A STUDY ON METALLURGY OF METALLIC BERYLLIUM
ON REDUCING BERYLLIUM OXIDE WITH CALCIUM

HACHIE SAWAMOTO, TAKEO OKI and AKIRA NISHINA

Department of Metallurgical Engineering

(Received May 31, 1960)

We have studied on metallurgy of beryllium (the pile material) by reducing beryllium oxide with calcium. We produced beryllium-calcium alloy, and then extracted metallic beryllium from beryllium-calcium alloy. And we obtained the following results;

A. Beryllium-calcium alloy production.
1. Every mixing method may be used in this case.
2. The optimum conditions were

Reaction temperature ; $> 1{,}200°$ C
Reaction time ; > 5 hrs.
Mixing weight-ratio of calcium to beryllium oxide ; > 6

In this case the yield percentage of beryllium was one hundred percent.

B. Extraction of beryllium
3. Ammonium chloride cold solution process was better than high temperature vacuum process.
4. Metallic beryllium powders (produced by ammonium chloride process) were chemically pure and they had spectrographical traces of iron, aluminium, magnesium and calcium.

This smelting process is very useful, and has one hundred percentage utilization of beryllium oxide, and the produced metallic powders are convenient in beryllium powder metallurgy.

1. Introduction

In the recent atomic energy age the metals used in atomic pile have been closed up, especially the metallic beryllium is most valuable, which is used as reflector, moderator and so on. The metal for this purpose must be very pure in a view point of the absorption area for thermal neutron. The present production methods[1)2)3)] for the metallic beryllium are electrolysis of fused salts with beryllium fluoride, metal reduction beryllium fluoride, etc. These processes have many difficulties such as fluorination and contamination of impurities. In previous reports[4)] we had some difficulties in reduction of beryllium oxide with calcium carbide. Then in this paper we try to obtain the metallic beryllium by reduction of beryllium oxide with calcium directly, or to extract the metallic beryllium with either cold NH_4Cl solution or vacuum treatment after we get calcium-beryllium alloy from reaction between beryllium oxide and excessive calcium, thus we let removal of

impurities in metallic beryllium be easier, while we using strong reducibility of metallic calcium.

2. Experimental Details

2.1. Possibility of reaction

Here we discuss the possibility of the reducing reaction. When beryllium oxide is reduced by calcium according to the above idea at a view point of free energy change of the reducing reaction, ΔF° values are as follows;

$$\mathrm{BeO} + \mathrm{Ca} = \mathrm{Be} + \mathrm{CaO}$$

$$\begin{aligned}\Delta F^\circ = &-7{,}370 + 2.86\,T\log T - 9.11\,T \quad (298^\circ\text{–}1{,}124^\circ\,\mathrm{K})\\ &-9{,}600 + 2.86\,T\log T - 7.13\,T \quad (1{,}124^\circ\text{–}1{,}556^\circ\,\mathrm{K})\\ &-4{,}450 + 6.91\,T\log T - 23.41\,T \quad (1{,}156^\circ\text{–}1{,}760^\circ\,\mathrm{K}).\end{aligned}$$

When we use calcium in excess and make calcium beryllium alloy, the reaction is as follows;

$$\mathrm{BeO} + \mathrm{Ca} = \mathrm{Be}\ (\text{in Ca}) + \mathrm{CaO}.$$

For the free energy changes at each temperature

$$\Delta F_T = \Delta F^\circ + RT\ln\frac{[\mathrm{Be}]f_{\mathrm{Be}}}{[\mathrm{Ca}]f_{\mathrm{Ca}}}$$

f_{Be}; Activity co-efficient of Be in Ca-Be alloy
f_{Ca}; Activity co-efficient of Ca in Ca-Be alloy.

By the above formula, we understand that in the case of using calcium in excess we let the reducing reaction of calcium be easier than in no excess, that is, by using calcium very much we can decrease activity of beryllium and give no change to activity of calcium.

Also, as calcium reacts with oxygen very easily we cannot perform the experiment in air atomosphere. Therefore we try to obtain beryllium-calcium alloy and beryllium powder including calcium by acting the reducing reaction in argon atmosphere and reducing beryllium oxide with calcium usefully. On the basis of these points and pre-experiment, we use the following variables;

Reaction temperature; 1,000°–1,300° C
Reaction time; 1–10 hours
Mixing ratio (weight); BaO : Ca 1 : 4 . . . 9.

We examine changes of yield percentages, extraction percentages and purity of beryllium according to the above conditions.

2.2. Specimens and experimental apparatus

Beryllium oxide is used in the state of Reagent Special Grade or chemically pure, and calcium, which is produced by re-distillation of electrolytical calcium at 850° C and 10^{-4} mmHg, is 99.99% in purity.

Experimental apparatus (it is shown in Fig. 1), has reaction system, where the specimen is placed in a crucible made of magnesia or mild steel which was set in a stainless steel retort, and vacuum system, which has argon supply system and temperature control system, but temperature is observed at outside of the retort.

