Kinetic Studies of the Reduction of FeO and $FeWO_4$ by Hydrogen

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The kinetics of the reduction of FeO and $FeWO_4$ have been investigated by thermogravimetric method in the temperature ranges of 1023 to 1173 K and 823 to 1173 K, respectively. The experiments were conducted under isothermal conditions in flowing hydrogen gas. The activation energies for the reduction of the pure iron oxide and iron tungstate were found to be 42.7 kJ/mol and 85.1 kJ/mol, respectively. The results obtained show that the reduction of iron tungstate proceeds in one single step from $FeWO_4$ to Fe_3W_2 and W. The experimental data are compared with the information available in the literature, and the correlations between the results obtained in pure oxide systems and complex systems are discussed.

I. INTRODUCTION

THE advances in high technology have led to the development of a new generation of materials with improved properties. In this respect, metal-matrix composites have found a variety of high-technology applications. The reduction of complex oxides appears to be a potential production route for composite materials with a metal matrix. This route offers a unique advantage, as the materials produced under well-defined conditions have enough active centers to achieve good chemical bonding between the dispersed material and the matrix during the production process itself. A number of reduction studies were carried out at the division of Theoretical Metallurgy (Royal Institute of Technology, Stockholm, Sweden) toward the production of tungsten-dispersed nickel and cobalt[1–5] by hydrogen reduction of tungstates. The results obtained show that the reduction route chosen for these experiments was extremely promising for the production of composite materials where a uniform dispersion of the fine additives is required. The present study was carried out with the view to extend the investigation to iron-based alloys. Tungsten-iron heavy alloys, in addition to their use in metallurgy, have found numerous applications as kinetic energy penetrators, radiation shields, and counterbalances and in a number of other defense applications.[6]

It is important to point out that the reduction of iron tungstate is also of theoretical interest. The activation energy of iron tungstate reduction is a function of the metal-oxygen interactions and, thus, a function of the thermodynamic stability of iron tungstate in comparison to that of pure tungsten oxide and pure iron oxide. In the case of the reduction of nickel tungstate, it has been shown[2] that the activation energy is the sum of the activation energies of the reduction of pure nickel oxide and pure tungsten oxide. And, in this case, the reduction was found to proceed in two stages. In the case of cobalt tungstate, however, the reduction proceeds in a single step and the activation energy is close to that of WO_2.[4]

A comparison of the thermodynamic stabilities of the tungstates of iron, cobalt, and nickel reveals that the Gibbs-free energy of formation decreases with increasing atomic number. The relationship between the activation energies of the reduction of iron tungstate compared with those of the component oxides, obtained under identical conditions, has not been investigated. One of the aims of this present study on the reduction of iron tungstates has been to see if the reduction kinetics of this system can be predicted from those of the component oxides.

II. PREVIOUS WORK

A number of investigations on the reduction of iron oxides have been carried out by different groups of investigators over the years, and these are presented in Table I. The results from the different investigations, however, are not in agreement with each other. The activation energy for the reduction of wüstite (FeO) reported in recent publications is much lower than those reported earlier, which perhaps could be attributed to improvements in the experimental technique. Hayashi and Iguchi[7] and Turkdogan and Winters[9] have conducted the reduction experiments under somewhat similar experimental conditions to the present study. The former report an activation energy value of less than half of the one reported by the latter. Edström[11] has made a summary of the most important work done up to 1953, and he also presents the reduction mechanisms of the different iron oxides.

III. EXPERIMENTAL

A. *Materials*

Wüstite was prepared from pure iron and hematite. All the materials used in the present work are stated in Table II, along with information regarding the material's supplier, its purity, and any pretreatment made to the material.

