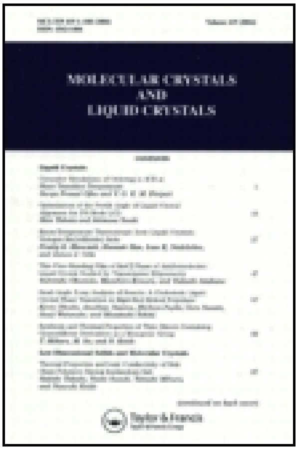

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On the Ternary System Graphite-Sodium-Potassium

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The intercalation of sodium-potassium alloys into graphite leads, at room temperature, to compounds close to KC_8. Graphite powder fits to large amounts of the alloy : up to compositions close to MC_2, but the stable state is a mixture of KC_8 and alloy excess. In spite of the presence of large quantities of free alloy, liquid at room temperature, the powder does not agglomerate and constitutes an important solid reservoir for alkali metals.

Keywords: alkali metals; graphite intercalation compounds; differential scanning calorimetry; XRD

INTRODUCTION

The potassium-sodium system presents a eutectic which melts at -12.62°C and whose composition is close to NaK_2 [1]. By stirring, at room temperature, this eutectic with graphite powder, a rapid intercalation occurs into graphite which turns to a shiny yellow color, characteristic of stage one graphite intercalation compounds with alkali metals. The reaction is done under the inert atmosphere of a glove box containing purified argon.

The composition NaK_2C_{12} was particularly studied since it corresponds to the minimum alloy content which leads readily to a first stage compound. Higher metal content powders can be obtained with metal/carbon ratios up to 1/3 or 1/2 (depending on the initial graphite particle size : respectively 150 and 10 μm) without any agglomeration of the powder. In all cases, the intercalated phase is similar to KC_8 (color, repeat distance along the c axis), but is not stable and turns to a mixture of KC_8 and free metal. Anyway, even when the initial composition was NaK_2C_6, and after the decomposition, the powder does not agglomerate, in spite of the presence of about 60% of a free alloy which is liquid at room temperature [2].

The aging of the compounds was studied as well as the mechanisms of intercalation and deintercalation.

EXPERIMENTAL

In order to determine the possible excess of metal and the intercalation-deintercalation mechanisms, we have made Differential Scanning Calorimetry (DSC) measurement on the powder. This method is particularly sensitive to the presence of free alloys or metals in the powder. The experiments are performed with either a Perkin Elmer DSC 7 or a Mettler DSC 30, in the range -30 to 450°C.

The heats of fusion of sodium and potassium are well known[3], but not that of their alloys. We have measured them for different compositions between $Na_{0.1}K_{0.9}$ to $Na_{0.9}K_{0.1}$. The higher heat of fusion corresponds to Na_2K, in good agreement with the fact that Na_2K is the only defined compound in the Na-K binary system.

Aging

There are always two successive heatings for one given compound, the second one is performed a few minutes after the sample was cooled down to -30°C. In general, as the compound was either aged (for at least 6 days), annealed at 200°C for 2 days or compressed, the first and second heating give the same result which means that the first heating up to 450°C for a few minutes involves the aging of the sample. The results are given in table I.

Just after the synthesis, at the first heating, there are 4 endothermic peaks at -12 and +7°C, (eutectic and peritectic of Na-K), 97.5°C (sodium melting), and 386°C, (2D melting of the intercalated species). The ratio between the eutectic and peritectic corresponds to a composition $Na_{0.6}K_{0.4}$ for the free alloy. The simultaneous presence of those peaks and that of the sodium melting is incompatible with the Na-K phase diagram. This means that the sodium and alloy are separated and this gives some indications on the intercalation-deintercalation processes since the formation of the Na-K alloys is immediate, already at room temperature. The intercalated phase corresponds to $Na_{0.38}K_{1.67}C_{12}$.

At the second heating, one gets a quite different result : the eutectic and sodium fusions have disappeared whereas a shoulder on the peritectic indicates a liquidus temperature corresponding to a new composition for the free alloy : $Na_{0.7}K_{0.3}$, in good agreement with the disappearance of free sodium. The composition of the intercalated phase is $K_{1.55}C_{12}$.

After 6 days at room temperature, the DSC curve at the first and second heatings is already similar to that of the second heating observed previously, with an intercalated phase corresponding to $Na_{0.09}K_{1.57}C_{12}$.

After 2 days at -15°C, one observes a behaviour different from that of the compound kept at room temperature, but also from the fresh sample, which means that, in spite of a low temperature supposed to prevent a decomposition, there is some evolution. The DSC pattern exhibits one peak at 7°C and a second one at 97°C, characteristic of the melting of sodium, but much smaller than just after preparation. This means that part of the sodium has reacted with some potassium or alloy in spite of the low temperature. This fact confirms that both should be very close in the starting material.

After annealing at 200°C for 2 days, one observes roughly the same results than the second heating for the compound as prepared. The final intercalated phase presents a composition close to $Na_{0.04}K_{1.5}C_{12}$.

