METALLURGICAL STUDY OF CALCIUM BY PYROLYSIS OF CALCIUM CARBIDE

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1. Introduction

Calcium recently has been closed up as a strong reductant, with which we smelt important metals (U, Th, etc.) in atomic force industry. There are a few methods of calcium production, which are electrolysis of fused $CaCl_2$ salts,[1] and reduction of CaO with Al,[2] Fe-Si,[3] and so on. But as they have many inconvinient points, we tried to produce metallic calcium by pyrolysis of commercial calcium carbide at high temperature and high vacuum, which is cheap and at hand as a source of calcium.

2. Thermodynamical Pre-Consideration

In order to consider the possibility of pyrolysis of calcium carbide, we tried to caliculate the free energy changes of its decomposition. The free energy changes[4] of it under the standard condition and specified conditions are shown in Fig. 1. We can understand from Fig. 1 that the decomposing reaction is nearly impossible at 1 atomosphere and low temperature but quite possible at very high temperature. At low atomosphere the reaction begins to occur at 1,860°K 1 mmHg, 1,380°K 10^{-2} mmHg, 1,230°K 10^{-3} mmHg, and so on. The higher the vacuum degree and temperature, the easier the reaction occurs. The temperature at the begining of the reaction is low at higher vacuum degree.

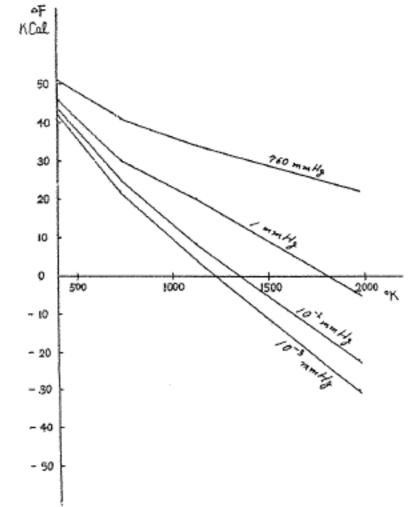


FIG. 1. Free energy changes under each atomosphere.

As stated above, we recognized the possibility of easy decomposition of calcium carbide at high temperature from a view point of free energy changes, but the reaction velocity is not clear. Therefore, first, we examined the weight change of calcium carbide at elevated temperatures by means of the thermo-balance and the weight changes at constant temperature with variation of time.

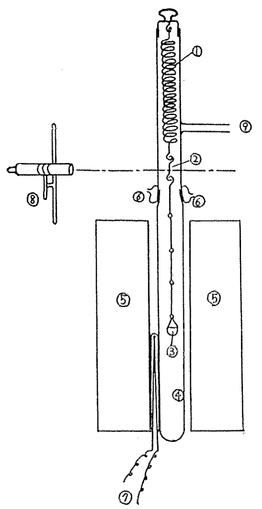
Then, we examined the metallurgy of calcium, and we obtained the yield percentage, which changes pretty with the changes of some conditions.

3. Experimental Details

A) *Fundamental study by the thermo-balance on the decomposition of Ca-carbide.*

Experimental specimen: It is commercial calcium carbide, whose components by the chemical analysis is shown as follows; CaC_2; 71.90%, Fe; 1.39%, Al; 1.25 %, Mg; 10.48%, Si; 1.59%, C; 2.40%.

Experimental apparatus: It is consisted of vacuum system, reaction system, and temperature controll system. Details of the reaction system is shown in Fig. 2, that is, platinum vessel is hung from the silica-spring balance by platinum chains. And we read the graduation by cathetometer searching a mark on the silica-spring balance.



① Silica spring balance
② A mark
③ Pt crucible
④ Silica tube
⑤ Siliconit electric furnace
⑥ Water jacket
⑦ Pt-PtRh (13%) thermocouple
⑧ Cathetometer
⑨ To vacuum pump

FIG. 2. Experimental apparat for thermo-balance test.

Experimental procedure: In the case of the weight changes with the variations of the temperature, the sample ground below 80 mesh is hung from silica-spring balance at room temperature and the reaction tube is closed up. Then the reaction tube is pumped under the ultimate vacuum 10^{-2}–10^{-3} mmHg at room temperature. Then, heating the reaction tube up to 1,200°C at the rate of 50°C/hr, 100°C/hr or 200°C/hr, we read the changes of the mark on a silica-spring at intervals of 50°C by cathetometer. In an other case of the weight changes with time variations, the sample is charged as stated above, and the tube is degassed below 800°C and at the ultimate vacuum 10^{-2}–10^{-3} mmHg, the temperature is elevated to the specified point quickly, and we read the changes of the mark on silica-spring every 30 minutes.

4. Experimental Results and Consideration (A)

Experimental results are shown in Fig. 3 and Fig. 4.

