addition.

and Razvorotneva, 1998). HCl molecules penetrate through cracks into particles and there occurs a selective chromite dissolution. The presence of the maximum on the solubility curve suggests that the additive, with which chromite is ground, may cause both an increase and a decrease in the chromite solubility (Fig. 7, curve (▼)). IR spectra allow to control the amount of hydrotalcite-like compounds and its decomposition products in the X-ray amorphous region. X-ray powder diffraction patterns show a low intensity background signal in the region from
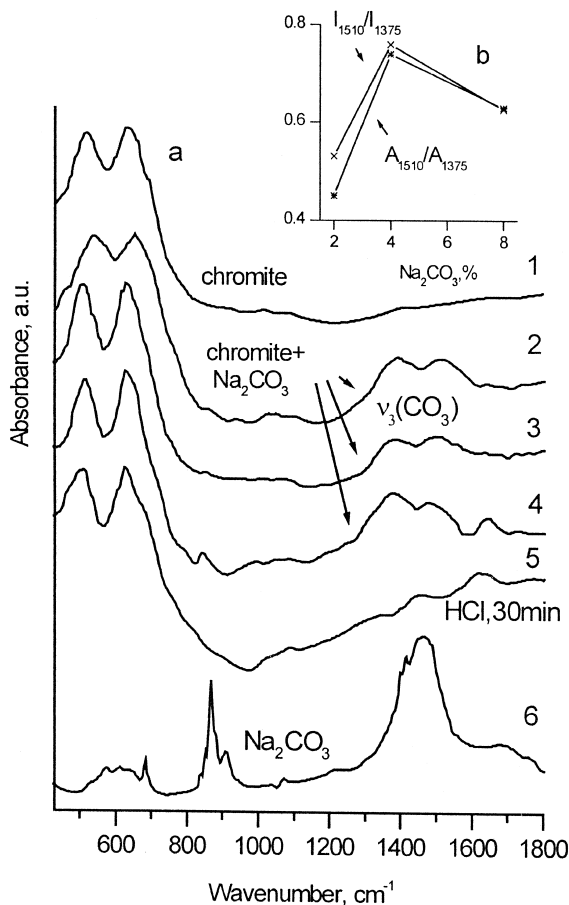

Fig. 7. Relationship between solubility (▼) (specific surface (○)) of chromite (after mechanical treatment for 5 min) with different amounts of solid Na_2CO_3.

$10°$ to $25°$ $2\theta(CuK_\alpha)$. The method of sample preparation can be used for determining platinum group elements (Tsimbalist et al., 1999). This method combines the mechanical activation of the sample with the introduction of a solid-phase inorganic salt (4%). In this way, we can intensify decomposition of the most stable mineral to mechanical and chemical explosions.

4. Conclusions

The hydrotalcite–spinel conversion is a rather complicated process, which is accompanied by the formation of various intermediate products depending on many static and kinetic factors. So in this paper, it has been demonstrated that the nature of the products resulting from the thermal decomposition of hydrotalcite-like minerals depends on the presence of impurities as well as the environment and the conditions of the applied heat treatment (temperature, pressure, heating program).

We have used chromite to illustrate the influence of the mechanical activation on the return process from the spinel to hydrotalcite-like structure. Infrared spectra indicated the formation of both hydrotalcite-like and hydrotalcite destruction phases in the resulting material. This phenomenon enhanced destruction of chromite and raised its solubility. Small amount of surface-bound solid-phase inorganic salts has been found to facilitate structural transformation upon mechanical and chemical treatment.

Fig. 6. (a) IR spectra of chromite after 10 min mechanical treatment (1) with 2 wt.% (2), 4 wt.% (3), 8 wt.% solid Na_2CO_3 (4), respectively. IR spectrum of chromite after 10 min mechanical treatment with 4 wt.% solid Na_2CO_3 have been dissolved in HCl (5). IR spectrum of Na_2CO_3 (6). (b) The results of the band component analysis of the ν_3 carbonate stretching region of the IR spectra (this figure, curves 2, 3, 4) of treatment chromite with Na_2CO_3 additions.
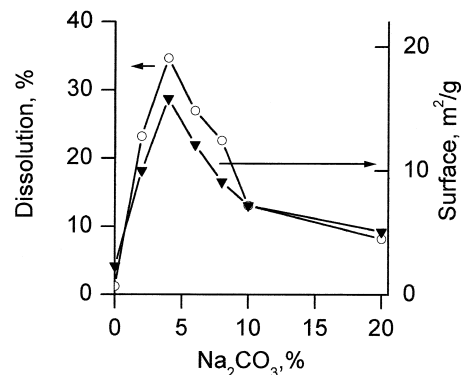
References

Allman, R., Jepsen, H.P., 1969. Structure of hydrotalcite. Neues Jahrb. Mineral., Monatsh. 12, 544–551, (in German, with English abstract).