Finally, the natural aging at room temperature for a month or more leads always to a mixture of KC_8 and free Na_2K, in good agreement with the following equation :

$$2\,NaK_2 + 24\,C \quad \rightarrow \quad Na_2K + 3\,KC_8 \qquad (1)$$

TABLE I : Differential Scanning Calorimetry on NaK_2C_{12}.

NaK_2C_{12}		$T_{liquidus}$ (°C), (Na_xK_y)	ΔH_m (J/g)	Free metal (at. /NaK_2C_{12})	Composition of intercalated phase
as prepared	1st heating	8.8°C, ($Na_{0.6}K_{0.4}$) 97.5°C, (Na)	11.2 1.3	$Na_{0.5}K_{0.33}$ 0.12 Na	$Na_{0.38}K_{1.67}C_{12}$
	2nd heating	32.5°C, ($Na_{0.74}K_{0.26}$)	18.3	$NaK_{0.45}$	$K_{1.55}C_{12}$
after 6 days at room temperature		20.6°C, ($Na_{0.67}K_{0.33}$)	16.5	$Na_{0.91}K_{0.43}$	$Na_{0.09}K_{1.57}C_{12}$
after 2 days at -15°C	1st heating	10.4°C, ($Na_{0.6}K_{0.4}$) 97.6°C, (Na)	15.1 0.8	$Na_{0.7}K_{0.4}$ 0.07 Na	$Na_{0.23}K_{1.6}C_{12}$
	2nd heating	28.2°C, ($Na_{0.72}K_{0.28}$)	21.2	$NaK_{0.5}$	$K_{1.5}C_{12}$
after 2 days annealing at 200°C		21.5°C, ($Na_{0.68}K_{0.32}$)	19.6	$Na_{0.96}K_{0.5}$	$Na_{0.04}K_{1.5}C_{12}$

One has to note here that, according to equation (1), the free alloy, which is liquid at room temperature, represents 30% in volume and must be in the graphite particles (probably as inclusions) since the color of the powder is that of a first stage of a GIC with alkali metals and there is no agglomeration of the powder.

Compression

By applying a *non isostatic compression* on the compounds, one can extract a part of the alloy. The composition of this alloy is always Na_2K, independent of the history of the powder : as prepared, annealed or aged... the difference consists in the amount of the extracted alloy, lower when the compound was annealed (1/6 of the total amount of metal), than for the compound as prepared (1/4). The compressed pellets contain some remaining free alloy as shown by DSC and the composition of the intercalated phase is close to KC_8.

The corresponding pellet (called B in table II) was annealed at 200°C for two days, and, then, compressed again. A small quantity of alloy can be extracted, pointing out that the composition was not exactly KC_8 after the first compression. Anyway, the compounds cannot be exactly KC_8 in the presence of alloy excess containing sodium ; it should be rather at least a ternary compound $Na_xK_{1-x}C_8$ even with x very small [4].

TABLE II : Effect of an uniaxial pressure on NaK_2C_{12}

Compression of NaK_2C_{12}	**extracted metal**	**Composition of the pellet (*A*)**	**$T_{liquidus}$ (°C), (Na_xK_y)**	**ΔH_m (J/g)**	**Free metal (at/*A*)**	**Composition intercalated phase**
as prepared	0.91 $Na_{0.64}K_{0.36}$	$Na_{0.42}K_{1.67}C_{12}$	24°C, ($Na_{0.7}K_{0.3}$)	6.9	$Na_{0.35}K_{0.15}$	$Na_{0.07}K_{1.52}C_{12}$ **(*B*)**
after annealing at 200°C for 2 days	0.6 $Na_{0.65}K_{0.35}$	$Na_{0.61}K_{1.79}C_{12}$	36.2°C, ($Na_{0.76}K_{0.24}$)	11.7	$Na_{0.76}K_{0.24}$	$K_{1.55}C_{12}$

A NaK_2C_{12} compound freshly prepared was compressed by a *quasi hydrostatic method*. Between 15 and 17 kbars, it transforms in $M_{2.5}C_{12}$ (Figure 1), which means that a part of the metal is still not intercalated under that pressure, whereas in the case of pure potassium, the limit is KC_4 under these conditions. This accounts for a higher limit for the formation of a sodium NaC_3 superdense compound : 45 kbars [5].