FeO was prepared by mixing dry hematite and pure iron in equimolar quantities.[12] The mixture was heated to 1373 K in a sealed, alumina-lined iron crucible for 20 hours and then quenched. The crucible was then opened and the metastabile ''FeO'' thus prepared was subjected to X-ray diffraction (XRD) analysis. The absence of metallic iron as

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Table I. Literature Data for the Reduction of FeO

Method of Investigation	Reducing Media	Activation Energy (kJ/mol)	Temperature Interval (K)	Year of Publication	Reference Number	Remarks and Material
Thermogravimetry	H_2	418	973 to 1273	1994	7	Samarco iron ore
Fluidized bed	N_2-H_2 mixture	110	1723 to 1823	1994	8	reduction of liquid iron ore fines in gas-conveyed systems
Thermogravimetry	H_2	80.3*	1073 to 1473	1972	9	apparent activation energy hematite*
Thermogravimetry	H_2-H_2O mixture	159	973 to 1323	1966	10	synthetic wüstite
Horizontal tube furnace and microscopic analysis	H_2 and different mixtures of CO/CO_2	—	723 to 1273	1953	11	results obtained by quenching samples after different reaction times: hematite, magnetite, and wüstite

well as other oxides of iron was confirmed by this method. From the XRD pattern, the lattice parameter of the FeO produced was calculated to be 4.317 Å. This value compares well with the reference value from the TADD database, *viz.*, 4.307 Å for pure wüstite.

Some reduction experiments of wüstite in hydrogen were carried out to find out the oxygen content of the FeO prepared. In these experiments, a maximum weight reduction of 22.91 wt pct was obtained, indicating that the composition corresponds to $Fe_{0.96}O$. Thus, the purity as well as the composition of the metastabile FeO was considered to be well defined in the present work. Hydrogen reduction experiments of the iron tungstate examined in the present work showed a maximum weight reduction of 21.02 pct, which is very close to the theoretical value of 21.07 pct for complete oxygen removal. No weight loss due to evaporation of water could be detected during the heating of this sample. Hence, no pretreatment of the iron tungstate was carried out before the reduction experiments.

Table II. The Materials Used in This Investigation

Material	Stated Purity (Pct)	Supplier	Remarks
Fe_2O_3	99.9	Johnson Matthey	dried at 573 K for 10 h before use
Fe	99.5	Merck	—
$FeWO_4$	99	Johnson Matthey	—
Ar	99.9997	AGA*	—
H_2	100	AGA*	—

*AGA Special Gas, Stockholm.

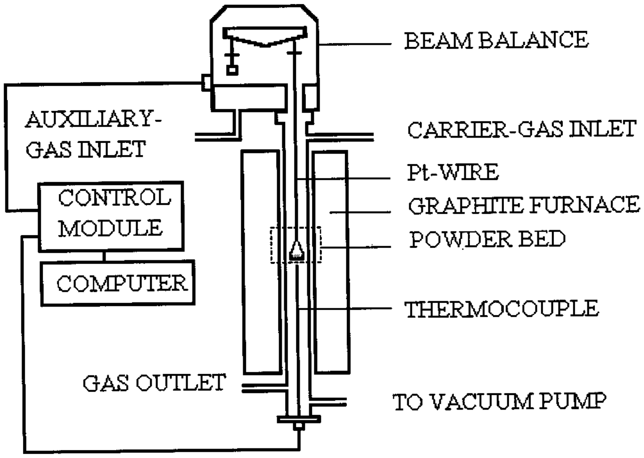

Fig. 1—The experimental setup.

B. *Apparatus and Procedure*

The apparatus and procedure used in this study have been described in detail in an earlier publication;[13] therefore, only a brief account of the important features will be given in this article. The apparatus is a SETARAM, TGA 92 (France) thermogravimetric instrument, with a detection limit of 1 μg. The apparatus is schematically shown in Figure 1. The system is fully controlled by an IBM PC* through a CS92 control unit.

