CALCIUM SOLUBILITY IN MOLTEN CALCIUM CHLORIDE

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ABSTRACT

In order to develop a new process for a direct titanium powder production in a molten calcium chloride media, calcium solubility and calcium diffusion coefficient has been determined in this melt at temperatures ranging from 850°C to 900°C.

The corresponding results are compared to those of the literature, which show rather large discrepancies. Nevertheless, a fair agreement is obtained with the latest studies.

INTRODUCTION

Metal solubility in its molten chloride is a phenomenon which has called chemists attention for a large period of almost 200 years (1-4). The case of Ca in molten CaCl₂ seems the more striking, but reliable descriptions had to wait until the second part of the 20th century. For example, in 1949, Cubicciotti and his co-workers (5) claimed a Ca solubility value in its molten chloride as high as 16 moles%, obtained by determinations on Ca-CaCl₂ liquidus curves.

Ten years later, Peterson and coll. (6) obtained much lower values (S_Ca = 3.8 moles%) and explained that such a difference can be ascribed to the unavoidable pollution by oxygen and water of CaCl₂ and the very reactive calcium metal.

Phase diagrams of Ca-CaCl₂ system have partially been determined par various authors, with different techniques, such as chemical analysis, in Dworkin's (7) and Sharma's (8) works, vapor pressure measurements, in Van Westenburg's work (9), and electrochemical determinations, in Dosaj's one (10).

According to Sanchez et Monier (11), results may differ as they are obtained by static or dynamic methods, due to the relatively long time necessary to reach equilibrium. These authors have determined the whole Ca-crucial phase diagram by differential thermal analysis (DTA).
Very recently, Axler et DePoorter (12) have measured the calcium solubility by using \( \text{CaCl}_2 \) and Ca, as pure as 99.995%.

As shown in table I, the set of results obtained from the above mentioned studies, exhibits rather large discrepancies in calcium solubilities values in molten \( \text{CaCl}_2 \).

In the frame of an industrial program aimed to the development of a new process for titanium powder production, direct reduction of TiCl\(_4\) by calcium dissolved in molten calcium chloride has been studied extensively. In order to avoid any doubt on a parameter which plays a crucial part on the reduction process in this melt, new solubility values have been determined, by taking, for analysis, melt samples, previously saturated in Ca by agitating an excess of liquid Ca in molten CaCl\(_2\) at a given temperature.

**TABLE I : Ca solubility values in molten CaCl\(_2\)**

| \( T (^\circ\text{C}) \) | Ca Solubility in Moles % | Authors | Date   | Ref |
|-----------------|-------------------------|--------|--------|-----|
| 900             | 16.00                   | Cubicciotti and coll. | 1949   | 5   |
| 900             | 3.80                    | Peterson and coll.    | 1959   | 6   |
| 855             | 2.95                    | Dworkin and coll.      | 1961   | 7   |
| 860.5           | 3.57                    | Van Westenburg         | 1964   | 8   |
| 800             | 2.14                    | Sharma                | 1970   | 9   |
| 830             | 2.45                    |                      |        |     |
| 850             | 2.75                    |                      |        |     |
| 900             | 3.26                    |                      |        |     |
| 925             | 3.47                    |                      |        |     |
| 940             | 3.60                    |                      |        |     |
| 805             | 2.73                    |                      |        |     |
| 855             | 3.02                    | Dosaj, Morris and coll.| 1975   | 10  |
| 905             | 3.98                    |                      |        |     |
| 826.5           | 5.00                    | Sanchez and Monnier   | 1979   | 11  |
| 850             | 2.80                    | Axler and DePoorter   | 1991   | 12  |
| 900             | 3.70                    |                      |        |     |

**EXPERIMENTAL**

The experimental device used to perform these solubility values determinations is represented in figure 1, and is composed of:
- an electric furnace and its regulation device,
- a refractory stainless steel reactor,
- a 316 L steel crucible, containing the melt inside the reactor,
- a refractory stainless steel agitator,
- two thermocouples,
- a 316 L steel vessel, for metal calcium feed.