1. The weight changes with the variations of temperature (Fig. 3).

A pretty decrease appears at 250°C–400°C at all the rates, 50°C/hr, 100°C/hr and 200°C/hr. This phenomenon showed that CO_2 gas and H_2O gas are driven out by decomposition $CaCO_3$ and $Ca(OH)_2$ in the sample. The second *knick* appears at 800°C–900°C, where absorbed gasses are expelled and at the same time Ca vapor by the decomposition of calcium carbide is liberated, and at the temperature of 900°–950°C, the curve proceeds leniently, as the calcium condenses on the platinum chains. Then above 1,100°C the decomposing reaction of calcium carbide occurs so vigorously.

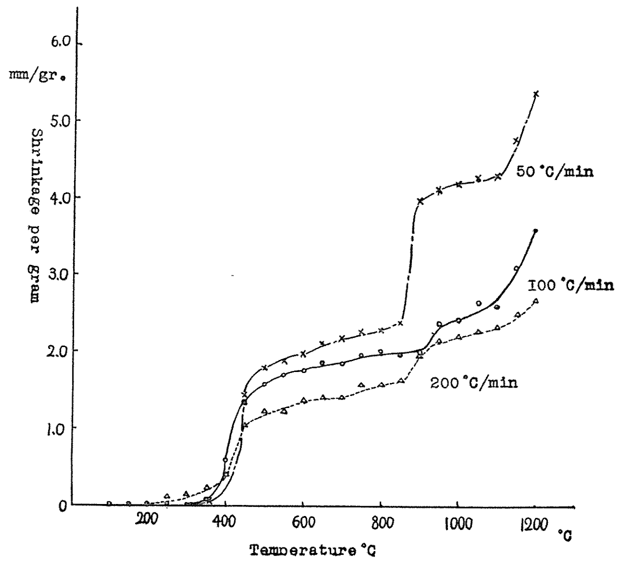


FIG. 3. Proportion of weight decrease to temperature increase.

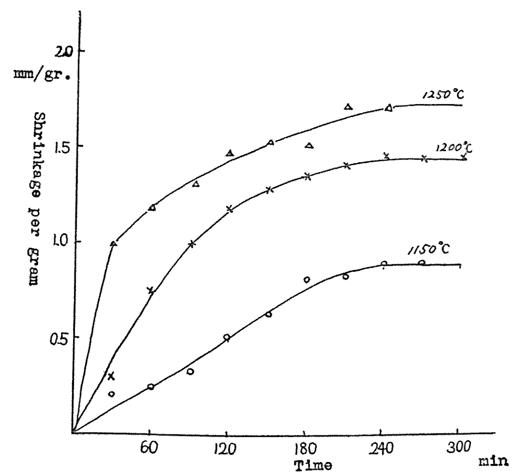


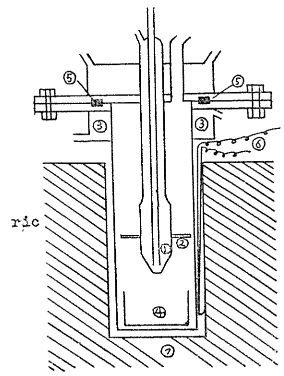
FIG. 4. Relation between weight decrease and time at each temperature.

2. The weight changes with the variations of time (Fig. 4).

We examined at 1,150°, 1,200°, and 1,250°C. The weight decreases liniarly at 1,150°C, but the relation crumbles a little and the acclivity of this curve increases. From this fact, we understand that the higher the temperature and the vacuum degree, the larger the reaction velocity is.

B) The metallurgy of calcium by the pyrolysis of calcium carbide.

The specimen is the same as in the case of the thermo-balance test and the experimental apparatus is shown in Fig. 5 in details.



① Condenser
② Dam plate for calcium vapor
③ Water jacket
④ 18-8 stainless steel crucible
⑤ Rubber packing
⑥ Pt-PtRh thermocouple
⑦ Siliconit electric furnace

FIG. 5. Apparatus for calcium production.

Experimental procedure: Take 100–110 grs. of the sample ground at a specified grain and mix calcium fluoride as an addition and insert the sample into the retort made of mild steel. Then put the retort into the electric-furnace, and degas it to the specified point, maintaining the vacuum degree. Let CaC_2 decompose during the specified hours, and then cool the retort in the state of the vacuum. Collect the calcium metal in a bottle, which is in argon flow, weigh that, and analize the metal.

5. Experimental Results and Consideration (B)

1. Influences of reaction temperature upon the yield percentage of Ca.

The results are shown in Fig. 6. Experimental conditions are; reaction time 7 hr, CaF_2 10%, grain size 80 mesh, the ultimate vacuum 10^{-2}–10^{-3} mmHg, and reaction temperature 1,200°C, 1,250°C, and 1,300°C. In this case, optimum temperature is 1,300°C, where we obtained 60% as a yield percentage of calcium.

2. Influences of calcium fluoride. The results are shown in Fig. 7. Experimental conditions are; reaction time 7 hr, grain size 80 mesh, reaction temperature 1,300°C, the ultimate vacuum 10^{-2}–10^{-3} mmHg, and mixing amounts of CaF_2 0, 5, 10, 15%. The yield percentage of calcium is 2% in 0% of CaF_2 and about 60% in 10% of CaF_2.

