Journal of Alloys and Compounds, 190 (1993) 143–147
JALCOM 398

Mechanisms governing tribochemical reduction of metals and non-metals from their oxides

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(Received February 3, 1992; in final form May 22, 1992)

Abstract

The paper describes the physical and chemical mechanisms governing the tribochemical reduction of metals and non-metals from their oxides. The reduction was started by a tribochemical activation of initial constituents in a vibrating mill used as a reactor. Powders of oxides of copper, iron, molybdenum, tungsten, vanadium, titanium and boron and also such chemically pure metals as magnesium, aluminium and titanium were used as reaction constituents. The triboactivation energy contribution needed to start the explosive mechanism reduction is found to increase as the heat of reaction decreases and the heat of formation of the associated product rises. Introducing oxygen into the reactor during the tribochemical activation of powders of oxides together with magnesium causes the intense oxidation of magnesium and stimulates the reduction process. To increase the yield of tungsten monocarbide from tungsten concentrate, the reduction process should be implemented in an atmosphere of hydrogen or hydrocarbons.

1. Introduction

Data on tribochemical reactions were first systematized by Carey-Lea at the end of the 19th century [1]. He showed that on pounding silver, gold, platinum and mercury halogenides with a pestle, they decompose to produce metals. In more recent years a large number of investigations of various tribochemical reactions have been carried out. Some of this research has been summarized in monographs by Thiessen *et al.* [2], Heinicke [3], and Avvakumov [4].

Recently, particular interest in tribochemical reactions has arisen owing to the possibility of carrying out tribological syntheses of carbides, silicides, borides [5] and sulphides [6] and of reducing metals from their oxides [7, 8]. In refs. 7 and 8 it is shown that the metallothermic reduction reactions initiated by tribochemical activation of the starting elements proceed by an explosive mechanism. The reaction proceeds spontaneously after starting and cannot be stopped. Here tribochemical activation enables the start of an exothermic reaction which then proceeds via heat release. Unlike the widely used methods of initiating metallothermic reactions (an open flame, a heated electric wire, an igniter, an electric discharge), the tribochemical method is not widely used and has been little studied. This is due to the fact that in the tribochemical activation of solid particles a number of effects occur which in combination initiate a metallothermic reaction. It is extremely difficult to differentiate and evaluate their respective roles in starting the metallothermic reaction. These effects include:

(a) splitting of the particles and the formation of new, highly reactive, clean surfaces on which, in the first instant, various substances may become adsorbed;

(b) plastic deformation of the particles, thereby creating many new solid state defects which are reflected by an additional energy increment stored in the lattice;

(c) friction and wear, which finally produce heat that dissipates.

In this connection we suggest introducing a quantity D (the tribochemical energy contribution, which is an integral value of the effects (a)–(c) above) to evaluate the level of tribochemical energy needed to start the metallothermic reaction. D need not strictly exhibit quantitative character. Its values merely allow us to make a comparative analysis of different metallothermic reactions initiated by tribochemical activation.

The aim of this paper is to elucidate the physical and chemical mechanisms governing the tribochemical reduction of metals and non-metals from their oxides as well as the formation of refractory compounds.

0925-8388/93/$6.00

2. Experimental procedures

Powders of chemically pure oxides (Cu_2O, MoO_3, FeO, WO_3, VO, TiO, B_2O_3, SiO_2) and metals (magnesium, aluminium, titanium) as well as a tungsten concentrate (54%–61% WO_3) were used as initial constituents in the experiment. The content of the basic substituent in the powders of the oxides being studied was not less than 97%; in aluminium powders, 98%; in titanium powders, 99.5%; in magnesium powders, 97%. The mean sizes of the initial constituents were as follows: Cu_2O, 0.05 mm; MoO_3, 0.05 mm; FeO, 0.05 mm; WO_3, 0.05 mm; VO, 0.05 mm; TiO, 0.05 mm; B_2O_3, 1–2 mm; SiO_2, 0.05–0.36 mm; magnesium, 0.2–0.3 mm; aluminium, 0.2–0.3 mm; titanium, 0.1–0.5 mm; tungsten concentrate, 0.1 mm. The tribochemical reduction of metals from their oxides and the formation of refractory compounds were carried out by the reaction

$$x\mathrm{MeO} + X\mathrm{Mg(Al)} + y\mathrm{C(Me)} \longrightarrow X\mathrm{MgO}(\mathrm{Al_2O_3}) + \mathrm{Me}_x\mathrm{C}_y + Q \quad (1)$$

where MeO is an oxide of a metal or non-metal, Me_xC_y is a carbide or another refractory compound and Q is the heat of reaction.