In the case of both wüstite and iron tungstate, an approximate sample weight of 50 mg ($\pm$0.1 mg) was used in the reduction experiments. The samples were suspended in the furnace chamber from the beam balance. The powder samples were contained in an alumina crucible of 8-mm diameter and 1-mm height. These conditions ensure that the chemical reaction rate is the rate-controlling step for the experiments. Some experiments were conducted by slightly varying the height of the bed; however, no change in the reduction rate could be observed. In both cases, the powder beds were very shallow, less than 0.5 mm. The reaction chamber was first evacuated down to a vacuum of 10 Pa, before argon was introduced into the furnace chamber through the auxiliary gas inlet. The temperature was then increased. When the temperature was stable at a preset level, hydrogen was introduced into the chamber through the carrier gas inlet. A constant hydrogen flow rate of 0.52 L/min (STP) was maintained during the entire course of the reduction. This gas flow corresponds to a linear velocity of 250 cm/min, and was found, in preliminary experiments, to exceed the starvation rate for the reduction reactions. The reduction experiments were carried out under isothermal conditions in the temperature range of 823 to 1173 K.

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*IBM PC is a trademark of International Business Machines Corporation, Armonk, NY.

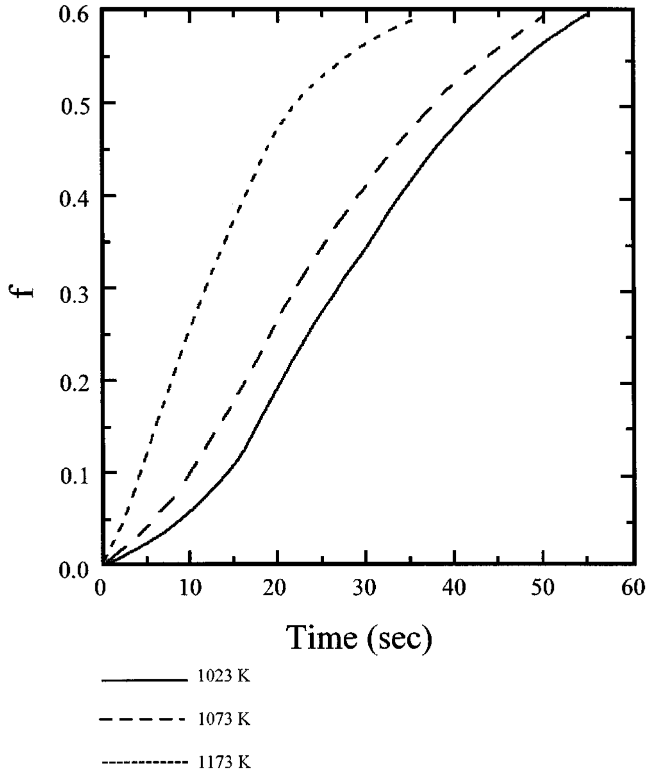

Fig. 2—Results of the hydrogen reduction experiments of wüstite.

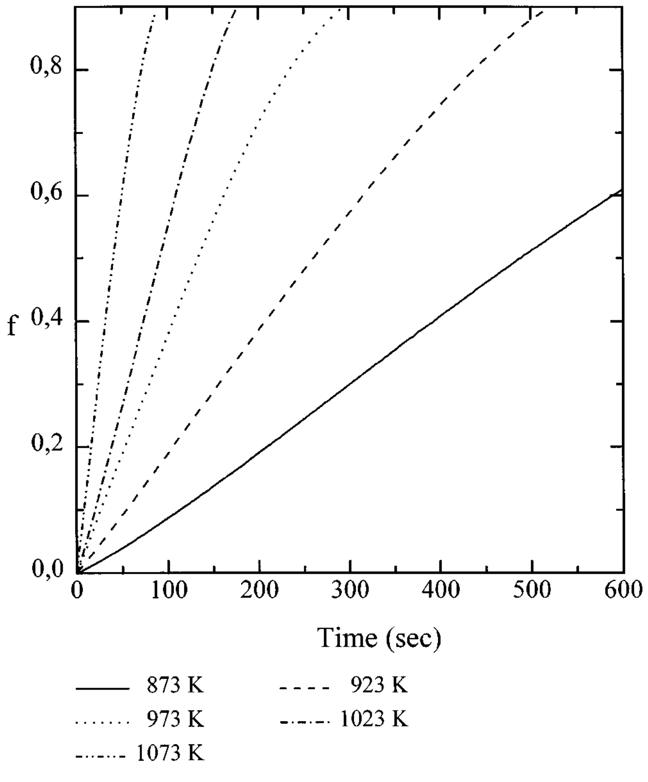

Fig. 3—Results of the hydrogen reduction experiments of iron tungstate.

