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ON THE DEHYDRATION ENTHALPIES OF SOME BETA-ALUMINAS

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The energetics of the dehydration reaction of single crystal (Na, Na 50%–Li, Li) and ceramic Na beta-aluminas have been studied.

From the dependence of the dehydration enthalpy values on the water content it has been deduced that lattice water can be bound in two different ways i.e. by ion-dipole interactions with conducting cations and by hydrogen bonds with spinel block oxygens. As expected, the first one gives binding energies depending on the nature of the monovalent cation ($\Delta H = 84.5$ and 59.4 kJ/mol H_2O for Li and Na beta-alumina respectively). In contrast, the enthalpy change associated with the second one is identical for the three beta-aluminas ($\Delta H = 15.1$ kJ/mol H_2O). The ceramic Na beta-alumina undergoes a surface reaction too (with CO_2) leading to the formation of carbonates and bicarbonates.

Beta-aluminas are non-stoichiometric oxides containing Al and a monovalent cation M^+. Their structure consists of well ordered spinel-like blocks interrupted by loosely packed planes. The M^+ ions lie in these planes and are responsible for the very high ionic conductivities of these compounds [1].

Water intake processes can, however, affect the transport properties as well as the sintering behaviour of beta-alumina [1]. Their study can then be of great technological interest in connection with the use of beta-aluminas as ceramic electrolytes in sodium-sulphur batteries.

Since 1980 a systematic study was undertaken by our group on the reactivity of beta-aluminas with air moisture. Once the members of the beta-alumina family that absorb water were identified [2], the maximum water amount that can enter the lattice was determined [3]. A model was then proposed to explain the hydration processes and the influence of absorbed water on the unit cell dimensions was analyzed [3].

Subsequently, the structure of the conduction planes of hydrated Na beta-alumina was defined [4]. Attention was then devoted to Li and Li–Na beta-

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aluminas: their hydration processes were characterized and the structure of Li beta-alumina was determined [5].

The study of the reactivity with air moisture was finally extended to ceramic beta-aluminas and it was shown that, different from single crystal beta-aluminas, carbonation processes take place simultaneously with hydration in these samples [6].

This work deals with the energetics of the interaction of beta-aluminas with water and refers on the dehydration enthalpy measurements performed on crystalline samples of Na, Li and Na–Li beta-aluminas and on a ceramic sample of Na beta-alumina.

Experimental

Crystalline samples have all been prepared from a melt grown single crystal of Na beta-alumina by Union Carbide. The composition of the crystal was $(Na_2O)_{1.22}$ $11\,Al_2O_3$. Li and Na (50%)–Li beta-aluminas have been obtained by cation exchange of slices of this crystal in molten LiCl at 650°.

Samples have been used in form of microcrystals (mean linear dimension less than 45 microns) obtained by grinding and sieving the corresponding single crystal.

The ceramic sample has been obtained by solid state reaction between Al_2O_3 and Na_2CO_3 at 1500°. For this sample too, particles with mean dimensions less than 45 microns have been selected by grinding and sieving.

Calorimetric measurements have been performed with a DuPont 1090 Thermal Analysis System equipped with a DuPont 910 Differential Scanning Calorimeter.

To determine the exact amount of water lost during the dehydration, a TG scan has been made under the same experimental conditions of each DSC scan. A DuPont 951 Thermogravimetric Analyzer has been used for TG measurements.

Results and discussion

Single crystal samples

The DSC traces of fully hydrated samples of Na, Na (50%)–Li and Li beta-aluminas are shown in Fig. 1. It can be seen that both the onset and the peak temperatures increase going from Na to Na–Li and Li beta-alumina. K beta-alumina does not absorb water and its DSC trace (also reported in Fig. 1) can be used as base-line for the best possible evaluation of peak areas.

Dehydration enthalpy values have been obtained for the fully hydrated samples

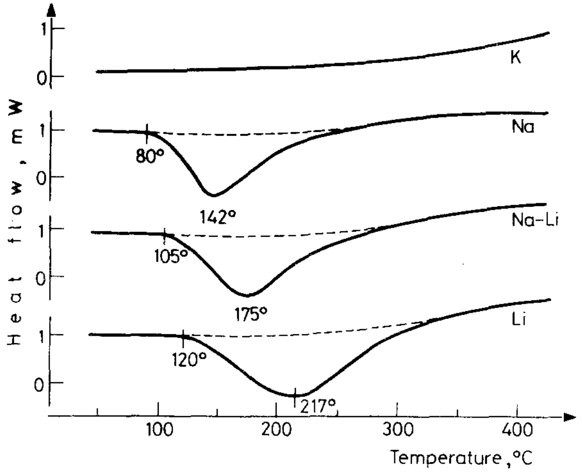

Fig. 1 DSC traces on fully hydrated samples of Na, Na-Li and Li beta-aluminas. K beta-alumina does not absorb water and its thermal trace, reported for comparison, can be used as base-line. Sample mass: 13 mg; heating rate: 5 deg/min

of 41.0, 47.7 and 61.9 kJ/mol H_2O for Na, Na-Li and Li beta-aluminas respectively.