Arakcheeva, A.V., Puscharovskii, D.U., Rastsvetaeva, R.K., Antensio, D., Lubman, G.U., 1996. Crystal structure and comparative crystal chemistry of $Al_2Mg_4(OH)_2(CO_3)\cdot 3H_2O$, a new mineral from the hydrotalcite–manasseite group. Crystallogr. Rep. 41, 972–981.

Aramendia, M.A., Aviles, Y., Benitez, J.A., Borau, V., Jimenez, C., Marinas, J.M., Ruiz, J.R., Urbano, F.J., 1999. Comparative study of Mg/Al and Mg/Ga layered double hydroxides. Microporous Mesoporous. Mater. 29, 319–328.

Bail, C., Thamassin, J.H., Touray, J.C., 1987. Hydrotalcite like solid solutions with variable SO_4^{2-} and CO_3^{2-} contents at 500°C: an X-ray diffraction and Raman spectrometry study. Phys. Chem. Miner. 14, 377–382.

Barriga, C., Crespo, I., Ulibarri, M.A., Malet, P., Rives, V., 1999. An X-ray diffraction and absorption study of the phases formed upon calcination of Zn–Al–Fe hydrotalcites. Abstracts of Euroclay'99 Conference. 59.

Braithwaite, R.S.W., Dunn, P.J., Pritchard, R.G., Paar, W.H., 1994. Iowaite, a re-investigation. Mineral. Mag. 58, 79–85.

Dritz, V.A., Sokolova, T.N., Sokolova, G.V., Cherkashin, V.I., 1987. New members of the hydrotalcite–manasseite group. Clays Clay Miner. 35, 401–417.

Gadsden, J.A., 1975. Infrared Spectra of Minerals and Related Inorganic Compounds. Butterworths, Chichester, 277 pp.

Hansen, H.C.B., Poulsen, I.F., 1999. Interaction of synthetic sulphate "green rust" with phosphate and the crystallization of vivianite. Clays Clay Miner. 47, 312–318.

Hashi, K., Kikkawa, S., Koizumi, M., 1983. Preparation and properties of pyroaurite-like hydroxy minerals. Clays Clay Miner. 31, 152–154.

Hernandes-Moreno, M.J., Ulibarry, M.A., Rendon, J.L., Serna, J.C., 1985. IR characteristics of hydrotalcite-like compounds. Phys. Chem. Miner. 12, 34–38.

Hibino, T., Tsunashima, A., 1997. Formation on spinel from a hydrotalcite-like compound at low temperature: reaction between edges of crystallites. Clays Clay Miner. 45, 842–853.

Hibino, T., Tsunashima, A., 1998. Characterization of repeatedly reconstructed Mg–Al hydrotalcite-like compounds: gradual segregation of aluminum from the structure. Chem. Mater. 10, 4055–4061.

Hibino, T., Yamashita, Y., Kosuge, K., Tsunashima, A., 1995. Decarbonation behavior of Mg–Al–CO$_3$ hydrotalcite like compounds during heat treatment. Clays Clay Miner. 43, 427–432.

Kloprogge, J.T., Frost, R.L., 1999a. Infrared emission spectroscopic study of the thermal transformation of Mg-, Ni- and Co-hydrotalcites. Appl. Catal., A 184, 61–71.

Kloprogge, J.T., Frost, R.L., 1999b. Infrared emission spectroscopic study of the dehydroxylation of synthetic Mg/Al and Mg/Zn/Al-hydrotalcites. Phys. Chem. Chem. Phys. 1, 1641–1648.

Kohls, D.W., Rodda, J.L., 1967. Iowaite, a new hydrous magnesium hydroxide–ferric oxychloride from the precambrian of Iowa. Am. Mineral. 52, 1261–1271.

