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Investigation on Reduction of $CoAl_2O_4$ by Hydrogen Gas Using TGA

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The reduction of metallic oxides is an important route for the production of metal and ceramic matrix composites for high technology applications. Experimental investigation on reduction of metallic oxides by hydrogen has special relevance in potential use of natural gas as a reducing agent. In view of this, the Department of Metallurgy, Royal Institute of Technology, has been pursuing kinetic studies on reduction of various complex metallic oxides.[1–5] The present work aims at a study of the reduction kinetics of $CoAl_2O_4$. While the study is partially initiated from a theoretical point of view to investigate reduction characteristics of this complex oxide, it is hoped that the investigation could also result in new information and could pave the way to innovation of newer processes.

The reduction studies of $CoAl_2O_4$ were carried out using a Setaram (Caluire Cedex, France), TGA 92 thermogravimetric analyzer. A schematic drawing of the TGA unit is presented in Figure 1. The analyzer has the resolution of 1 mg and is fully controlled by an IBM PC* through a CS92 controller. A detailed description of the apparatus has been given in an earlier publication.[6]

Cobalt aluminate having a purity of >99 mass pct (approximately 10 μm in particle size) was supplied by Johnson Matthey (Karlsruhe, Germany). In a general run, approximately 20 mg of fine aluminate particles in the form of loosely packed powder bed was kept in a shallow alumina crucible of 8-mm i.d. and 1-mm inner height. The crucible was hung by a Pt suspension wire in the thermobalance and was introduced into the alumina reaction tube. The loosely packed shallow powder bed would allow the reducing gas to have good access to all individual particles. The use of fine particle size would ensure that the diffusion distance for both H_2 and H_2O was short enough, so that it was possible to focus the study on the chemical reaction at the initial stages of reduction.

Before heating, the reaction chamber was first evacuated down to vacuum of 10 Pa and argon gas was introduced through the auxiliary gas inlet. The argon gas having a PLUS grade quality, *i.e.*, 99.999 pct pure, was supplied by AGA GAS (Stockholm). The furnace was then heated to the desired reaction temperature under constant argon flow. When the sample temperature was stabilized, argon supply was terminated and the reducing gas, hydrogen (PLUS grade quality, *i.e.*, 99.999 pct pure, supplied by AGA GAS), was introduced to the furnace chamber through the carrier gas inlet. A constant flow of hydrogen was maintained during the entire course of reduction. The gas flow corresponds to a linear velocity of 300 N cm/min. It was confirmed by preliminary experiments that the hydrogen flow used was above the starvation rate of reactions. The weight changes were registered by the computer at intervals of 2 seconds.

In order to examine the products of the reduction, a sample in the form of loosely packed pellet was reduced at 1473 K and was subjected to scanning electron microscope (SEM) analysis. For this purpose, a Hitachi (Ibarki, Japan) Microscope Model S-3500N attached with an energy-dispersive X-ray analyzer (model ISIS series 300, Oxford, United Kingdom) was employed.

The experiments were carried out in the temperature range 1173 to 1473 K. The reduction curves are shown in Figure 2, in which the fraction f denotes the ratio of instant mass loss to the theoretical mass change corresponding to the loss of one oxygen atom from $CoAl_2O_4$.

It is clearly seen that the reduction curves corresponding to the temperatures at and higher than 1273 K cross the expected maximum value of 1. In order to examine the possibility of the weight loss due to the formation of volatile species of Al_2O_2 and Al_2O during the reduction, thermodynamic calculation was carried out using the literature data.[7] The calculated results show that the equilibrium pressure of Al_2O_2, $P_{Al_2O_2}$, due to the reaction

$$Al_2O_3 + H_2\,(g) = Al_2O_2\,(g) + H_2O\,(g) \qquad [1]$$

is lower than 10^{-11} bar at 1500 K under hydrogen pressure of 1 bar. In the case of Al_2O, the reaction is considered to be

$$Al_2O_3 + 2H_2\,(g) = Al_2O\,(g) + 2H_2O\,(g) \qquad [2]$$

The standard Gibbs energy of Reaction [2] reveals that at equilibrium, the product of $P_{Al_2O} \cdot P^2_{H_2O}$ has a value of $4.6 \cdot 10^{-22}$ at 1500 K under hydrogen pressure of 1 bar. The low values of $P_{Al_2O_2}$ and P_{Al_2O} indicate that both Reactions [1] and [2] would not take place to an appreciable extent at the present experimental temperatures. This aspect was further confirmed by the experiment, in which an alumina crucible containing Al_2O_3 powder was hung in the hydrogen gas stream at 1473 K for a few hours. The undetectable weight change of the sample during this experiment has further ruled out the possibility of appreciable volatilization of Al_2O_2 and Al_2O during the reduction in the present experimental temperature range. The degree of the reduction being higher than 1 at and above 1273 K would indicate that some amount of Al_2O_3 has probably been reduced to Al.