However, these are not the only dehydration enthalpy values that can be obtained for the beta-aluminas analyzed and measurements performed on samples with different water contents show a dependence of the dehydration enthalpy on the water content. The results are shown in Fig. 2 where dehydration enthalpies are represented as a function of the water content.

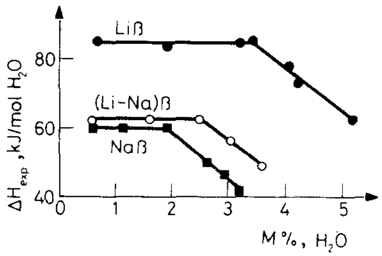

Fig. 2 Dehydration enthalpy value as a function of the water content

It can be seen that constant dehydration enthalpy values (ΔH_c) are obtained for each beta-alumina up to a certain water content ($M\%_c$). For water contents ($M\%$) higher than $M\%_c$ the dehydration enthalpy values (ΔH_{exp}) decrease linearly with $M\%$ and for each beta-alumina the lowest value (ΔH_{min}) is obtained where the water content is maximum ($M\%_{max}$).

Table 1 $M\%_c$ and $M\%_{max}$ values for Na, Na–Li and Li beta-aluminas. The corresponding ΔH values (ΔH_c and ΔH_{min}) are also reported (kJ/mol H_2O)

Beta-alumina	$M\%_c$	ΔH_c	$M\%_{max}$	ΔH_{min}
Na	1.9	59.4	3.2	41.0
Na–Li	2.5	61.9	3.6	47.7
Li	3.5	84.5	5.2	61.9

Values of $M\%_c$, ΔH_c, $M\%_{max}$ and ΔH_{min} are summarized in Table 1. It can be seen that the ΔH_c value of Na–Li beta-alumina is lower than expected on the basis of the additivity of the pertinent values of pure Na and Li beta-aluminas: a similar behaviour has already been observed for the electrical conductivity and is known as "mixed alkali effect" [7].

From a phenomenological point of view the dependence of the experimental dehydration enthalpy values (ΔH_{exp}) on the water content (Fig. 2) can be explained by considering that for $M\% > M\%_c$ a second enthalpy contribution arises (ΔH_e) that makes ΔH_{exp} a linear combination of ΔH_c and ΔH_e. In more detail:

$$\Delta H_{exp} = \frac{\Delta H_c M\%_c + \Delta H_e(M\% - M\%_c)}{M\%}$$

The ΔH_e value of 15.1 ± 1.7 kJ/mol H_2O obtained in this way is common to the three beta-aluminas analyzed.

Na beta-alumina ceramic sample

One month of exposure to air moisture was necessary for this sample to reach its maximum water content.

TG and DSC scans performed under the same experimental conditions on a fully hydrated sample are shown in Fig. 3. It can be seen that a much higher weight loss occurs than with crystalline sample and that in the temperature range of the weight decrease three thermal effects are evident in the DSC trace beginning at about 80, 110 and 220° respectively. If, however, after the first heating the sample is cooled to room temperature and here exposed for some hours to air moisture, the TG and DSC traces obtained on a second heating are very similar to those of the crystalline sample exposure to air moisture. On the basis of parameters such as peak corresponding weight decrease amounts to about 3%.

The thermal traces of Fig. 3 are, however, newly reproduced after one month of sample exposure o air moisture. On the basis of parameters such as peak temperature, weight loss and dehydration enthalpy the conclusion can be drawn that the second of the three effects observable on a fully hydrated ceramic sample corresponds to the dehydration process observed on the crystalline sample.

