

A STUDY ON REDUCTION OF BARIUM OXIDE WITH ALUMINIUM

HACHIE SAWAMOTO, TAKEO OKI and TERUYOSHI UMEMURA

Department of Metallurgical Engineering

(Received May 31, 1960)

Introduction

Metallic barium is now produced by reduction of barium oxide with aluminium; namely, barium oxide and aluminium inserted in a vacuum retort, reacting at high temperature, change to barium aluminate and barium vapor. This reaction has been assumed to obey the following formula;



The formula manifests that the residue which is formed as a result of the reaction is 3Ba-aluminate, and so the maximum yield percentage is 50%.

In our experimental barium production, however, the yield percentage exceeds 50%. This fact suggests a formation of other aluminate which has less barium than 3Ba-aluminate.

X-ray diffraction analysis is applied to investigate the form of barium aluminate, which is the most important factor for determination of the mechanism of this reaction.

Stability of Barium Aluminate

For the purpose of investigation of stability of barium aluminate, a mixture of barium oxide and alumina is heated at from 1,000° to 1,400° C, and then a synthetic barium aluminate is consequently prepared and examined by X-ray diffraction analysis.

One of the X-ray diffraction chart of a synthetic barium aluminate is illustrated in Fig. 1. For the preparation of the barium aluminate, barium oxide and alumina are mixed at the compounding-ratio of 1 to 1 in mole and heated at 1,000° C for 4 hrs.

All the distinguished peaks (shown in Fig. 1) which have the maximum intensity at 3.16 Å, the second at 4.55 Å, the third at 2.62 Å and so on, are undoubtedly corresponding to those of 1Ba-aluminate ($\text{BaO} \cdot \text{Al}_2\text{O}_3$) recorded in ASTM card. While, in Fig. 2, which is obtained from a mixture of richer barium oxide (2 to 1) under the same experimental conditions, here exist another group of peaks, which have the maximum intensity at 2.92 Å, the second at 4.14 Å and so on. The heights of these new peaks increase with the richness of barium oxide in the mixture to be synthesized, while the other peaks of 1B-aluminate decrease. The group of these new peaks must indicate the formation of some other barium aluminate which has more barium than 1B-aluminate. Excepting of 1Ba-aluminate the data of X-ray diffraction on barium aluminate seems to have been still unknown,

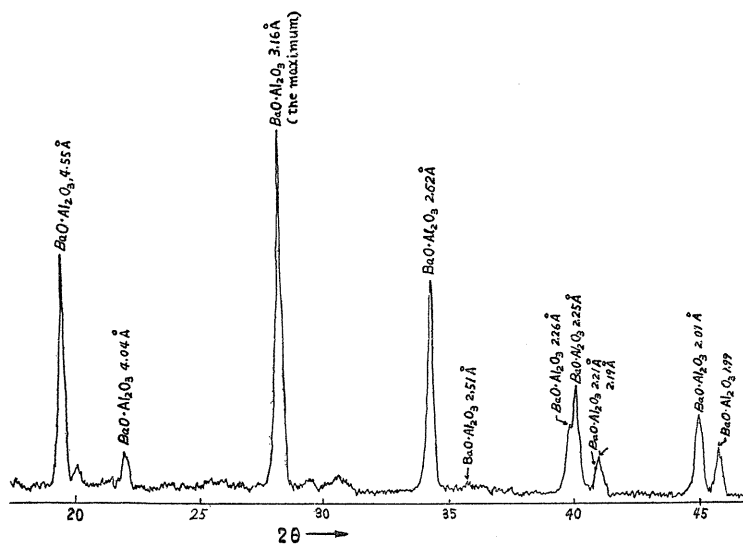


FIG. 1. X-ray diffraction chart of synthetic barium aluminate which was synthesized from the mixture: $\text{BaO}/\text{Al}_2\text{O}_3=1/1$ in mole.

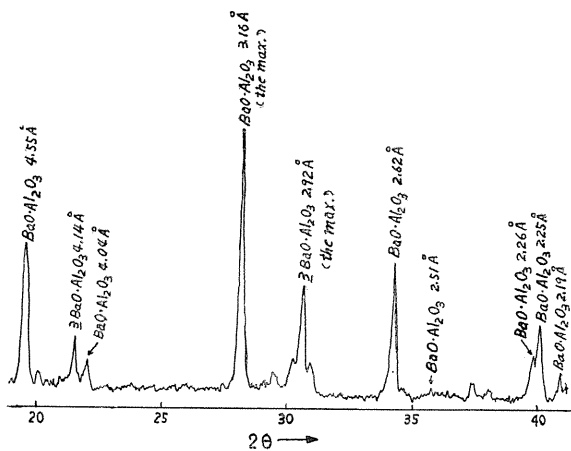


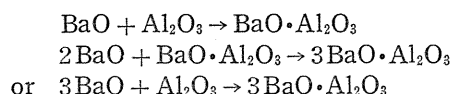
FIG. 2. X-ray diffraction chart of synthetic barium aluminate which was synthesized from the mixture: $\text{BaO}/\text{Al}_2\text{O}_3=2/1$ in mole.