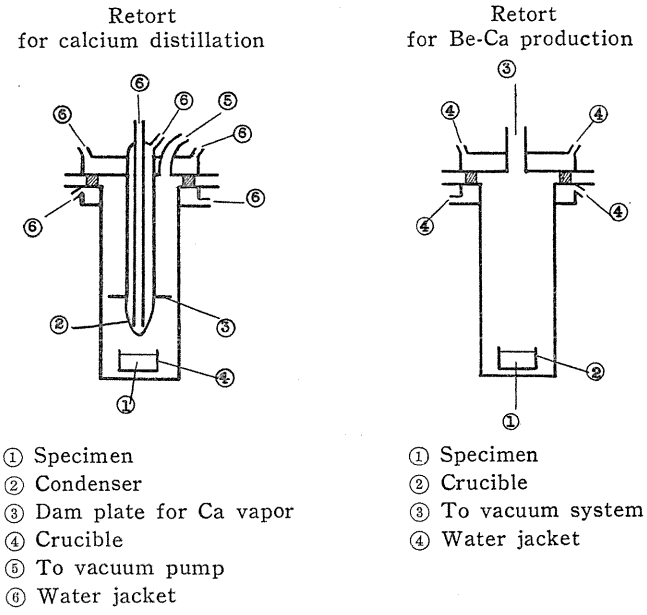

FIG. 1. Experimental apparatus

2.3. Experimental procedure

2.3.1. Production process of beryllium- calcium alloy

Put beryllium oxide and calcium, mixed at the specified ratio, in the crucible in the stainless steel retort. Close the retort and pumped into vacuum. After the vacuum degree reaches 10^{-2}–10^{-3} mmHg at room temperature, degas at 400°–500° C, and then fill the reaction system with 1 atm. argon gas and elevate temperature up to the specified point, and after reaction of the specified time, cool the retort and put out the mixture and treat by proper methods.

2.3.2. Extraction process of metallic beryllium

1. 1st method. In case good beryllium-calcium alloy was produced, we let calcium included in the specimen evaporate at high temperature and high vacuum degree in a magnesia crucible.

2. 2nd method. Extract pure beryllium by treating the beryllium-calcium alloy with ammonium chloride cold solution.

3. Experimental Results and Considerations

3.1. On the mixing process of beryllium oxide and calcium

1. To mix beryllium oxide and calcium naturally.
2. To place beryllium oxide on the calcium block.
3. To drop beryllium oxide on the fused calcium

By three methods, we obtain one hundred yield percentage of beryllium at 1,200° C, 5 hrs. and 6 : 1 (Ca: BeO weight-ratio). Therefore any mixing method is good in this case, as at 1 atm. argon atmosphere calcium vaporizes pretty and calcium vapor reacts with contacting beryllium oxide. Then we use the handly

mixing method at the experiments from the next time onward.

3.2. Influences of reaction temperature and reaction time on the yield percentage

The results are shown in Figs. 2, 3. In Fig. 2 at 1,000° C and 1,100° C, some beryllium oxide remains unreacted, but at 1,200° C and 1,300° C there is perfectly formed beryllium-calcium alloy, showing no unreacted beryllium oxide, 100 percent yield of beryllium. At low temperatures calcium oxide remains in beryllium-calcium alloy, but at high temperatures forms good beryllium-calcium alloy which includes some trace of calcium oxide frequently. Though we do not prove on the yield percentage, as it include relation with reaction time, considering activity of calcium for disoluting beryllium, reaction velocity, complicate elements of contact reaction and so forth, at above 1,200° C the reduction reaction may occur without the initial contact reaction. Influences of reaction time on the yield percentage is shown in Fig. 3. For above 5 hrs. we obtain 100 percent in yield, but for below 5 hrs., unreacted beryllium oxide remains. This is concerned with only reaction velocity. So, we use 1,200° C as a reaction temperature, and 5 hrs. as a reaction time from the next time onward.

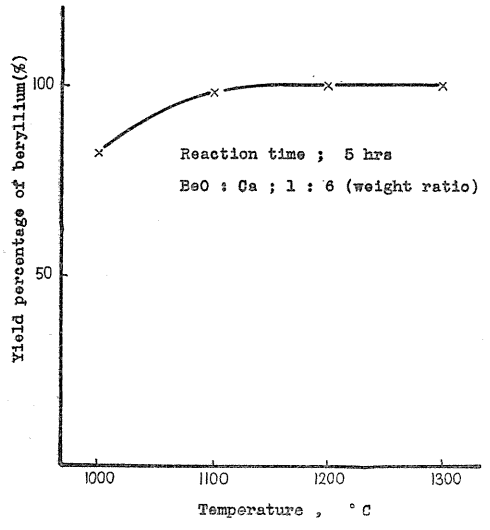

FIG. 2. Relation between yield percentage and reaction temperature.

