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PREPARATION OF HIGH PURITY ALKALI METALS BY NEAR MELTING POINT SEGREGATION

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Abstract

Pure alkali metal preparation is a complex problem: in most available commercial samples, all of them are simultaneously present. Conventional separation techniques are not always effective enough to reach parts per million total impurity levels. However, near the melting point, superficial segregation occurs. A zone melting derived technique coupled with a specifically developed solvent extraction process allows the total impurity content of sodium to be lowered below a few parts per million. The described thermal process, although using chemical reactions, is purely physically steered : it purifies as well potassium containing sodium as sodium containing potassium. 4 alkali metals are considered : Li, Na; K, and Cs.

Keywords: alkali metals, solvent extraction, zone melting

Introduction

Thermal segregation near the melting point is a very common phenomenon. Alkali metal purification is a complex problem, since most of them are simultaneously present at trace level concentrations in most of the available samples. Direct extraction from the liquid phase is often difficult because of the high reciprocal solubility in the liquid state far from the melting point. For the same reason, conventional zone melting does not work well on such systems, since capillary effects at the grain boundaries carry the interfacial impurity enriched liquid phase back to the purified solid core.

The described technique is based on coupling three effects:

1) impurity concentration in the liquid phase at the melting (or better: crystallizing) metal-metal interface.

2) impurity segregation at the metal-organic solvent interface, leading to extremely high (sometimes more than four orders of magnitude) surface concentration enhancements [2].

3) continuous surface dissolution, carrying permanently away the segregated impurity species.

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Thermodynamics

A chemical reaction involving soluble alcoxyde formation by a diluted alcohol mixed with an inert solvent such as *n*-octane allows the dissolution of the sample surface. The alcohol reacts with alkali metals following

$$\text{R–OH} + \text{M} \rightarrow \text{ROM} + 0.5\text{H}_2$$

R–OH: alcohol; *M*: alkali metal; ROM: formed alcoxyde

Thus, since the foreign atoms are surface segregated near the melting point, they are permanently eliminated from the melting zone. This way, the above mentioned retrodiffusion phenomena are blocked, and high purification efficiency is reached. The thermodynamic processes allowing the impurities to be eliminated have been examined on hand of the system sodium matrix – traces of caesium in a previous work [1]. Further, it has been shown [2] that with diluted alcohols, the specific reactivities (corrected by the size of the superficial atoms) of sodium, potassium and caesium are identical, excepted for lithium, the reactivity of which is approximatively ten times lower (Fig. 1). That shows that at least for sodium, potassium and caesium, the reaction speeds are proportional to the surface concentrations of the reacting atoms.

Since impurity segregation can enhance the surface concentration more than 10000 times [2] (in comparison with the average impurity concentration in the metallic sample), this will result in high impurity dissolution rates.

Besides this kinetic factor based on an interfacial equilibrium constant, once they are in the solution as alcoxydes, the alcoxyde alkali metal atoms are exchangeable, so that near the interface, the local composition depends on the reciprocal equilibrium constants between alcoxydes and metals. Such exchange reactions allow

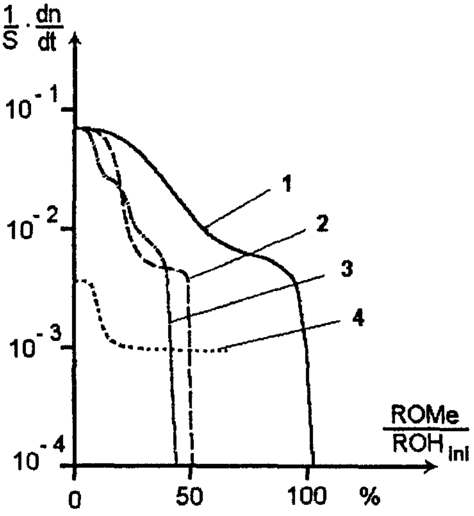

Fig. 1 Compared reactivities of Li, Na, K and Cs. Reaction rates *vs*. molar ratio of % formed alcoxyde to initial alcohol 1) Na; 2) K; 3) Cs; 4) Li

short equilibrium time constants so that the system shows permanently near to equilibrium conditions. The solvent being continuously removed, the sharing constant of the impurity between the solvent and the metallic phase will contribute to a second thermodynamically steered reaction speed. The impurity transfer rate from the metal to the solvent is controlled by the slowest process, which generally is the diffusion of the impurity through the metallic phase towards its surface. As shown by [1] temperatures between eutectic and melting temperature result in high concentrations of the impurities in the liquid intergranular grain boundaries. At melting temperature, while melting goes on, these concentrated liquid zones are enabled to diffuse towards the surface, (since the diffusion coefficients in liquid metals are about 200 to 600 times higher than in the solid state [3], [4]) and effective segregation takes place.

