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THE PRODUCTION OF METALS AND ALLOYS BY THE DECOMPOSITION OF OXYSALTS

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ABSTRACT

The production of metals from the thermal decomposition of oxysalts is an interesting process because the metals are produced below their melting point in a highly active particulate form. In many instances the production of the metal as the primary reaction mechanism is obscured because the environmental conditions allow the production of oxide products as a further reaction process. Thermodynamic considerations can be applied which show when the production of the metal is to be expected as the prime product in an inert atmosphere. This had previously been applied to oxalates, but the same reasoning is shown here to be applicable to formate decompositions and probably applies to other oxysalt systems. The types of kinetic expressions which govern such decompositions are outlined, and correlations are made between the kinetic mechanism of decomposition and the change in surface area. The correlation between density and surface area takes the form

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2} \cdot (N)^{1/2}$$

where V_1 and V_2 are the molar volumes of the oxysalt and the metal product, S_1 and S_2 are the molar surface areas, and N is the number of particles of metal produced from one particle of oxysalt.

In the present study it is shown that thermal analysis techniques can be used to produce powdered alloys at temperatures far below the melting point of the metals by the decomposition of suitable complex oxysalts or mixtures of oxysalts.

INTRODUCTION

The decomposition of oxysalts by thermal methods will lead eventually to the production of either a metal or an oxide as an end product. The production of a metal as a primary product of decomposition is often masked when the decomposition is carried out in air by the violent oxidation of the metal, so not only does the reaction appear exceptionally vigorous but one may be misled into believing that the primary route is to the oxide. The present study could lead to the production of powdered alloys by the

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decomposition of complex oxysalts or mixed oxysalts in inert or reducing atmospheres.

The diverse behaviour of oxysalts upon heating may be exemplified by considering the thermal decomposition of oxalates. Calcium oxalate decomposes by the following sequence of steps, all seen on thermal analysis equipment

$$CaC_2O_4 \cdot 2H_2O \longrightarrow CaC_2O_4 + 2\ H_2O$$

The dehydration step is endothermic under all conditions.

The next step is

$$CaC_2O_4 \longrightarrow CaCO_3 + CO$$

This is basically endothermic, but if excessive areas of metal are available then the catalyzed exothermic reaction

$$CO + 1/2\ O_2 \longrightarrow CO_2$$

might produce an exothermic reaction overall.

The final decomposition step is the endothermic decomposition of the carbonate

$$CaCO_3 \longrightarrow CaO + CO_2$$

Zinc oxalate, on the other hand, decomposes by a different sequence of reactions. The first is the endothermic dehydration

$$ZnC_2O_4 \cdot 2H_2O \longrightarrow ZnC_2O_4 + 2\ H_2O$$

This is followed by an endothermic decomposition to zinc oxide in an atmosphere of nitrogen

$$ZnC_2O_4 \longrightarrow ZnO + CO + CO_2$$

In air this reaction becomes exothermic due to the catalytic oxidation of CO to CO_2 on the surface of the product ZnO.

Nickel oxalate shows the same change from an endothermic decomposition to an exothermic process upon changing the environmental atmosphere from nitrogen to air, but for an entirely different reason. The dehydration is endothermic

$$NiC_2O_4 \cdot 2\ H_2O \longrightarrow NiC_2O_4 + 2\ H_2O$$

The decomposition in nitrogen is to the metal

$$NiC_2O_4 \longrightarrow Ni + 2\ CO_2$$

The Ni is produced with such a high surface area that it is immediately oxidized in air in a violently exothermic manner, giving the overall process an exothermic character and a solid product oxide

$$Ni + 1/2\ O_2 \longrightarrow NiO$$

All these processes can be followed using thermal analysis equipment, and a review has recently been published [1].

A further group of oxalates, the rare earth oxalates, often decompose with the appearance of a carbon residue in varying amounts. Mercury, silver and copper oxalates decompose exothermically in nitrogen.