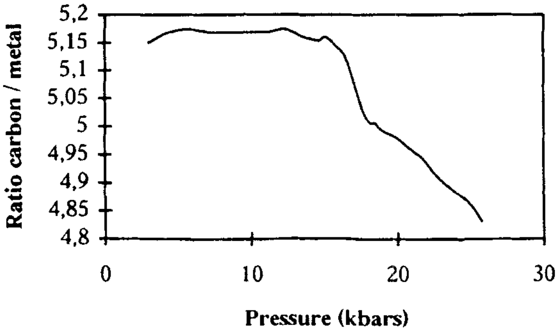

FIGURE 1 : Effect of hydrostatic pressure on the intercalation

X-ray diffraction

The X-ray diagrams are in good agreement with that of KC_8 : all peaks can be indexed in the orthorhombic unit cell with a = 4.92 Å, b = 8.52 Å and c = $4I_c$= 21.40 Å. However, two differences appear :

- the relative intensity of the 00*l* reflections, which is sensitive to the amount of intercalated species, is quite different from that of KC_8. If one considers a first stage M_xC_y compound with one intercalated layer in the medium plane between the graphite planes, the structural factor F_{00l} can be expressed by the following relation :

$$F_{00l} = x * f_M * (-1)^{l/4} + y * f_C \qquad (2)$$

where f_M and f_C are the atomic diffusion factors of the metal and carbon. For instance, the relative intensity of the 004 and 008 reflections are different from that of pure KC_8. In particular, the ratio I_{004}/I_{008} should be, with a powder, around 1.18. This ratio is often, but not always, smaller (about 0.9) and presents an evolution towards that of KC_8 by aging. A smaller value of this ratio corresponds to a higher metal content, according to relation (2).

- the hkl reflections are more modulated than in a pure KC_8 freshly synthesized (for instance, the 022 peak, much weaker than its theoretical value for a Fddd orthorhombic unit cell, reaches its normal intensity only after a few days at room temperature). This is probably due to the difference of preparation temperature : room temperature for our ternary phases, around 250-300°C for KC_8.

Melting properties, intercalation-deintercalation mechanisms

The melting temperatures of the free alloys and sodium in the compounds are that of the bulk. This means that the size of the inclusions of metal as inclusions between the graphene planes should be larger than 100 Å [6]. However the background of the X-ray diagrams is not larger than with pure KC_8 which assumes that the graphene planes are not too much deformed. This means that, probably, the shape of those metallic inclusions is lenticular.

A 2D melting of the intercalated species occurs at a temperature of 386-388°C. This 2D melting was compared to that of potassium in KC_8, at 398°C (about 10°C higher than with a ternary compound), which is significant taking into account the accuracy of the temperature determination. Secondly, the 2D heat of fusion of K in KC_8 is much smaller than that of the alloy in the ternary phases : 3500 J instead of 5000 J per intercalated atom. The corresponding 2D entropies of melting are respectively 5.3 $J.K^{-1}.mol^{-1}$ (pure K) and 7.6 $J.K^{-1}.mol^{-1}$ (Na-K). To our knowledge, there are no literature data for comparison. The trends which are observed in 2D melting are similar to those which are known in bulk metals. The entropies of melting of pure Na and K are both nearly 7 $J.K^{-1}.mol^{-1}$ [3] while that of K-Na alloys are systematically higher because of their greater enthalpies of melting and lower temperatures of fusion than the pure metals.

Those investigations give some idea about the intercalation and deintercalation mechanisms : during the intercalation process, the whole of the alloy, driven by the affinity of potassium towards graphite penetrates between the graphene planes. Since, under these conditions, the stable phase is close to the MC_8 composition, there is a partial deintercalation and the excess of metal : Na_2K, according to equation (1) gets off the intercalated phase and, at room temperature, the alloy remains in the interlayers, and gathers as inclusions. In fact, the intercalated phase contains more metal than KC_8, probably some excess of sodium which deintercalates and forms a separate phase, as seen in fresh compounds. The converse process does not occur : if sodium was firstly deintercalated, the liquid alloy will pass on the metallic sodium and form with it a higher sodium content molten alloy, as it occurs at the second heating.

CONCLUSION

The intercalation of NaK_2 into graphite powder at room temperature leads to a mixture of a compound close to KC_8 (but which contains, initially more metal per carbon atom) and metal excess.

This preparation is very convenient to prepare important quantities of a material which behaves like a powder at room temperature and contains large amounts of alkali metals : up to one metal for two carbons.

The powders suggest several potential applications in electrochemistry, as rapid heat provider, catalyst... [7].

References

[1] T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak, *in Binary Alloy Phase Diagrams, Second Edition,* (ASM International, 1990) **3,** p. 2377.

[2] L. Antoine, J.C. Gachon, D.E. Sklovsky, A. Filatov, V. A. Nalimova and D. Guérard, Proc. Int. Symp. on Carbon, Science and Technology for New Carbons, Tokyo, 1998, p. 130.

[3] R. Hultgren, P. D. Desay, D. T. Hawkins, M. Gleiser, K. K. Kelley, D. D. Wagman, Selected values of the thermodynamic properties of the elements.

[4] D. Billaud, B. Carton, A. Métrot and A. Hérold, *B.S.C.F.* **7–8,** 2259, (1973) American society for Metals, Metal Park, Ohio, 1973.

[5] V.V. Avdeev, V.A. Nalimova and K.N. Semenenko, Synth. Met. **40**, 267, (1991).

[6] J.P. Borel, Surface Science, **106,** 1, (1981).

[7] G. Leichter, D. Guérard and J.C. Gachon, Fr 9505398, PCT/FR96/00687.