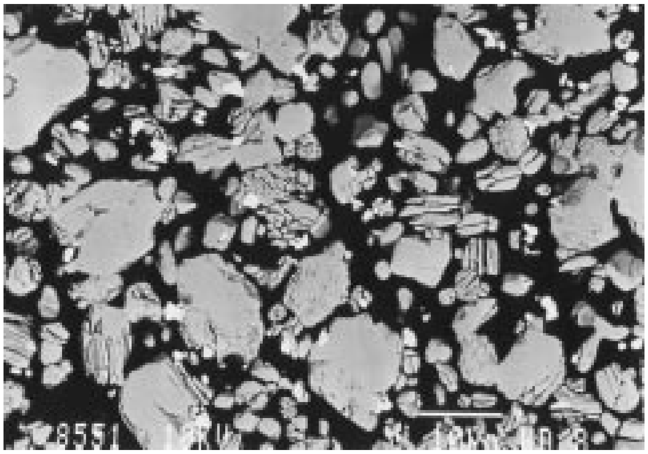

Fig. 4—Micrograph of the partially reduced iron tungstate sample (53 pct reduction).

IV. RESULTS

A. *FeO Reduction*

Since FeO has been investigated previously by a number of scientists, with differing results, a brief investigation was conducted at high temperature to ensure conditions identical to those used for the tungstate investigation reported in this article. The temperature range for these reduction studies was 1023 to 1173 K. The maximum temperature limit was set by the fact that the reaction rate became extremely fast beyond 1173 K and the experimental data became unreliable.

The results of the reduction experiments are presented in Figure 2. The figure shows the fraction of reduction *f, i.e.*, the ratio of the instant mass loss to the theoretical final mass loss, as a function of time for the different temperatures. The reduction of wüstite was quite fast, as can be seen in the figure. In fact, the reduction was almost complete within 1 minute, even at the lowest experimental temperature, *viz.*, 1023 K.

B. *$FeWO_4$ Reduction*

The reduction curves for the iron-tungstate are presented in Figure 3. In this figure, the mass loss has been converted to the fraction of reduction. It can be seen that, even in this case, the rate of reduction was high. The reduction at the highest temperature in the chosen temperature interval (823 to 1173 K) was almost complete within 2 minutes.

In order to confirm the reduction mechanism, one sample was prepared as a loosely compacted briquette (6-mm diameter and approximately 1-mm height, weighing approximately 200 mg). The reaction was arrested at approximately 53 pct reduction by flushing the reaction chamber with argon and cooling the furnace at a rate of 100 K/min. The partially reduced briquette was examined by scanning electron microscopy (SEM) analysis. The micrograph of this sample is presented in Figure 4. The presence of the phases Fe_3W_2 (light phase) and $FeWO_4$ (dark phase) have been identified by energy dispersive spectrometry (EDS) analysis.

Because of the difficulties determining the existence of pure tungsten in the partly reduced sample by SEM and EDS, a partly reduced sample with approximately 60 pct reduction was examined by XRD analysis. The presence of pure tungsten could thereby be confirmed in the X-ray results, while no oxides of tungsten (WO_2, WO_3, *etc.*) could be detected. This is in support of the proposed process route.