Similar trends can be observed in the decomposition of other oxysalts such as formates, acetates, citrates, stearates etc.; although systematic studies are lacking, the preparation of metals from such decomposition routes is reported. Thus, the preparation of nickel catalyst in hardened oil flakes provides an important example of an unusual "inert" environment. The nickel formate decomposes initially to the metal powder by two concurrent routes [2]

$$\mathrm{Ni(COOH)_2} \longrightarrow \mathrm{Ni + H_2O + CO + CO_2}$$

and

$$\mathrm{Ni(COOH)_2} \longrightarrow \mathrm{Ni + H_2 + 2\,CO_2}$$

In air the nickel would be oxidized to the oxide, but in the "inert" environment of the oil the metal powder is stable. The oil is chosen so that it sets to a hard wax on cooling and the wax flakes can be used as an inert storage and handling medium for the nickel catalyst.

Nitrate decompositions provide an example of an oxysalt type where the acidic group has oxidizing capabilities and the decomposition process in all atmospheres is usually to the highest oxide form, with good stoichiometric composition. Carbonates always decompose endothermically to produce the oxide. With these diverse reactions to consider it seems worthwhile to examine the thermodynamic, kinetic and textural features which lead to metal formation by the decomposition of oxysalts.

THERMODYNAMIC FACTORS

A typical case of oxide dissociation can be represented as

$$\mathrm{MO_2(s)} \longrightarrow \mathrm{M(s) + O_2(g)}$$

and is no different in principle to the thermal decomposition of an oxysalt to a metal with the liberation of one gaseous species, again represented as

$$\mathrm{MA(s)} \longrightarrow \mathrm{M(s) + A(g)}$$

In the above two reaction equations, M is a divalent metal and A is a divalent acid ion. The treatment outlined here for the oxide is the same as for the salt MA. The integrated van 't Hoff equation applies

$$\ln K_\mathrm{p} = \frac{-\Delta H}{RT} + \text{constant} \tag{1}$$

With one gaseous species evolved this takes the form

$$\ln P = \frac{-\Delta H}{RT} + \text{constant} \tag{2}$$

where K_p = equilibrium constant, P = equilibrium pressure of product gas, ΔH = heat of reaction, R = gas constant, and T = absolute temperature.

As, however, all phases involved are solid except for the gaseous product, then

$$\ln P = \ln K_p$$

It should be noted that the true equilibrium constant requires that the solid be subjected to a total pressure of 1 atm. However, in normal experiments this is not strictly adhered to, although it is followed in thermal analysis experiments [3].

This approach for oxysalt decompositions, in which the system consists of two solids and one gas, gives the partial pressure at which dissociation occurs. If product gas is present in the experimental environment during decomposition, then the decomposition temperature corresponds to the temperatures obtained by substituting appropriate values of P in the above equations. The oxide (or salt MA) can be put in the differential thermal analysis (DTA) unit and heated under a partial pressure of oxygen (or A) at a total pressure of 1 atm. This is then repeated at various partial pressures of oxygen. The temperature at which decomposition is noticed is recorded; Fig. 1 represents the type of relationship usually noted between log P and $1/T$. In DTA experiments the onset temperature of the peak is usually chosen.

However, in oxalate degradation where two decomposition routes can occur, it is possible to use the thermodynamic treatment to decide which oxalate will decompose to a metal in an inert atmosphere and which will

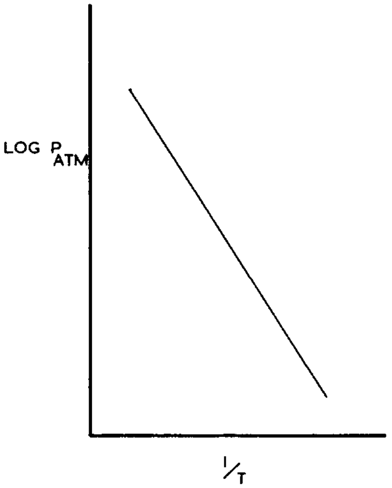


Fig. 1. Schematic relationship observed between log P and $1/T$ for oxide dissociation.