but in thermodynamic data there are found two compounds of barium aluminate; namely, 1Ba-aluminate and 3Ba-aluminate. Although, as far as our investigation is concerned, it can not be exactly confirmed, the compound represented by these new peaks is most likely 3Ba-aluminate.

Under the various experimental conditions the synthetic barium aluminates are prepared, from which the X-ray diffraction charts are obtained. And the intensities of their maximum peaks are checked out as their characterized peaks,

which are at 3.16 Å and at 2.92 Å for 1Ba-aluminate and 3Ba-aluminate respectively.

Fig. 3 shows the relationship between diffraction intensity and synthetic temperature. The curves indicate the intensity of 1Ba-aluminate and the dotted lines indicate the intensity of 3Ba-aluminate. It is the most noticeable thing in this diagram that at the temperature of 1,150°C the intensities of 1Ba-aluminate rapidly decrease with the rapid increases of 3Ba-aluminate, and at the higher temperature the former increase rapidly again while the latter decrease. These are observed in all the samples that are synthesized from mixtures of richer barium oxide than 1/1 (BaO/Al₂O₃ in mole). These may be explained as follows; at the lower temperature than 1,150°C, both 1Ba-aluminate and 3Ba-aluminate may be formed by the following formula;



but 3Ba-aluminate may be more stable than 1Ba-aluminate at that temperature, therefore, 1Ba-aluminate can change to 3Ba-aluminate. And at the vicinity of 1,150°C the rate of the reaction rapidly increases, so that the amount of 1Ba-aluminate decreases. The temperature exceeding 1,150°C, however, 3Ba-aluminate may be, decomposed as follows:



so the amount of 1Ba-aluminate increases again, while 3Ba-aluminate is hardly detected.

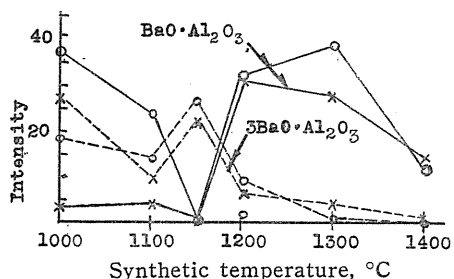


FIG. 3. Relationship between X-ray diffraction intensities of barium aluminate and its synthetic temperature.

○: synthesized from mix.; BaO/Al₂O₃=3/1.

×: synthesized from mix.; BaO/Al₂O₃=4/1.

Experimental Barium Production

A cylindrical retort made of stainless steel is vacuumed at about 5×10^{-3} mmHg, in which a reactor, a crucible of stainless steel, containing barium oxide and aluminium, is set. The barium vapour evolves from the reactor, diffusing in the retort, condenses on a condenser of common steel which is previously cooled with water. Barium is recovered from this condenser in an inert gas atmosphere. Temperature is measured out-side of the retort.

Varying experimental conditions, such as temperature, compounding ratio of barium oxide to aluminium, reaction time and grain sizes of aluminium, or adding calcium fluoride as a catalyst, the yield percentages of barium are measured and the reaction residues are examined by X-ray diffraction analysis. On the reaction

residues, it is established that there are no difference of notice between their X-ray diffraction charts and those of the synthetic barium aluminate mentioned before; *i.e.*, the materials constituting the reaction residues are 1Ba-aluminate and 3Ba-aluminate. Thereby, the maximum peak of each aluminate is checked out also as before and compared with the yield percentages.

Fig. 4 shows the relationship between reaction temperature and yield percentage and diffraction intensity. Aluminium as a reductant is used is a form of powder and the reactions are continued for 4 hrs. in this case. The most noticeable thing in this diagram is a sudden rise of the yield percentage as well as of the intensity of 1Ba-aluminate at the temperature of 1,150° C. On the other hand, the intensity of 3Ba-aluminate does not rise at that temperature. This is, however, incompatible with the fact mentioned before; *i.e.*, though at the temperature of 1,150° C the 3Ba-aluminate must be formed rapidly, the intensity of 3Ba-aluminate does not rise but the intensity of 1Ba-aluminate does. This is explained that the inner energy of the reactants may have been at higher level than the reactants

in synthetic reaction mentioned before; in practice also, the temperature in the reactor may be higher than the temperature measured on account of its exothermic reaction. Therefore, 3Ba-aluminate may be decomposing to 1Ba-aluminate at that temperature. The sudden rise of the yield percentage may be owing to the decomposing reaction.