The tribochemical activation was carried out in the vibrating mill developed by the Far Eastern Polytechnic Institute at a vibration frequency of 12 Hz and a vibration amplitude of 90 mm. The mill used as a reactor was filled with steel balls 19.5 mm in diameter to 0.5–0.6 of its capacity. The ball-to-sample ratio varied from 10 to 20. The temperature of the reactor was monitored with an IKR-4M IR radiometer to a precision of ± 0.5 °C and with a thermocouple inserted in the wall of the reactor. The reduction process was studied by examining temperature–time thermograms and data from X-ray diffraction analysis of the end products. The gas composition of the reactor atmosphere was analysed with a GAZOKHROM 3401 chromatograph.

3. Results and discussion

In order to classify the experimental data on the tribochemical reduction of metals, a comparison between the free energy of oxide formation and the triboactivation energy contribution has been made. The tribochemical energy contribution was estimated by the formula

$$D = \frac{Et}{m}$$

where D (kJ g^{-1}) is the tribochemical energy contribution, E (W) is the rating of the mill, m (g) is the mass of initial constituents loaded and t (s) is the triboactivation time for reaction (1).

As shown in Table 1, the tribochemical energy contribution needed to start the explosive reduction increases with a decrease in reduction heat (except for boron anhydride).

For boron anhydride a larger amount of tribochemical starting energy is found to be necessary when the amount of magnesium in the reduction reaction is increased. For example, the stoichiometry of $2B_2O_3 + 3Mg$ requires an energy contribution of $D = 3.1$ kJ g^{-1}, but for $2B_2O_3 + 6Mg$ the value must be 9 kJ g^{-1}. The phase composition of the end product and the content of amorphous magnesium polyboride depend on the stoichiometry of the reduction reactants boron anhydride and magnesium (Fig. 1). The maximum amount of amorphous boron (80.67%) was produced when the B_2O_3:Mg ratio was 2:4.75. Unlike the boron produced by self-propagating high temperature synthesis, this boron has a light brown colour and contains a larger amount of elemental boron. A significant factor affecting the reaction under study is the presence of an oxygen-containing atmosphere in the reactor. Performing the oxidation–reduction reaction in an oxygen atmosphere leads to the appearance of an exothermic peak in the thermogram at a smaller tribochemical energy contribution than that for the reaction in an argon atmosphere (Fig. 2). This is attributed to the oxidation of magnesium by the reaction $2Mg + O_2 \rightarrow 2MgO + Q$. The reaction is accompanied by a heat release, favouring the reduction of boron from its oxide. As shown in Fig. 2, the oxygen atmosphere allows the tribochemical energy contribution to be reduced from 9 to 1.3 kJ g^{-1}.

However, according to the results of the chemical analysis, the content of boron in magnesium polyboride produced in an oxygen atmosphere equals 73.6%, which is less than the boron content when it is produced in argon atmosphere.

Thus the quality of the end product is lowered but the oxygen atmosphere process takes less time. The triboactivation atmosphere also significantly affects the formation of tungsten monocarbide from tungsten oxide. The reaction of $WO_3 + Mg +$ graphite in air leads to the formation of $W_2C + MgO$, but the same reaction with carbon black as one of the initial constituents results in the formation of $WC + W_2C + MgO$.

To elucidate under what conditions tungsten monocarbide is formed, the gaseous composition of the reactor atmosphere after reaction completion has been analysed. In the case of carbon black the reactor atmosphere contained up to 20% hydrogen, but in the case of graphite, hydrogen was not detected. It seems that in the presence of carbon black a gas phase carbonization occurs along with the solid phase reaction;

TABLE 1. Values of the tribochemical energy contribution (D), reaction heat (Q) and formation heat ($-\Delta G^0$) of some oxides for the reactions $Me_xO_y + yMg \rightarrow xMe + yMgO$ and $3Me_xO_y + 2yAl \rightarrow 3xMe + yAl_2O_3$

Oxide Reducing agent	Cu_2O Mg	MoO_3 Mg	FeO Mg	WO_3 Mg	VO Mg	TiO Mg	B_2O_3 Mg	Cu_2O Al	FeO Al
D (kJ g^{-1})	0.31	0.50	0.55	0.70	0.72	1.25	9.0	0.16	1.08
Q (kJ)	430	350	340	320	170	80	180	575	440
$-\Delta G^0$ (kJ)	175	250	265	280	430	525	420	260	400