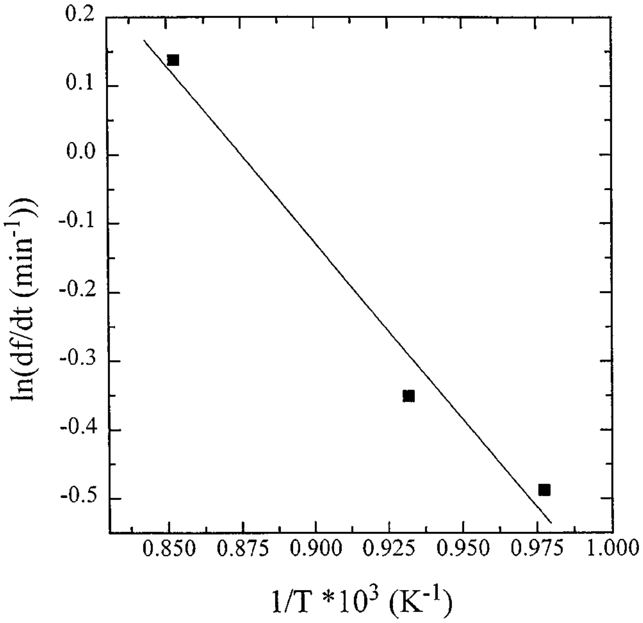

Fig. 5—Arrhenius plot of the initial reduction rate of wüstite *vs* reciprocal temperature.

V. DISCUSSION

The experimental conditions are summarized briefly as follows:
(1) shallow powder bed, less than 0.5 mm;
(2) low crucible, approximately 1-mm deep;
(3) high hydrogen gas flow, 0.5 L/min; and
(4) both FeO and $FeWO_4$
were powders with very fine grain size, less than 5 μm.

These conditions should ensure good contact between the reducing gas, H_2, and all the individual particles in the bed. The product gas, H_2O, should also have an easy escape from the bed, and thereby it should be safe to rule out transport in the gas phase, as well as mass transfer in the solid phase, as controlling steps in the reduction process. As mentioned earlier, slight changes in the bed height had no noticeable effect on the reaction rate. Therefore, the chemical reaction could be expected to be the rate-controlling step, especially in the initial stages of the reduction.

A. *FeO Reduction*

The reduction of FeO proceeds according to the reaction:

$$Fe_{0.96}O\ (s) + H_2\ (g) = 0.96Fe\ (s) + H_2O\ (s). \quad [1]$$

Figure 5 shows the Arrhenius plot for the initial reduction rate for the reduction experiments. From the slope of the plot, the activation energy was evaluated to be 42.7 kJ/mol. The results obtained in the reduction of FeO agree well with the results obtained by Hayashi and Iguchi.[7]

It would be interesting to compare the activation energies for the hydrogen reduction of different transition metal oxides having the wüstite structure. Such a comparison is made in Table III. It can be seen that the activation energy for NiO is lowest and that for CoO is highest, while the value corresponding to FeO is in between. The enthalpies of formation of these oxides at 298 K have been listed in Table III. If enthalpies can be considered as a measure of the bond strengths, it should be reasonable to expect that the reduction of FeO should have the highest activation energy.

In the case of FeO, it should be remembered that the number of Fe-O bonds are reduced to 0.96 × Avogadro's number of bonds. In order to compare the activation energies, it would be reasonable to divide the experimental activation energy value by 0.96, which would lead to a value of 44.5 kJ/mol. This would not seriously affect the situation. The reason for the change in the trend for the activation energy shown in Table III is not certain. One possible reason could be that, in the case of NiO, the reductant hydrogen dissolves in the metallic Ni phase formed during the initial stages of reduction, and further reduction could take place by the fast diffusion of the atomic hydrogen followed by the chemical reaction,

$$NiO\ (s) + 2H\ (g) = Ni\ (s) + H_2O\ (g) \quad [2]$$

in addition to the gas-solid reaction:

$$NiO\ (s) + H_2\ (g) = Ni\ (s) + H_2O\ (g). \quad [3]$$

Consequently, the activation energy, measured in the case of NiO, could correspond to a situation of Reactions [2] and [3] occurring simultaneously. This is supported by the fact that the solubility of hydrogen in Ni at 893 K is significantly higher than those for Co and Fe.[16] It is possible that even the relative differences in the sintering effects during reduction for the three oxides could affect the activation energies, as this could result in a serious decrease in the surface area available for the reduction reaction. It should be noted that the temperature of reduction in the case of Ni is much lower compared to that for the other oxides.