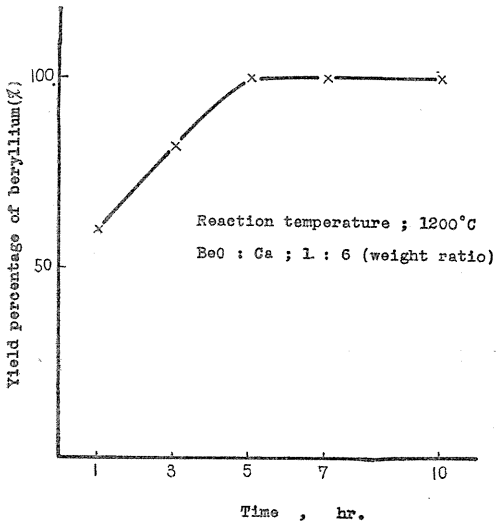

FIG. 3. Relation between yield percentage and reaction time.

3.3. Influences of mixing-ratio on yield percentage

The results are shown in Fig. 4. In case mixing-ratio is above 1 : 5 (BeO : Ca weight ratio) we obtain yield percentage of 100%, where beryllium oxide reacts unperfectly with calcium below the mixing-ratio, presenting unreacted beryllium oxide. This is owe to activity of calcium decreased on account of alloying with beryllium, loss of calcium for its vaporizing, and non-contact of calcium vapor with beryllium oxide by vaporizing direction, etc., though 1 : 5 mixture (BeO : Ca weight-ratio) contains sufficient calcium enough to reduce sufficiently beryllium oxide in the reaction formula.

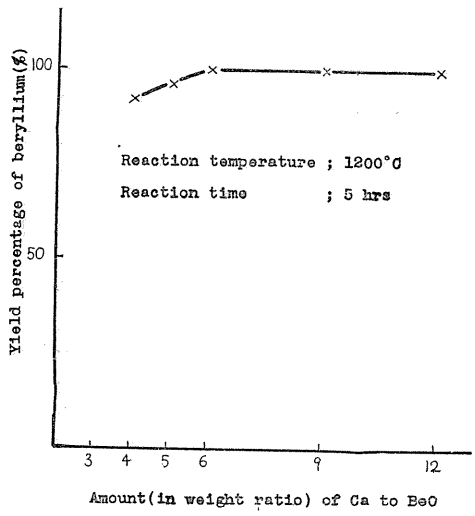

FIG. 4. Relation between yield percentage and mixing ratio.

3.4. Extraction of beryllium by vacuum distillation process from beryllium-calcium alloy

This process is a method removing calcium from calcium-beryllium alloy by application of high temperature and high vacuum degree. In this method we can not obtain pure beryllium, but 85% beryllium. This phenomenon is due to the non-metallic inclusion, calcium oxide, in the calcium-beryllium alloy, and non-decomposition property at this point of intermetallic compound Ca_xBe_y, though the phase diagram of beryllium-calcium alloy is not clear.

Anyhow this method is not quite a good method for removing calcium. Though it is better to treat at higher temperature, we have many difficulties such as evaporation of beryllium, etc.

3.5. Extraction of beryllium from calcium-beryllium alloy by ammonium chloride cold solution process

This is a process removing calcium and calcium oxide by treating with ammonium chloride cold solution. We obtain chemically pure beryllium metal powder by using 200 g/l solution of ammonium chloride from a beryllium alloy of any composition, and this metal powder includes traces of iron, calcium, magnesium and aluminium spectrographically. Thus ammonium chloride cold solution process is a good extraction process for beryllium and produces beryllium metal powder, which is very useful for beryllium powder metallurgy.

From the above results, (there is little source of beryllium in Japan and beryllium oxide is valuable) by using this beryllium production method, we obtain 100% yield percentage of beryllium and its should be specially mentioned that the produced metal is high pure powder.

4. Conclusion

1. In producing calcium-beryllium alloy, mixing process of beryllium oxide and calcium is all good, showing 100% yield percentage, reacting perfectly in conditions like (2).

2. The optimum conditions are, reaction temperature: 1,200°C, reaction time; 5 hr., mixing-ratio; 1 : 6 (BeO : Ca weight-ratio).

3. In the extraction processes from calcium-beryllium alloy, calcium distillation process at high temperature and high vacuum degree is not good for some reasons, but ammonium chloride cold solution process is very useful, by which produced beryllium metal is very chemically pure powder, and includes traces of magnesium, iron, aluminium and calcium, spectrographically.

4. By this process, we can obtain metallic beryllium for atomic pile material, which is convinient for beryllium powder metallurgy, using 100% of valuable beryllium oxide.

In conclusion we express thanks for Bureau of Education of Japan to give us the Expense for Research and Exam. Research of Science of Japan to accomplish this research.

References

1) Lecture for experimental chemistry, Vol. **10**, pp. 179–186 (Marzen).
2) D. W. White and J. E. Burke: The metal beryllium, pp. 49–124 (A.S.M. 1955).
3) Handbook for metal, pp. 468 (Marzen 1954).
4) Sawamoto, Sugiura, Nishina: J. Min. Met. Inst. of Japan, Vol. **76**, No. 862, p. 37 (Syn).