In a first step, a quantity of 5 Kg of CaCl2, is dehydrated by heating and melting under a chlorine flow, according to a procedure recommended by White (13) and Combes and coll. (14). After the removal of the air in the reactor by a vacuum pump, argon gas is injected to maintain an inert atmosphere. In the next step, a large excess of Ca, in relation to its expected solubility according to the more reliable values mentionned in the litterature is added to the melt.

Then, a regular and slow agitation is maintained, in order to provide an homogeneous solution, without making an emulsion of calcium in its salt. Melt samples are taken at regular time intervals, by means of a refractory stainless steel tube, in contact with the crucible bottom. These samples are solidified and cooled down in air proof vessels and are dissolved in freshly boiled distilled water. Their calcium content is determined by hydrogen evolution, according to a classical analytical method (15). The corresponding results are checked against those obtained by an acid titration, in order to be sure that none, or negligible amount of calcium oxide, is present.

**RESULTS**

These determinations, performed at three different temperatures, provided the calcium solubility values collected in table II.

In figure 2, the mole fractions of soluble Ca, are plotted against time for experiment n°1, and give a fair idea on the kinetics of the melt saturation in calcium.

| TABLE II: Calcium solubility values |
|-------------------------------------|
| Experiment 1 | Experiment 2 | Experiment 3 |
| -------------- | -------------- | -------------- |
| CaCl2 (m(g))   | mole          | CaCl2 (m(g))   | mole          | CaCl2 (m(g))   | mole          |
| 5000           | 45.05         | 5000           | 45.05         | 5000           | 45.05         |
| Ca (mole)      |               | Ca (mole)      |               | Ca (mole)      |               |
| 150            | 3.74          | 150            | 3.74          | 150            | 3.74          |
| T (°C)         | 870           | 900            | 850           |
| Number of samples | 5          | 2             | 1             |
| Duration (min) | Moles% Ca     |                |               |
| 7              | 1.73          | -              | -              |
| 14             | 2.19          | -              | -              |
| 19             | 2.27          | -              | -              |
| 25             | 2.35          | 2.67           | -              |
| 60             | 2.37          | 2.67           | 2.27           |

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DISCUSSION

Two kinds of interpretations can be obtained from these results: the first one is related to the kinetics of dissolution, and the second one is related to the solubility value itself and its comparison to previous ones.

As shown in figure 2, it is possible to assume that Ca saturation in this melt is obtained fairly rapidly (around 20 minutes). This is confirmed by the equal solubility values obtained in experiment 2, respectively after 25 and 60 minutes.

Moreover, the kind of curve obtained suggests a Ca diffusion in this melt, obeying to the Fick's law:

\[ \frac{V}{d} \frac{dX}{dt} = - \frac{DS}{d} X \]  

where:

- \( X = C^o - C \) is equal to the difference between Ca concentration at saturation (\( C^o \)) and its value at a time \( t \),
- \( D \) is the Ca diffusion coefficient,
- \( V \) is the melt volume,
- \( S \) is the Ca diffusion surface in the melt,
- \( d \) is the diffusion layer thickness.

By integrating equation [1] from 0 to \( t \)

\[ \int_0^t \frac{dX}{X} = \int_0^t - \frac{DS}{Vd} dt \]

one obtains:

\[ \ln \frac{C - C^o}{C^o} = - \frac{DS}{Vd} t \]  

as, \( X = C^o \), when \( t = 0 \).
By plotting the values of $\ln \frac{C_{\bullet} - C}{C_{\bullet}}$, obtained in experiment 1, versus time, a line, of slope $3.0 \times 10^{-3}$ sec$^{-1}$, can be fitted by the least squares method, as shown in figure 3.