B. *$FeWO_4$ Reduction*

According to the phase diagram of the Fe-W-O system,[14] shown in Figure 6, the reduction of iron tungstate should occur in a single step, the product being a mixture of Fe_3W_2 and W. This is in agreement with the reduction results, shown in Figure 3, where no discontinuity is seen in the reduction curves. The reduction reaction can thus be written as

$$FeWO_4\ (s) + 4H_2\ (g) = \frac{1}{3}Fe_3W_2\ (s) + \frac{1}{3}W\ (s) + 4H_2O \quad (4)$$

It should be mentioned that the pure tungsten phase could not be detected by EDS analysis in the sample. This could be due to the tungsten phase being well dispersed in the metal matrix.

Figure 7 presents the Arrhenius plot for the initial reaction rate for the reduction of $FeWO_4$. From this plot, the activation energy for the reduction of iron-tungstate by hydrogen was evaluated to be 85.1 kJ/mol.

The activation energies for hydrogen reduction of the three transition metal tungstates are presented in Table IV.[2,4] It can be seen that the activation energies for the reduction of the selected tungstates are very close, but there is a tendency for the values to increase with increasing atomic number. Experiments in this and previous studies have shown that both iron and cobalt tungstates are reduced in one step, while nickel tungstate is reduced in two. Ac-

Table III. Comparison of the Activation Energy for the Reduction of Fe, Co, and Ni Oxides by Hydrogen

Oxide	Atomic Number of Metallic Constituent	Activation Energy (kJ/mol)	Heat of Formation,[15] kJ/mol ($T = 298$ K)	Standard Gibbs Free Energy,[15] kJ/mol ($T = 900$ K)
FeO	26	42.7	−265.96	6.85
CoO	27	54.3	−237.94	−27.99
NiO	28	18	−239.74	−40.47

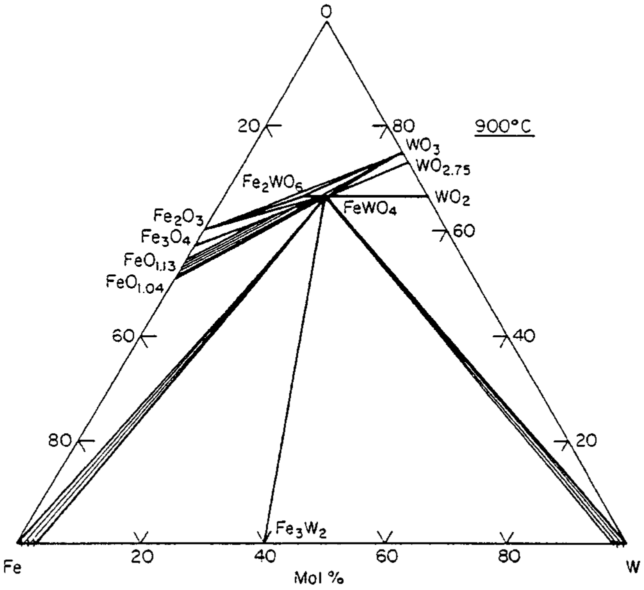

Fig. 6—Phase diagram of the system Fe-W-O at 900 °C.

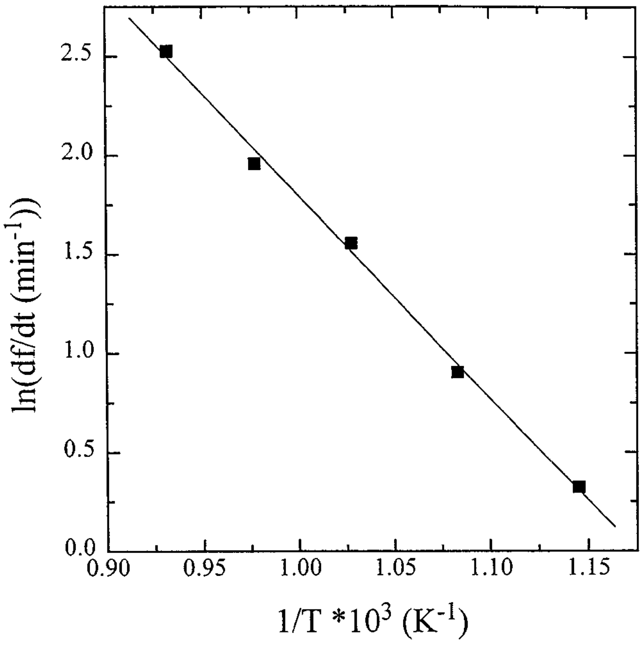

Fig. 7—Arrhenius plot of the initial reduction rate of iron tungstate *vs* reciprocal temperature.