It is thus essential to extract the impurities while melting or solidification takes place. Thus, the extracting device must be thermally controlled in order to allow several successive melting-crystallization cycles.

Results and discussion

The experimental device is shown by Fig. 2. The main reactor is a double-walled 30 mm diameter PYREX glass tubing (5). The solvent, a mixture of 5 to 20% vol. butylcellosolve (glycolmonobutylether) and ligroin (boiling point: 120–150°C) is fed to this tubing through a solvent heater by means of a volumetric pump (7). The solvent heating is obtained by an immersed 30 ohm double folded 3 mm wide nickel-chromium ribbon resistor. Thus, thermal inertia is as low as possible.

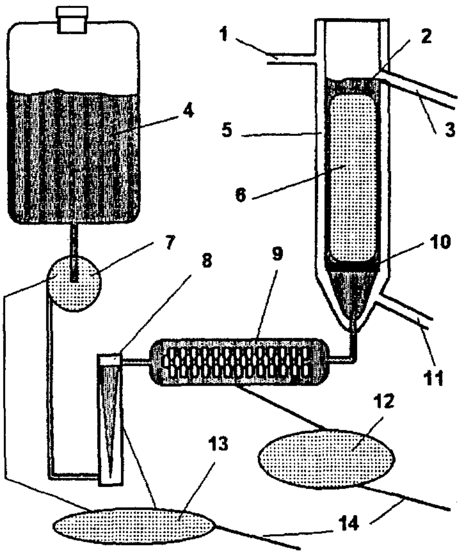

Fig. 2 Experimental device. 1) hot air inlet, 2) organic solvent, 3) solvent overflow, 4) solvent tank, 5) double sidewall, 6) alkali metal sample, 7) controlled solvent pump, 8) flow rate meter, 9) solvent heater, 10) sintered glass (porosity 1), 11) hot air outlet, 12) solvent heater control, 13) solvent pump control, 14) mains

The heater control (12) is steered by a K-type thermocouple measuring the temperature just below the sintered glass filter (10). To avoid thermal loss through the sidewalls, hot air from a heat gun is blown through the inlet (1). The power of the heat gun is controlled by adjusting the air temperature to the value measured at the solvent heater.

Since the density of the solvent and of alkali metals (especially sodium and potassium) are approximatively the same, due to its surface tension, the alkali metal does not drop through the filter, although its porosity is coarse.

The thermal program runs from a few degrees below the melting point to some degrees above it and back. One complete cycle requires about half an hour for a 30 mm diameter reactor, accepting sodium samples up to 250 g . Due to diffusion phenomena, the required time increases with the square of the reactor size. Thus, the molten zone moves from the bottom to the solvent overflow, that is the same direction as the eliminated impurities. During cooling back, the crystallizing zone moves the same way.

The overflowing solvent is fed to a VARIAN AA-6 modified spectrometer (Fig. 2), determining the matrix (Li, Na or K) by flame emission and the eliminated impurity (Li, Na, K, or Cs) by atomic absorption. The purification process is stopped when the monitored impurity signal decreases below the detection limit.

Since the properties of rubidium are very close to those of caesium, we assumed their behaviors to be similar. Caesium could not be tested as a matrix since our device just could heat the solvent. The low temperatures needed for caesium crystallization would require a specially designed cooling device.

As far as the diffusion rates are proportional to the concentration gradients and the dissolution rates are proportional to the reaction surfaces, one can define an extraction efficiency coefficient E :

$$E = (C_{\mathrm{i_S}}/C_{\mathrm{m_S}})(M_{\mathrm{i}}/M_{\mathrm{m}})^{-1}(V_{\mathrm{m}}/S_{\mathrm{m}})$$

$C_{\mathrm{i_S}}$: impurity concentration in the solvent; $C_{\mathrm{m_S}}$: matrix concentration in the solvent; $M_{\mathrm{i}}/M_{\mathrm{m}}$: % impurity in the metal; $V_{\mathrm{m}}/S_{\mathrm{m}}$: specific surface of the metal sample (volume to surface ratio).

The efficiency coefficient E, the dimension of which is homogeneous with a length, is a direct index for the estimation of the purification efficiency for different systems : for Li, K and Cs in metallic sodium purified by a 5% vol butylcellosolve solution, the values of E are respectively:

Li: 20 cm; K: 3 cm; and Cs: 30 cm.