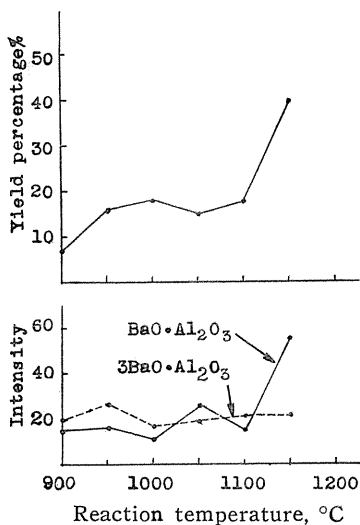


FIG. 4. Relationship between reaction temperature and yield percentage of barium and X-ray diffraction intensity of the reaction residue.

With variation of compounding-ratio we obtain a result shown in Fig. 5. According to the increase of barium oxide from 3/2 to 2/1, a depression of the yield percentage appears, and the intensity of 1Ba-aluminate decreases identically in spite of continuous rising of 3Ba-aluminate. This indicates that the yield percentage is not associated with the formation of 3Ba-aluminate, but associated with the formation of 1Ba-aluminate.

Fig. 6 shows the influence of grain size of aluminium. The experiment is carried on at the reaction temperature of 1,150° C for 4 hrs. and the compounding-ratio is 3/2 for BaO/Al in mole. Under these conditions, the yield percentages exceed 50% and the maximum gets to 55.0%. The yield percentage, in general, increases with the decrease of grain size. But in the case of powder decreases the yield percentage. This may be account for its overmuch reactivity; which brings about a so much a quick reduction of barium oxide that the barium vapor can not be quite recovered on the condenser.

Fig. 7 shows the relationship between reaction time and yield percentage.

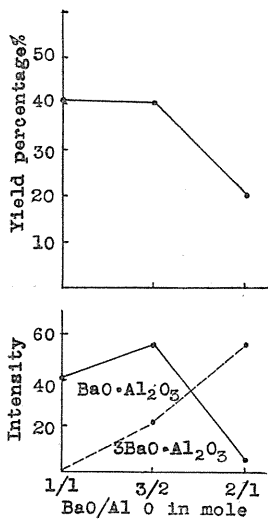


FIG. 5

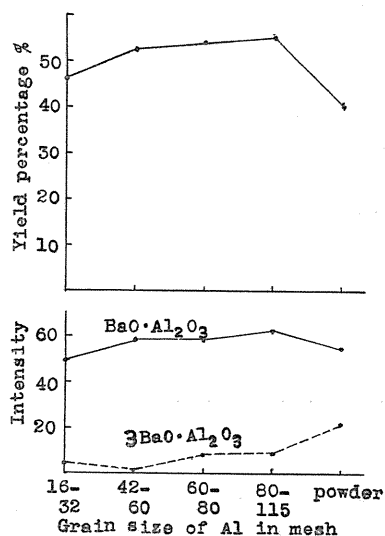


FIG. 6

FIG. 5. Relationship between compounding ratio and yield percentage of barium and X-ray diffraction intensity of the residue.

FIG. 6. Influence of grain size of aluminium on yield percentage of barium and X-ray diffraction intensity of the reaction residue.

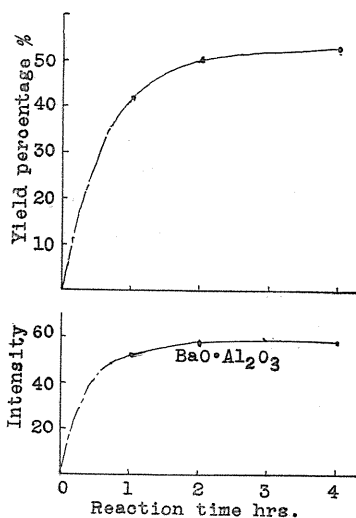


FIG. 7

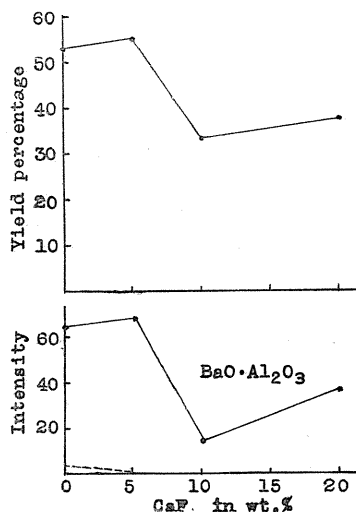


FIG. 8

FIG. 7. Relationship between reaction time and yield percentage of barium and X-ray diffraction intensity of the reaction residue.