cording to earlier publications, the activation energy of reduction of WO_3 to WO_2 is 75.9 kJ/mol,[1] and the activation energy for NiO is 18 kJ/mol.[3] The sum of the activation energies of the two component oxides is 93.9 kJ/mol, which is very close to the activation energy of the nickel tungstate reduction to WO_2 and Ni reported by Sridhar *et al.*[2] *viz.*, 95.3 kJ/mol. In the two-step reaction for $NiWO_4$, the breakdown of the Ni-O bonding could be the main reaction step, followed by the reduction of WO_3 to WO_2 before WO_2 is reduced to W. This would probably explain the additive behavior of the activation energies. In this case, even the reduction occurring through the dissolution of H_2 in Ni, and a possible reduction by atomic hydrogen, could be part of the overall reduction of $NiWO_4$.

In the case of the single-step reduction, the reaction is likely to proceed by the breakdown of the WO_4 complex. The strength of the W-O bonds is weakened due to the attraction of Fe or Co to oxygen. The difference between the activation energy of a tungstate and that of a corresponding pure oxide would probably correspond to the energy for breaking down W-O bonds, which should be independent of the transition metal. This value is 40.6 kJ/mol for iron tungstate, and 35.7 kJ/mol for cobalt tungstate.

The micrograph presented in Figure 4 shows that the phases present are iron tungstate ($FeWO_4$), viewed as the dark phase in the picture, and iron-tungsten alloy (Fe_3W_2), viewed as the light phase. The phase diagram for the Fe-W-O system, presented in Figure 6, is in agreement with the results obtained in this study.

The normal processing route for tungsten-heavy alloys today includes sintering mixed powders of tungsten and appropriate binder materials at a temperature where the minor constituents form a liquid.[6] The liquid formed at the sintering temperature takes tungsten into solution and reprecipitates it onto existing tungsten grains. This process of sintering-reprecipitation aids the densification and results in significant grain growth. The process would also result in a material with considerable property variations.[6] This must be attributed to the difficulties in controlling the composition in all the different parts of the sintered body. Mixing tungsten and a tungstate of the minor constituent (usually cobalt, iron, and/or nickel) and sintering in a reducing atmosphere should result in better control of the grain size and the composition. This processing route would also be favorable in the production of tungsten-reinforced steel, because of the fine dispersion of tungsten in the metal matrix.

VI. SUMMARY AND CONCLUSIONS

In the present work, the reduction kinetics of FeO and $FeWO_4$ by hydrogen were investigated by a thermogravimetric method. The reduction experiments were conducted on powder samples in shallow powder beds. The reduction experiments were carried out in the temperature ranges of 848 to 1173 K for wüstite and 823 to 1173 K for iron tungstate. The activation energies for the reduction of wüs-

Table IV. Comparison of the Activation Energy for the Reduction of and the Heat of Formation of Fe, Co, and Ni Tungstates

Material and the Solid Product	Activation Energy (kJ/mol)	Heat of Formation,[15] kJ/mol (T = 298 K)	Standard Gibbs Free Energy,[15] kJ/mol (T = 800 K)
$FeWO_4$ = Fe−W	85.1	−1184.42	92.5
$CoWO_4$ = Co−W	90	−1142.65	46.34
$NiWO_4$ = Ni + WO_2	95.3	−1127.84	21.46

tite and iron tungstate were found to be to 42.7 and 85.1 kJ/mol, respectively. The results from this investigation were compared with results obtained previously in similar systems. The difference between the activation energy for the reduction of the simple oxide and the corresponding tungstate was found to be similar in the case of both iron and cobalt.

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