That means that since caesium shows a ten times higher coefficient than potassium, the removing of a given amount of potassium from sodium does not require less time than the elimination of the same concentration of caesium in a ten times larger sample of sodium. Paradoxically, although the reactivity of lithium is ten times lower than the potassium reactivity, its E value is 20, the same order of magnitude as for Cs. This has to be correlated with the corresponding sharing coefficients χ: The sharing coefficients χ are defined by the ratio of the trace metal concentration in the solvent (g ml^{-1}) to the trace metal concentration in the metallic matrix (g/g). For Li, K and Cs present at trace levels in sodium, the sharing coefficients χ measured with 5% vol (about 0.4 mol $^{-1}$) glycolmonobutylether are:

$$\text{Li: } 70 \text{ g ml}^{-1}; \ \text{K: } 0.1 \text{ g ml}^{-1}; \ \text{Cs: } 0.7 \text{ g ml}^{-1}$$

The extremely high sharing coefficient of lithium leads to very low lithium activities in the organic solvent. The resulting high chemical potential gradient across the metal-solvent interface leads to high diffusion rates and compensates its relatively poor reactivity .

Typical purification curves are shown by Fig. 3. The temperature measured in the metallic phase remains constant during melting and solidification steps. Beyond the melting point, the thermal ramp rate is inverted. In sodium, the best extracted metals are lithium and caesium, the behaviors of which are practically identical, showing superimposed lines (3 and 4, Fig. 3). After one cycle, the total amount of impurity has been eliminated so that no more signal can be observed when running a second cycle. For potassium in sodium (2), a small quantity of impurity (about 1%) is left in the matrix, and requires a second thermal cycle to be completely eliminated. The worst situation is shown when potassium is contaminated by sodium (1): three cycles ore more are required until the sodium signal in the overflowing solvent becomes weak. (The analytical sensitivities of Na and K are approximatively the same by atomic absorption.)

Figure 4 shows the melting curve of a 100 g sodium sample. From the binary alkali metal diagrams [5], the lowering of the melting point of sodium due to impurity contamination can be estimated near 2.5 K/% mol. Thus, assuming that the impurities are completely segregated in the liquid phase, the TOTAL impurity amount

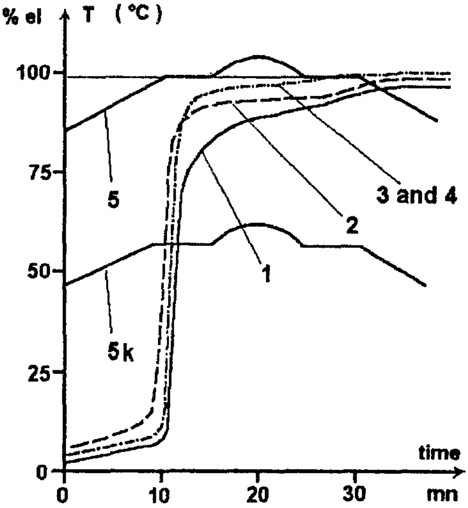

Fig. 3 Eliminated impurity percent and temperature *vs.* time. 1) sodium extraction from potassium matrix, 2) potassium extraction from sodium matrix, 3) lithium extraction from sodium matrix, 4) caesium extraction from sodium matrix, 5) sodium temperature, 5k) potassium temperature

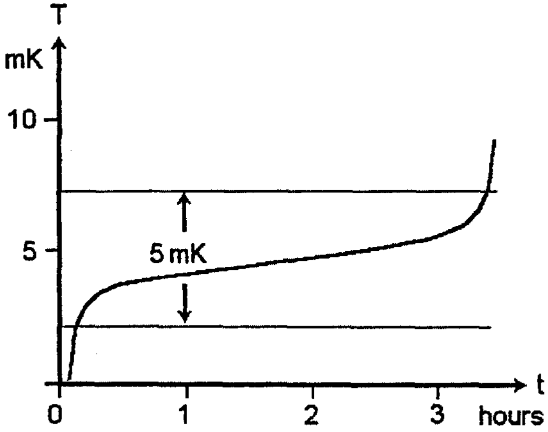

Fig. 4 Melting of a purified 100 g sodium sample. Temperature evolution *vs.* time

(alkali metals, non determined other metals, oxygen, hydrogen and carbon compounds...) of the sample is in the range 10–20 molar parts per million after purification and transfer into the measuring cell, which always leads to slight contamination. By atomic absorption, by complete dissolution of the sample just after purification, contamination levels lower than 0.02 part per million Cs and 0.005 K and Li have been measured.

Conclusion

The obtained results clearly show that the purification is not due to differences in reactivity of the impurities with the alcohol (used as the active solvent) but only depend on thermally induced segregation phenomena.

This technique is not only very suitable for preparation purposes, but it leads also to very sensitive analytical methods when coupled with hyphenated techniques such as atomic absorption spectrometry.

Moreover, it has been used to develop a near 100°C thermometric standard: due to its low changes in volume by melting, such a standard is much more pressure independent than boiling water.

The thermodynamic principles of the described method can be applied successfully to other systems, provided they show similar binary phase diagrams.

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