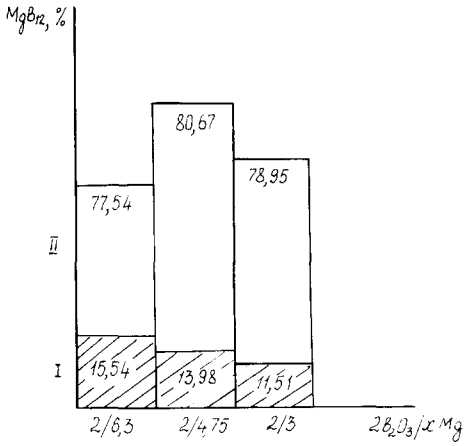

Fig. 1. Effect of the stoichiometry of the charge for the reduction of boron anhydride with magnesium on the content of magnesium polyboride in the end product (I) uncleared of magnesium oxide and (II) after the removal of magnesium oxide.

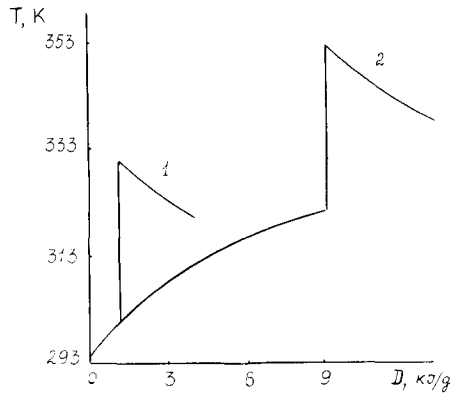

Fig. 2. Thermograms of the magnesiothermic reduction of boron anhydride in atmospheres of (1) oxygen and (2) argon.

$$2C + H_2 \longrightarrow C_2H_2 \quad (2)$$

$$C + 2H_2 \longrightarrow CH_4 \quad (3)$$

$$2W + C_2H_2 \longrightarrow 2WC + H_2 \quad (4)$$

$$W + CH_4 \longrightarrow WC + 2H_2 \quad (5)$$

As is known, the vapour pressure of acetylene over tungsten particles is lower than that over carbon black particles, so carbon atoms are transferred from carbon black particles onto tungsten particles.

Thus the reaction $WO_3 + Mg +$ carbon black in an atmosphere of hydrogen or hydrocarbons should produce WC but not W_2C. This is corroborated by the experimental results of the phase analysis of the products obtained in different atmospheres (Fig. 3). As shown, tribochemical activation of the composition $WO_3 + Mg +$ carbon black in a hydrogen atmosphere leads to a 100% yield of WC, whereas the yield is half this value in air. Similar results have also been obtained for the synthesis of silicon carbide by the reaction

$$SiO_2 + 2Mg + C \xrightarrow{C_xH_y} SiC + 2MgO \quad (6)$$

The yield of silicon carbide formed in the presence of hydrocarbons is found to increase and free silicon is not observed in the end products.

The use of scheelite instead of tungsten trioxide as an initial constituent reveals new features. Firstly, scheelite is a complex chemical compound corresponding to the formula $CaWO_4$. Secondly, its rich concentrate contains 60%–65% WO_3, the rest being inert matter. Besides, the concentrate is contaminated with carbonate, sulphate, arsenate and phosphate. In this connection we outline here only the principal points concerning the possibility of direct reduction of tungsten from its concentrate and the synthesis of tungsten monocarbide. We will deal with the development and improvement

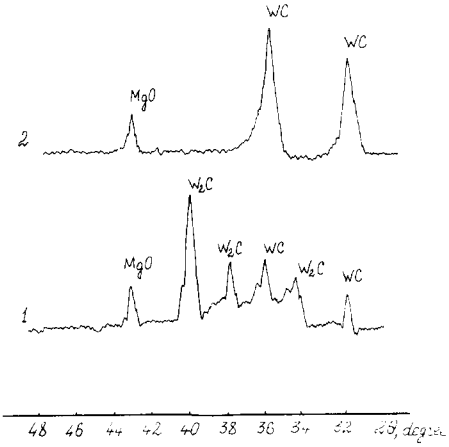

Fig. 3. X-ray diffraction patterns of the products of the reaction $WO_3 + Mg +$ carbon black carried out in atmospheres of (1) air and (2) hydrogen.

of the process of production and purification of end products from contaminations in a subsequent paper.