3. Infuluences of reaction time. The results are shown in Fig. 8. Experimental conditions are; reaction temperature 1,300°C, CaF_2 10%, grain size 80 mesh, the ultimate vacuum 10^{-2}–10^{-3} mmHg, and reaction time 5, 7 and 10 hrs.

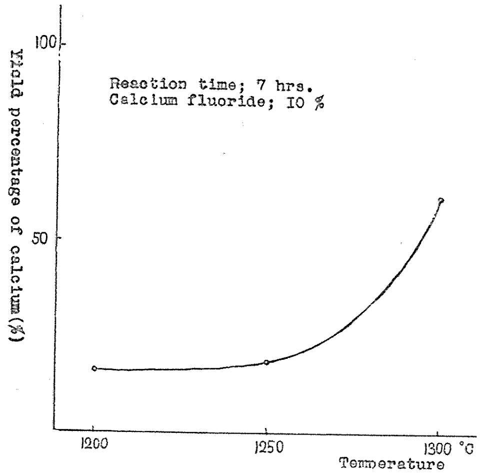


FIG. 6. Relation between yield percentage and reaction temperature.

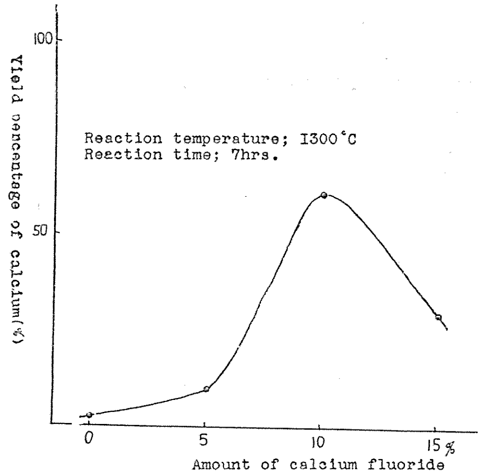


FIG. 7. Relation between yield percentage and calcium fluoride.

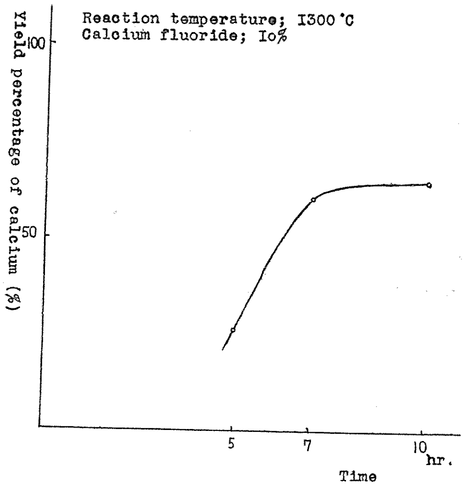


FIG. 8. Relation between yield percentage and reaction time.

In this case optimum time is 10 hrs and the yield percentage of calcium is 63%.

Now we give some considerations. In relation between temperature and yield percentage of calcium, the yield percentage increases suddenly at 1,250°–1,300°C. We understand this fact in a view point of free energy. At these temperature the possibility of reaction increases and at the same time the reaction velocity increases, we think, and if the apperatus is constructed strongly, we can obtain the higher yield percentage at higher temperature. As for addition of CaF_2, in case there was no addition we had low yield percentage, while addition of ten percentage gave the highest value, 63% of the yield percentage of calcium, for in the case of CaF_2 below 10%, its catalytic action is little, but above 10%, the yield percentage is low because of sintering action of CaF_2 disturbing the vaporization of calcium, which we see in condition of residues and chemical analysis, although its catalytic action increases. According to the relation between reaction time and yield percentage of calcium, the longer the time the higher the yield percentage is, and we had the yield percentage of 63% at 10 hr, but we cannot expect to increase remarkably the yield percentage even if we do longer than this. Chemical analytical values of the metallic calcium produced are as follows; Ca; 95.84%, Fe; 1.35%, Al; tr, C; tr, gas components; 2.81%. By re-distillation this produced calcium has 99.98% Ca etc.

6. Summary

1. From thermodynamical consideration the following reaction, or decomposition of calcium carbide, is nearly impossible at one atomosphere but quite possible at higher vacuum state, $CaC_2 = Ca + 2\,C$.

2. From the thermo-balance test, we found that the higher the temperature the larger the reaction velocity is.

3. The yield percentage is better at higher temperature, and at 1,300°C the yield percentage is 59%.

4. As for addition of CaF_2, in the case of an addition of 10% CaF_2 the yield percentage is maximum, giving no good result either for below 10% or above 10% CaF_2.

5. The longer the reaction time the better the yield percentage is.

6. Purity of the calcium metal produced is 95.84% Ca, but by re-distillation it becomes 99.98% Ca.

Acknowledgements

In conclusion, the present authors wish to express their cordial thanks to Mr. J. Hirai for his zealous co-operation throughout this research.

References

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3) H. Sawamoto, T. Sugiura, A. Nishina; Suiyokai-shi 13, 673 (1958).

4) Electro-Chemical Handbook (Maruzen), p. 96 (1953).