Figure 3 shows the SEM micrographs of a completely reduced sample at 1473 K. Energy dispersive spectroscopy (EDS) analysis showed that in the gray areas marked "A" in the figure, cobalt metal was well mixed with alumina. In the light phase, marked "B" in the figure, metallic cobalt was found to coexist with Al. The atomic percent of Al in

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Manuscript submitted October 20, 1999.

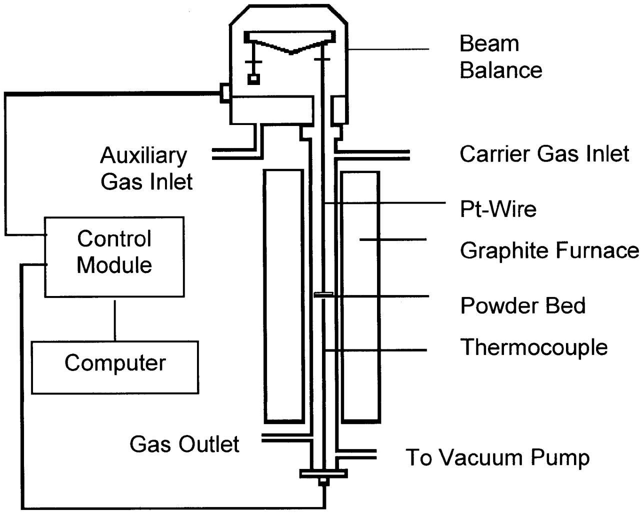

Fig. 1—Experimental setup.

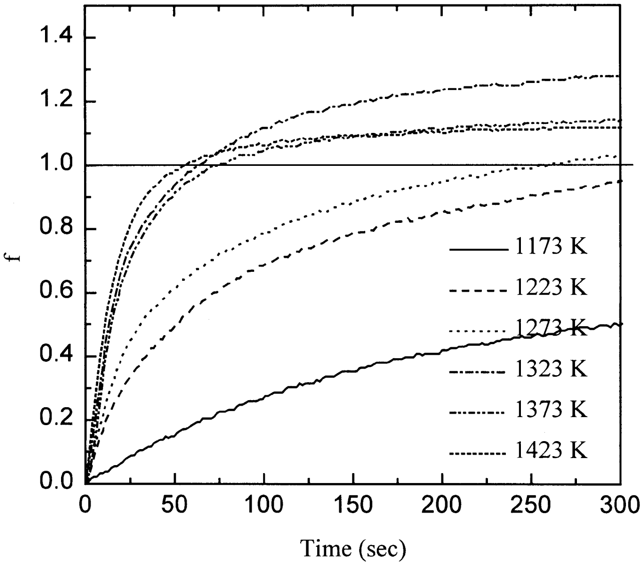

Fig. 2—Weight loss curves for $CoAl_2O_4$.

this light phase was about 40. It is noted that the total amount of the Co-Al phase is small in the reduced sample. In the middle part of the figure, a particle, marked "C," was detected to be pure Co. It should be pointed out that this was the only particle observed in the specimen. It is reasonable to believe that the pure cobalt particle was formed from Cobalt oxide, which might be there as impurity in the original $CoAl_2O_4$ sample.