From this result, $D$ can be calculated numerically, by using the following experimental data:
- $S = 150$ cm$^2$, cross-section of the reaction crucible,
- $V = 2500$ cm$^3$, melt volume,
- $d$ has been taken from Chemla's and Lantelme's work (16) and assumed to be equal to $5 \times 10^{-3}$ cm,

$$D = 2.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}.$$

This value, which is of the same order of magnitude as Na$^+$ one in NaCl (18) at 838 °C ($10^{-4} \text{ cm}^2 \text{ s}^{-1}$), is relatively high, but can be explained by the fact that soluble Ca is nothing more than the solvated electron.

The second kind of interpretation is related to the Ca solubility values obtained in this work. They vary from 2.27 to 2.67 moles% at 850 and 900°C respectively, and can be compared to those of Sharma, Dosaj and Axler in a close range of temperature: 800-940°C. All these values have been plotted against the reciprocal of absolute temperature in figure 4. Though a fairly comparable behaviour versus $1/T$ be observed, the solubility values obtained by the above mentioned authors are 20 to 30% higher than this work's ones: a difference which can be ascribed to the possible pollution of calcium by its oxide in the previous works.

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REFERENCES

1. Davy, Trans. Roy. Soc. (London), 97, 1 (1807).
2. Bunsen, Kirchhoff, Pogg. Ann., 113, 364 (1861).
3. Stockem, Z. Angew. Chim., 17, 341 (1904).
4. Guntz, Benoit, Bull. Soc. Chim., 35(4), 709 (1924).

5. D. D. Cubicciotti, C. D. Thurmond, J. Amer. Chem. Soc, 71, 2149 (1949).

6. D. T. Peterson, J. A. Hinkenbein, J. Phys. Chem., 63, 1360 (1959).

7. A. S. Dworkin, H. R. Bronstein, M. A. Bredig, Discussions Faraday Soc., 32, 188 (1961).

8. R. A. Sharma, The Journal of Physical Chemistry, 74, 22, 3896 (1970).

9. J. A. Van Westenburg, Dissertation Abstracts, 25 (2), 1129 (1964).

10. V. Dosaj, C. Aksaranan, D. R. Morris, J. Chem. Soc., Faraday Trans., I, 71, 1083 (1975).

11. J. A. Sanchez, R. Monnier, Rev. Int. Hautes Tempér. Réfract., 16, 5 (1979).

12. K. M. Axler, G. L. DePoorter, "Molten Salt Chemistry and Technology", p. 19 Ed. M. Chemla and D. Devilliers, (1991).

13. S. White, in "Ionic Liquids", Plenum Press, New-York, (1981)

14. R. Combes, B. Trémillon, F. de Andrade, M. Lopes, A. Ferreira, Anal. Letters, 15, p. A20 (1982).

15. G. Charlot, "Chimie Analytique Quantitative", 6ème edition, Paris, Masson, (1974).

16. D. Damianacos, F. Lantelme, M. Chemla, Electrochim. Acta, 28, 217 (1983).

17. E. Janz, "Molten Salts Handbook", Academic Press, New York, (1967)
Figure 1: Experimental device used in order to perform Ca solubility determinations in molten CaCl₂

\[
\text{mole}\%\ \text{Ca} = f(t)
\]

Figure 2: Mole fractions of soluble Ca versus time, for experiment n°1, at \( t = 870 \, ^\circ\text{C} \)
Figure 3: $\ln \frac{C^* - C}{C^*}$ values versus time in experiment 1 at 870 °C

Figure 4: Logarithm of Ca solubility values (mole fractions), versus the reciprocal of the absolute temperature $T$. 

$X_s = \text{Ca mole fraction}$

$T = \text{temperature in K}$

- $-\log X_s(\text{this work})$
- $-\log X_s(\text{Dosa})$
- $-\log X_s(\text{Axler})$
- $-\log X_s(\text{Sharma})$