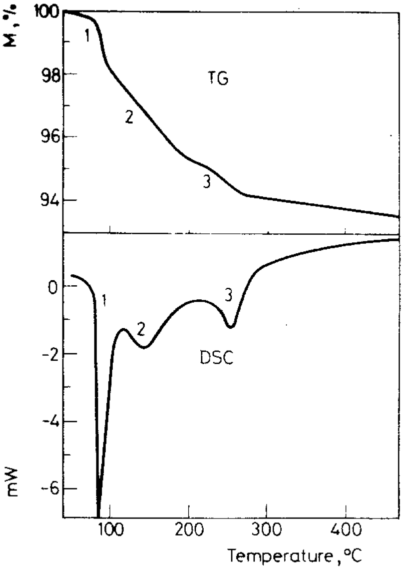

Fig. 3 TG and DSC curves for a fully hydrated sample of ceramic Na beta-alumina

To understand the other two effects different measurements have been performed [5] whose results are briefly summarized below:

— the weight increase recorded for initially anhydrous samples exposed at room temperature to fluxes of dry and wet gases (N_2, CO_2) is higher when wet CO_2 is used;

— Fourier transform infrared spectra of fully hydrated samples show the presence of absorption bands attributable to anhydrous and hydrated carbonates and bicarbonates. Moreover, the bands disappear if the sample is submitted to a thermal treatment up to $T > 800^\circ$;

— evolved gas analysis during TG of fully hydrated samples shows that while the second and the third process take place with only water release, both H_2O and CO_2 evolution are associated with the first one ($T \simeq 80^\circ$).

Some remarks can at this point be made on the results. As far as crystalline samples are concerned, the conclusion can be drawn that the water entering the conduction planes can be bound in two different ways. One part, whose amount is different for each beta-alumina (see $M\%_c$ in Table 1), shows dehydration enthalpy values (ΔH_c in Table 1) that can be attributed to ion-dipole interactions [8, 9]; the remaining part possesses the same binding energy (ΔH_e = 15.1 kJ/mol H_2O) for the three beta-aluminas, no matter which cation is contained in their structure. Such a behaviour can be attributed to the formation of hydrogen bonds between the water molecules and the spinel block oxygens of the layers immediately above and below the conduction planes [8]. For the ceramic Na beta-alumina, the results obtained indicate the formation of anhydrous and hydrated carbonates and bicarbonates too as a consequence of the surface reaction of the polycrystalline grains with CO_2 and H_2O. The fact that such a surface reactivity cannot be observed on the single crystal sample is probably due to the much smaller surface area this type of sample has in comparison with the ceramic one.

The sharp DSC peak with onset temperature at about 80° (Fig. 3) can be due to the transformation of a bicarbonate into a carbonate. While the second peak is due to the beta-alumina dehydration, the third one (onset temperature $\simeq 220°$) may be associated with the dehydration of an hydrated carbonate.

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Zusammenfassung — Die Energetik der Dehydratisierungsreaktion von Einkristallen von Na-, Na (50%)/Li- und Li- sowie von Na-β-Aluminiumoxid wurde untersucht. Aus der Abhängigkeit der Dehydratisierungsenthalpie vom Wassergehalt ergibt sich, daß Wasser auf zwei verschiedene Weisen gebunden ist, nämlich durch Ion-Dipol-Wechselwirkung mit leitenden Kationen und durch Wasserstoffbrückenbindungen mit Sauerstoffatomen. Wie zu erwarten war werden für die ersteren von der Natur der einwertigen Kationen abhängige Bindungsenergien ($\Delta H = 84.1$ kJ/Mol H_2O bzw. 59.4 kJ/Mol H_2O für Li- bzw. Na-β-Alumina) erhalten. Die auf die zweite Wechselwirkung zurückzuführenden Enthalpieänderung ist dagegen für die drei β-Aluminiumoxide identisch ($\Delta H = 15.1$ kJ/Mol H_2O). Das keramische Na-β-Aluminiumoxid zeigt auch eine Oberflächenreaktion mit CO_2, die zur Bildung von Carbonaten und Bicarbonaten führt.

Резюме — Изучена энергетика реакции дегидратации монокристаллического (Na, Na 50%-Li, Li) β-глинозема и керамического Па-β-глинозема. На основе зависимости энтальпии дегидратации от содержания воды было установлено два различных типа решеточной воды, связанной путем ион-дипольного взаимодействия с проводящими катионами и водородными связями с кислородными блоками шпинели. Как и следовало ожидать, энергия первого типа связи зависит от характера одновалентного катиона и ΔH для Li — и Na-β-глинозема составляет, соответственно, 84.5 и 59.4 кдж/моль H_2O. Для второго типа связанной воды, изменения энтальпии идентичны для всех трех β-глиноземов и ΔH составляет 15.1 кдж/моль H_2O. Керамический Na-β-глинозем показывает поверхностную реакцию с двуокисью углерода, приводящую к образованию карбонатов и бикарбонатов.