In spite of the significant amount of impurities in the scheelite (concentrates with 54% and 61% WO_3 were used), the magnesiothermal reaction is found to proceed by the mechanism of heat explosion. The phase composition of the end product includes tungsten, magnesium oxide, tungsten carbide (W_2C), calcium oxide and a negligible amount of the initial concentrate. The presence of tungsten carbide in the end product is attributed to the presence of carbon (0.6%) in the initial concentrate. The addition of carbon black to the initial constituents and the use of an atmosphere of hydrogen or hydrocarbons lead to the formation of tungsten monocarbide (WC), magnesium oxide and calcium oxide. The magnesium oxide was removed by a chemical method. After a single chemical processing the end product contained 94%–97% of tungsten monocarbide. Thus the tribochemical reaction of tungsten concentrate with magnesium under certain conditions makes it possible to produce tungsten monocarbide directly from tungsten concentrate. To produce tungsten powder from the concentrate, the latter should be cleared of carbon before the reaction proceeds. The simplest and rather effective method of removing carbon consists of heating the concentrate in air. After thermal processing of the concentrate at 850 °C for 2 h, the carbon content present as carbonate decreased from 0.6% to 0.01%. The tribochemical reaction of the processed concentrate with magnesium proceeded by the explosive mechanism. The phase composition of the end product included mainly tungsten, magnesium oxide and calcium oxide.

The next step of the experiment consisted of implementing a reaction in the B_2O_3–Mg–Ti system. The goal was to produce titanium borides of various stoichiometric compositions. The composition of the initial constituents is given in Table 2.

As follows from the experiments, irrespective of the charge composition, every reaction proceeded by the explosive mechanism. The tribochemical energy contribution was constant in every experiment, $D = 5.9$ kJ g^{-1}. X-ray diffraction analysis of the end products showed that their phase composition depended on the content of titanium in the initial charge (Fig. 4). The end product may consist of either titanium diboride and magnesium oxide, or titanium diboride, magnesium oxide and titanium. The two-phase end products ($TiB_2 + MgO$) are formed only when the Ti:B ratio is 1:2. As follows from the data of thermal and X-ray analysis, in the B_2O_3–Mg–Ti system a reduction occurs first to form amorphous boron and then titanium diboride is formed:

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO \quad (7)$$

$$2B + Ti \longrightarrow TiB_2 \quad (8)$$

Thus the phase composition of borides in the B_2O_3–Mg–Ti system is dependent on the magnesiothermal reaction which results in the formation of a single boride, namely TiB_2.

TABLE 2. Initial composition B_2O_3–Mg–Ti used for the production of Ti_xB_y

Composition number	x	y	Mass of initial constituents (g)		
			B_2O_3	Mg	Ti
1	1	4	6.4	6.7	2.2
2	1	2	5.6	5.9	3.9
3	3	4	5.0	5.2	5.1
4	1	1	4.5	4.7	6.2
5	5	4	3.7	3.9	7.7
6	3	2	3.2	3.3	8.8

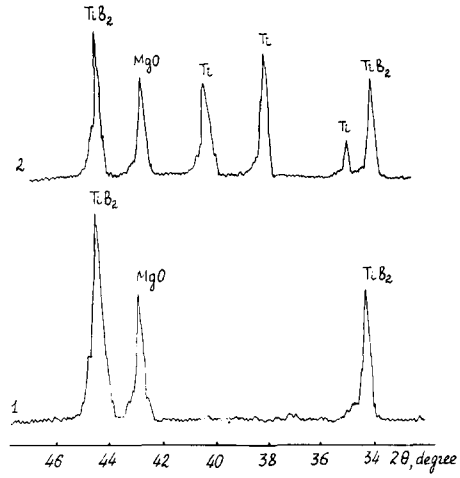

Fig. 4. X-ray diffraction patterns of the products of the reaction $B_2O_3 + Mg + Ti$ for Ti:B ratios of (1) 0.5 and (2) 1.

4. Conclusions

Estimates of the tribochemical energy contribution have been obtained at which the reduction of metals and non-metals from their oxides with magnesium and aluminium proceeds by the explosive mechanism. The tribochemical energy contribution needed to start an explosive reduction increases with a decrease in the heat of reaction and an increase in the formation energy of the associated product oxide. Introducing oxygen into the reactor in the process of tribochemical activation of oxide and magnesium powders causes an intense oxidation of magnesium and promotes the reduction reaction. The triboactivation reaction of $WO_3 + Mg +$ carbon black should be performed in an atmosphere of hydrogen to increase the yield of tungsten

monocarbide. The phase composition of borides in the B_2O_3–Mg–Ti reduction system is dependent on the progress of the magnesiothermal reaction which promotes the formation of a single boride, namely titanium diboride (TiB_2).

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