

1

2,789,896

PROCESS FOR REDUCING METAL OXIDES

Lynn Wallace Coffey, Columbus, Ohio, assignor to Climax Molybdenum Company, a corporation of Delaware

No Drawing. Application March 15, 1956,
Serial No. 571,594

1 Claim. (Cl. 75—27)

The present invention relates to the well known Goldschmidt process of reducing metal oxides which involves igniting a mixture of the metal oxide and a reducing agent consisting of another metal having a greater affinity for oxygen than the metal of the oxide.

In theory, any metal having a greater affinity for oxygen than another will, at some temperature, reduce the oxide of the other metal. However, the ignition process to which the present invention relates is an exothermic reaction; and, to be of practical effect, the heat generated by the reaction must be sufficient to melt the reduced metal and the resulting oxide of the reducing metal so that they may separate by gravity while in a molten state. As a result, the use of the process in cases where it was desired to reduce metal oxides has been limited to combinations of metal oxides and reducing metals which, upon reaction, release sufficient heat to produce a molten mass of the reaction products.

The amount of heat released by the reaction equals the difference between the heat released on oxidation of the reducing metal and the heat of formation of the metal oxide which is reduced. For that reason, it is preferred to use, as the reducing metal, a metal such as aluminum which is not only available at reasonable cost but has a high heat of formation of its oxide, Al_2O_3 (i. e., 399.09 kilo-calories per gram mole of the oxide). However, magnesium, silicon and calcium, or other metals having a greater affinity for oxygen than the metal of the oxide to be reduced may be used, if desired.

The quantity of heat released when aluminum is used to reduce a number of metal oxides is given in the following list of aluminum reduction reactions in kilo-calories per gram mole of the oxide which is reduced:

- (1) $3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3 - 295$ k-cal.
- (2) $CrO_3 + 2Al \rightarrow Cr + Al_2O_3 - 260$ k-cal.
- (3) $3Fe_3O_4 + 8Al \rightarrow 9Fe + 4Al_2O_3 - 265$ k-cal.
- (4) $MoO_3 + 2Al \rightarrow Mo + Al_2O_3 - 219$ k-cal.
- (5) $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 - 203$ k-cal.
- (6) $3Nb_2O_5 + 10Al \rightarrow 6Nb + 5Al_2O_3 - 202$ k-cal.
- (7) $Mn_2O_3 + 2Al \rightarrow 2Mn + Al_2O_3 - 167$ k-cal.
- (8) $3Ta_2O_5 + 10Al \rightarrow 6Ta + 5Al_2O_3 - 165$ k-cal.
- (9) $3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3 - 141$ k-cal.
- (10) $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 - 129$ k-cal.
- (11) $3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3 - 48$ k-cal.
- (12) $3ZrO_2 + 4Al \rightarrow 3Zr + 2Al_2O_3 - 10$ k-cal.

The values for the heat released which are given in the table are based on the heats of formation of the oxides at 25° C. and not the true heats of formation at the higher temperature at which the reaction actually occurs. Thus, the table indicates only relatively the amount of heat released by these reactions.

Whether or not the above reactions will result in satisfactory reduction of the metal oxide without added heat depends not only upon the quantity of heat released but the quantity and specific heat of the reaction products and also the melting point of the reaction products.

2

In the case of Reactions (1), (2), (3), (4), (5), and (9), the quantity of heat is sufficient to effect a fairly satisfactory reduction. Due to the higher melting points of the reduced metals or the smaller quantity of heat released, or a combination of both, the remaining reactions are not effective alone. However, Cr_2O_3 , Reaction (10), may be reduced if combined with a quantity of CrO_3 , Reaction (3). Similarly, Reaction (4) is used commercially in conjunction with Reactions (3) or (5) to produce an iron-molybdenum alloy, in which case the iron reduction not only increases the total heat released, but reduces melting point of the reduced alloy below that of molybdenum. This last type of combined reaction is useful only in the production of alloys.

It has also been proposed that other oxides be added to these reactions and reduced along with the metal oxide in question to increase the heat generated; but, except for barium oxide, which is expensive and not always effective, these either introduce undesirable impurities or cause an objectionable evolution of gas. Consequently, the Goldschmidt process has been of only limited application.

To overcome this limiting factor, it has also been proposed that external heat be applied to assist the process; but, to be effective on high melting point materials, the reaction must occur so rapidly that it has been found impossible to transmit the requisite heat to the mass from an external source during the reaction.

It is the object of the present invention to provide an improved method in accordance with which the heat released incident to the reducing reaction may be increased to any desired degree without otherwise impairing the effectiveness of the reaction. As a result, the increased heat released by ignition will make the process more effective when applied to oxides which have been reduced successfully by the Goldschmidt process and will also make the process applicable to oxides which have not been reduced successfully by the process.

In accordance with the present invention the heat released incident to the reduction of any metal oxide or mixture of metal oxides by any reducing metal is increased to any desired degree by combining liquid oxygen with the powdered reaction mixture and increasing the quantity of reducing metal so that it will react with all oxygen in the mixture. Since the oxidation of the reducing metal with pure oxygen releases a much greater quantity of heat than that released when the same reducing metal is oxidized by a metal oxide, the heat imparted to the total charge by the reducing reaction is increased markedly by the simultaneous reaction between the liquid oxygen and excess reducing metal even when relatively small amounts of the latter are added. Moreover, the amount of additional heat imparted to the charge may be increased to meet the requirements of any reducing reaction by simply increasing the amount of liquid oxygen and supplemental reducing metal which is added to the charge.

In accordance with standard practice the metal oxide and the reducing metal are powdered or reduced to small grains and are intimately mixed so that the reaction will occur very rapidly and uniformly throughout the charge once it is ignited. However, in accordance with the present invention, more reducing metal is added than is necessary to react with the oxide and produce the desired product or alloy, and sufficient liquid oxygen is added to the mixture to react with the excess reducing metal. The liquid oxygen is also mixed thoroughly and uniformly through the charge to ensure that it will react with the reducing metal as rapidly as possible and thus raise the temperature of the charge to the maximum degree. Due to the fact that the oxygen is in a liquid state, it is pos-