Kolesnikova, T.A., 1980. The rare spinel, climogumite and manasseite of Kuchimon deposit (Pamir). In: Petrov, V.P. (Ed.), Precious and Colour Stones. Science, Moscow, pp. 181–199, (in Russian).

Kornev, V.M., Razvorotneva, L.I., 1998. Brittle fracture of cracked solids as affected by surfactants. In: Carpinteri, A., Brebbia, C.A. (Eds.), Damage and Fracture Mechanics: Computer Aided Assessment and Control. Computational Mechanics Publications, Southampton, pp. 565–574.

Mackenzie, K.J.D., Meinhold, R.H., Sherriff, B.L., 1993. [27]Al and [25]Mg solid-state magic-angle spinning NMR study of hydrotalcite and its thermal decomposition sequence. J. Mater. Chem. 3, 1263–1269.

Mazurov, M.P., Korneva, T.A., Zhitova, L.M., Istomin, V.E., Palchik, N.A., Stolpovskaya, V.N., Titov, A.T., 2000. Iowaite from the Korshunovsk deposit (Siberian platform). Proc. Russ. Mineral. Soc. 129, 80–85, (in Russian).

Moroz, T.N., Arkhipenko, D.K., 1991. The crystal-chemical study of natural hydrotalcites. Sov. Geol. Geophys. 2, 52–58.

Moroz, T.N., Arkhipenko, D.K., 1993. Estimation hydrotalcite in serpentinites by X-ray and infrared spectroscopy. Acta Crystallogr., Sect. A 49, C-276.

Palchik, N.A., Ryabov, V.V., Stolpovskaia, V.N., Shevko, A.Ya., 1996. Iowaite from Talnakh (Norilsk region, Russia). Regularities of Evolution of the Earth Crust St.-Peterburg vol. 2, p. 281.

Pesic, L., Salipurovic, S., Marcovic, V., Vucelic, D., Kagunya, W., Jones, W., 1992. Thermal characteristics of synthetic hydrotalcite. J. Mater. Chem. 2, 1069–1073.

Strubel, G., Zimmer, S.H., 1982. Lexicon of Mineralogy. Ferdinand Enke Verlag, Stuttgart, 494 pp. (in German).

Sychev, M., Prihod'ko, R., Erdmann, K., Mangel, A., Santen, R.A., 2001. Hydrotalcites: relation between structural features, basicity and activity in the Wittig reaction. Appl. Clay Sci. 18, 103–110, (this issue).

Rebinder, P.A., Schreiner, L.A., Zhigach, S.F., 1944. Hardness Reducers in Rock Drilling. Academy of Science, USSR, Moscow, (in Russian).

Rebinder, P.A., Schreiner, L.A., Zhigach, S.F., 1948. Hardness Reducers in Rock Drilling. C.S.I.R.O. (translation, Melbourne).

Rebinder, P.A., 1966. In: Rebinder, P.A. (Ed.), Physicochemical Mechanics of Dispersion Structures. Science, Moscow, 400 pp. (in Russian).

Ross, S.D., Goldshmith, J., 1964. Factors affecting the infrared spectra of planar anions with D_{3h} symmetry—I. Carbonates of the main group and the first row transition elements. Spectrochim. Acta, Part A 20, 781–784.

Shabinin, L.I., 1973. Formation of Magnesian Skarns. Science, Moscow, 214 pp. (in Russian).

Titulaer, M.K., 1993. Porous structure and particle size of silica and hydrotalcite catalyst precursors. Geol. Uitraiectina 99, 207–267.

Tsimbalist, V.G., Razvorotneva, L.I., Anoshin, G.N., Yusupov, T.S., 1999. Problem of chromite dissolution in the determination of platinum-group elements. J. Anal. Chem. 54, 913–917.

Valcheva-Traykova, M.L., Davidova, N.P., Weiss, A.H., 1993. Thermal decomposition of Mg, Al-hydrotalcite materials. J. Mater. Sci. 28, 2157–2162.

White, W.B., 1974. The carbonate minerals. In: Farmer, V.C. (Ed.), The Infrared Spectra of Minerals. Mineralogy Society, London, pp. 227–284, Chap. 12.