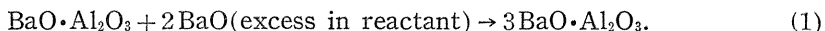
FIG. 8. Effect of calcium fluoride on the yield pt. of barium and the X-ray diffraction intensity of reaction residue.

The result is obtained under the same conditions as shown in Fig. 6, but the grain size of aluminium is from 42 to 60 in mesh. The curve seems to get to equilibrium in 3 or 4 hrs. and the curve of intensity showing the formation of 1Ba-aluminate is similar to that of the yield percentage also. The intensity of 3Ba-aluminate is so small that it can not be detected.

Adding calcium fluoride as a catalyst, under the same experimental conditions as shown in Fig. 7, a result is obtained which is shown in Fig. 8. Although there is a slight rise of yield percentage by such a little addition of calcium fluoride as it becomes 5%, the large amount of addition tends not only to prevent the reactants from contact but also to sinter them. A much similarity is found also between the two curves.

Discussion

In view of the stability of barium aluminate, it has been established that both 1Ba-aluminate and 3Ba-aluminate are formed at the lower temperatures than 1,150° C. Now, if the temperature is low and alumina is rich, *e.g.*, 1,000° C and 1/1 for BaO/Al₂O₃, 3Ba-aluminate is not formed at all but 1Ba-aluminate is. And if the temperature is low and alumina is not rich, *e.g.*, 1,000° C and 1/1 for BaO/Al₂O₃, 3Ba-aluminate is formed beside 1Ba-aluminate. On the other hand, when alumina is rich, *e.g.*, 1/1 for BaO/Al₂O₃, even at the temperature of 1,150° C that is to give the largest rate of reaction, 3Ba-aluminate is hardly formed. Therefore, the formation of 3Ba-aluminate may depend merely on the reaction between 1Ba-aluminate and excess barium oxide;



If this can be established also in the case of the reduction of barium oxide with aluminium, the formula indicates that the formation of 3Ba-aluminate does not take any part in the reduction of barium oxide. In practice, through the experimental results shown in Fig. 4 to Fig. 8, there is found no correlation between the yield percentage and the formation of 3Ba-aluminate, but found well between the yield percentage and the formation of 1Ba-aluminate with no exception. And that correlation indicates the reduction of barium oxide is owing merely to a reaction which brings about the formation of 1Ba-aluminate; namely, at the lower temperature than 1,150° C barium oxide is reduced as follows,



and the reaction (1) may occur if barium oxide is rich.

At the higher temperature than 1,150° C, even if 3Ba-aluminate is formed in the reactor, it will be decomposed to 1Ba-aluminate, so that the reducing reaction is expressed also by the formula (2). And its reaction rate, as mentioned in case of Fig. 4, will be very large at that temperature. By means of the formula (2), now, it has been indicated that the maximum yield percentage of barium is 75%. But in our experiments it attains only to 55%. It should not be thought that the reactions do not get to equilibrium, for the result shown in Fig. 7, but we think that the recovery of barium vapor is incomplete because of its contamination with impurities which appear in the retort, its adsorption on surface of reactants, etc. Especially the adsorption is visibly observed in case of the addition of calcium fluoride.

Conclusion

1. The mechanism of the reduction of barium oxide;
 (a), at the lower temperature than 1,150° C,
 the principal reaction;



when barium oxide is rich, as a supplementary reaction,



(b), at the higher temperature than 1,150° C,



2. The maximum yield percentage we obtained;	55.0%,
under the experimental conditions that,	
the reaction temperature;	1,150° C
the compounding-ratio;	BaO/Al = 3/2 in mole,
the reaction time;	4 hrs.,
the grain size of aluminium;	80-115 mesh,
3. The purity of barium;	97-98%,
the impurities; Al, 1-2%,	the others; Fe and gaseous comp.

In conclusion, we wish to express our gratitude to Mr. M. Koike and A. Nishina for their co-operation.

References

- 1) "Lecture for Experimental Chemistry" Vol. 10, p. 201 (1957).
- 2) Eichi Fujita, Government Chemical Industrial Research Institute, Tokyo, Vol. 46, No. 2.
- 3) Leo Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics", p. 14(1950).
- 4) O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochemistry", p. 232 (1956).