decompose to the oxide [4]. Taking the oxalate of the divalent metal ions, then two possible reactions are

$$MC_2O_4 \longrightarrow MO + CO + CO_2 \tag{3}$$

and

$$MC_2O_4 \longrightarrow M + 2\,CO_2 \tag{4}$$

If the discussion is confined to equilibrium conditions, then for reaction (3) the equilibrium constant (K_1) is given by

$$K_1 = \frac{[MO][CO][CO_2]}{[MC_2O_4]}$$

and for reaction (4) the equilibrium constant (K_2) is given by

$$K_2 = \frac{[M][CO_2]^2}{[MC_2O_4]}$$

In both instances the square brackets denote activities. Then

$$\frac{K_1}{K_2} = \frac{[MO][CO]}{[M][CO_2]}$$

A similar ratio can be obtained from a consideration of the reactions

$$2\,CO + O_2 = 2\,CO_2 \tag{5}$$

$$2\,M + O_2 = 2\,MO \tag{6}$$

i.e.

$$\left(\frac{K_4}{K_3}\right)^{1/2} = \frac{[MO][CO]}{[M][CO_2]}$$

where K_3 is the equilibrium constant for reaction (5) and K_4 that for reaction (6). Then

$$\frac{K_1}{K_2} = \left(\frac{K_4}{K_3}\right)^{1/2} \tag{7}$$

If the standard free energy of formation ($\Delta G^\circ = -RT \ln K$) for reaction (5) is denoted by ΔG_a and for reaction (6) by ΔG_b, then for $\Delta G_a > \Delta G_b$ there must exist the relationship $K_3 < K_4$, and from eqn. (7) it follows that $K_1 > K_2$. Therefore, if reactions (3) and (4) are considered at equilibrium, (3) is more to the product side than is (4); or alternatively, reaction (3) will predominate over reaction (4).

The variation in the free energy of formation of various oxides with temperature has been provided in graphical form by Ellingham [5,6]. A schematic representation of these graphs is portrayed in Fig. 2. In this diagram the various values of ΔG_b for several systems are given by the full lines while the values of ΔG_a are represented by the dotted line. When the

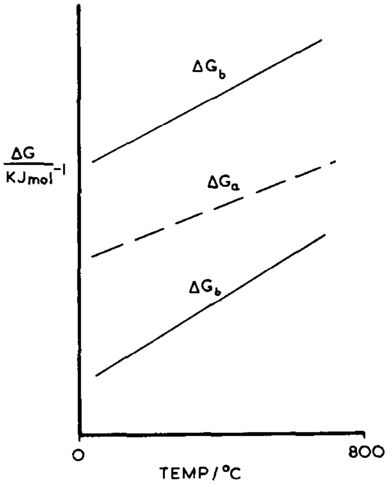


Fig. 2. Schematic portrayal of Ellingham free energy diagram.

ΔG_b line is above the ΔG_a line, as it is for copper, lead, nickel, cobalt and cadmium, then metal is the solid product. Ferrous iron is unique in that the ΔG_b line crosses the ΔG_a line at a temperature above 700 °C and lies only 17 kJ mol^{-1} above it at the decomposition temperature.