The observation of the existence of Co-Al phase in the reduced sample by SEM analysis is in accordance with the reduction curves shown in Figure 2. The reductions at and above 1273 K all proceeded beyond $f = 1$, indicating the reduction of Al_2O_3 to Al metal. Hence, the reduction of $CoAl_2O_4$ by hydrogen can be expressed as

$$\begin{aligned} r\mathrm{CoAl_2O_4} + \left(1 + \frac{3}{2}(1 - \alpha)X\right)H_2 &= X\mathrm{Co}_\alpha\mathrm{Al}_{1-\alpha} \\ &+ (1 - X\alpha)\mathrm{Co} + \left(1 - \frac{1}{2}(1 - \alpha)x\right)\mathrm{Al_2O_3} \\ &+ \left(1 + \frac{3}{2}(1 - \alpha)x\right)\mathrm{H_2O} \end{aligned} \qquad [3]$$

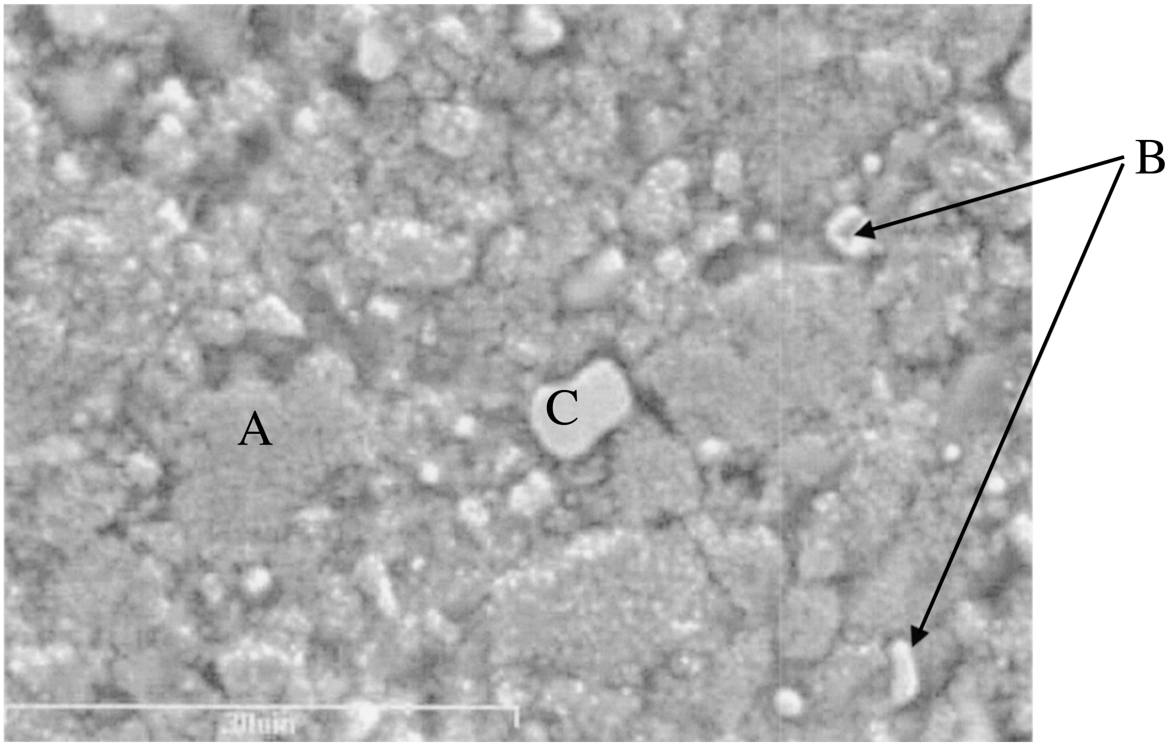

Fig. 3—Completely reduced $CoAl_2O_4$ sample at 1473 K: (A) Co-Al_2O_3 mixture, (B) Co-Al phase, and (C) Co.

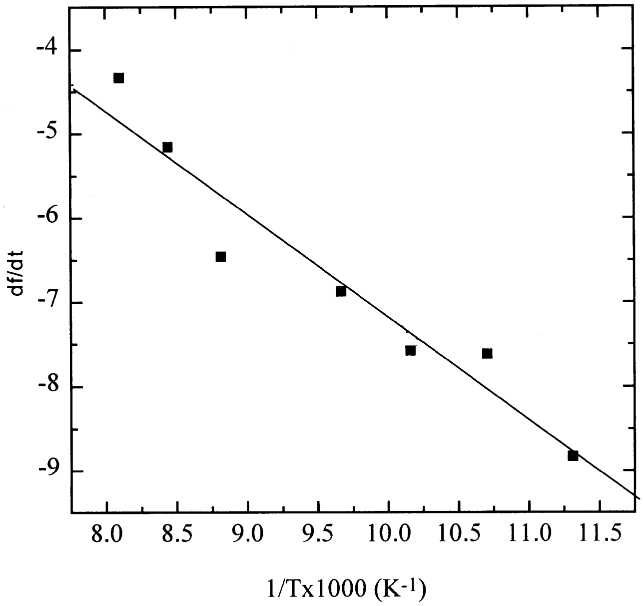

Fig. 4—Arrhenius plot for the reduction of $CoAl_2O_4$ by H_2.

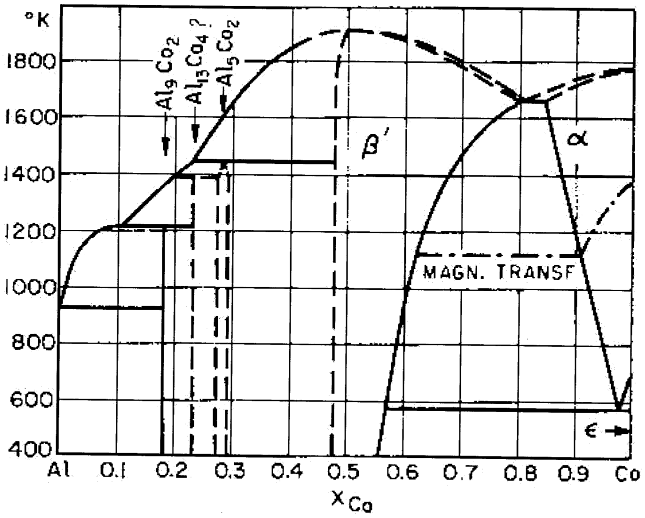

Fig. 5—Phase diagram of binary Co-Al.[8]

where α refers to the composition of the observed Al-Co alloy and X represents a constant.

It is clearly indicated by the Ellingam diagram[8] that alumina can only be reduced by hydrogen at very high temperatures. Even above 1773 K, the P_{H_2}/P_{H_2O} ratio needs to be above 10^{+7} to reduce alumina into aluminum metal. Hence, aluminum is mostly produced by electrolytic reduction. However, the present experimental findings clearly indicate the possibility of reducing aluminum oxide at lower temperatures. A thermodynamic explanation is expected to be found in the affinity of cobalt for aluminum.

The phase diagram of the Al-Co system[9] is reproduced in Figure 4. It shows that cobalt and aluminum form Co-Al solid solutions and a number of intermetallic compounds. The Co-Al phase found in the reduced sample has an aluminum content of about 40 at. pct, which would correspond to the β' solid solution. The enthalpy of mixing of the β' solution having a composition of $Co_{0.5}Al_{0.5}$ is reported to be -55229 J/mole atom.[10, 11] In addition, the trend suggests that the enthalpy is becoming increasingly negative as the aluminum content decreases. This clearly indicates a strong affinity of aluminum toward cobalt.

Based on the available thermodynamic information[7] on the β' solution, the Gibbs free energy change for the reaction depicted in Eq. [3] for $\alpha = 0.5$ was estimated at 1400 K. It was found that for $x < 0.35$, the standard Gibbs free energy change for the reaction given in Eq. [3] is negative, which is in line with the present experimental results.

Similar thermodynamic calculations for the reduction of $NiAl_2O_4$ by hydrogen show that the formation of AlNi intermetallic compound as one of the reduction products is also possible. However, experimental investigation[3] on the reduction of $NiAl_2O_4$ has not reported any Ni-Al alloy. The extremely small particle size of the produced metallic phase could have made the EDS analysis difficult.[3] Further, experimental investigation on the reduction of nickel aluminate is necessary to give more insight.

Since the powder bed was very shallow and the hydrogen flow rate was reasonably high, it could be expected that the reactant gas H_2 had access to all the small particles in the bed and H_2O could leave the site without much hindrance. Since the particles were very small, the reduction was controlled by the chemical reaction at the surfaces, at least in the initial stages. An Arrhenius plot using the initial reaction rates is presented in Figure 5. The apparent activation energy estimated for the reduction of $CoAl_2O_4$ from the Arrhenius plot was found to be 102 kJ/mole.

Financial support for this work from the Swedish Council for Technical Science (TFR) is gratefully acknowledged.

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