Similar arguments can be set out for oxalates of trivalent metals, for which three reactions are possible. Of these, two are analogous to reactions (3) and (4), namely

$$M_2(C_2O_4)_3 = 2\ MO + 4\ CO_2 + 2\ CO \tag{8}$$

$$M_2(C_2O_4)_3 = 2\ M + 6\ CO_2 \tag{9}$$

whereas the third would yield the oxide M_2O_3

$$M_2(C_2O_4)_3 = M_2O_3 + 3\ CO_2 + 3\ CO \tag{10}$$

If reactions (8) and (9) are set up as equilibria, reaction (8) is more to the product side than is reaction (9) if ΔG_a exceeds ΔG_b. Similarly, for reactions (8) and (10), the conditions $\Delta G_a > \Delta G_c$ (where ΔG_c is the free energy change for the reaction $4\ MO + O_2 = 2\ M_2O_3$) must be observed if reaction (10) is to be set up more to the product side than reaction (8). For reaction (10) to be set up, under equilibrium conditions, more to the product side than reaction (9), the condition is that $\Delta G_a > \Delta G_d$ (where ΔG_d is the free energy change for the reaction $4/3\ M + O_2 = 2/3\ M_2O_3$).

All these arguments apply to equilibrium conditions; removal of gaseous products as they are formed, e.g. in a stream of nitrogen, would favor the tendency shown by most systems to produce only one final solid product—i.e. the metal or the metal oxide—rather than a mixture. Where the thermodynamics suggest that a metal should predominate in the solid residue from the reaction in nitrogen, thermal decomposition is found to result only in the

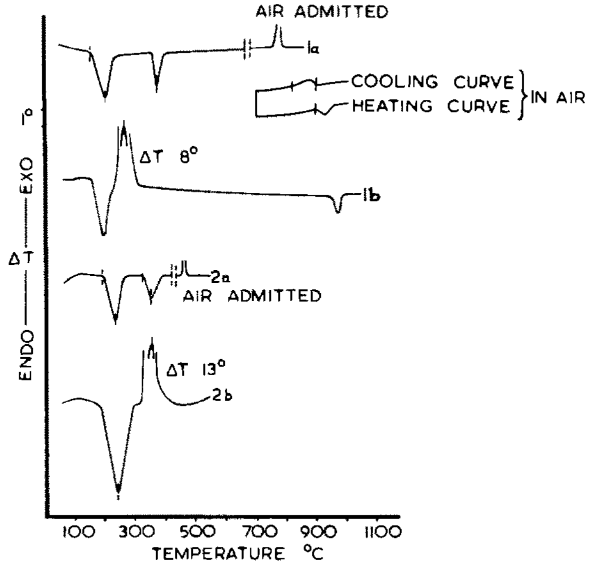


Fig. 3. DTA curves for cobalt and nickel oxalates in nitrogen and oxygen.
Cobalt oxalate:
1a (N_2): 149–197°, endo dehydration; 355–371°, endo decomposition to metal; 1100°, large exo on admission of air. Cooling curve in air: 896–821°, exo $CoO \rightarrow Co_3O_4$. Heating curve in air: 897–920°, endo $Co_3O_4 \rightarrow CoO$. 1b (O_2): 147–187°, endo dehydration; 219–261°, exo decomposition; 955–968°, endo $Co_3O_4 \rightarrow CoO$ (this last is reversible on the cooling curve).
Nickel oxalate:
2a (N_2): 185–231°, endo dehydration; 318–349°, endo decomposition; 450°, large exo on admission of air. 2b (O_2): 173–329°, endo dehydration; 312–350°, exo decomposition.

formation of the metal (e.g. for the oxalates of copper, nickel, cobalt and cadmium); in oxygen, of course, the oxide is produced. These observations are well exemplified by the DTA plot of nickel oxalate, which in nitrogen yields two endothermic peaks. The first of these represents dehydration, the second decomposition represents breakdown to the metal. In air or oxygen the second peak is exothermic due to the oxidation of the metal. All this can be seen by reference to Fig. 3, showing the DTA curves for cobalt and nickel oxalates [7].

This treatment could be extended to other oxysalts. Thus, we have for formates

$$M(COOH)_2 \longrightarrow M + H_2O + CO + CO_2 \qquad (11)$$

$$M(COOH)_2 \longrightarrow M + H_2 + 2\,CO_2 \qquad (12)$$

$$M(COOH)_2 \longrightarrow MO + H_2O + 2\,CO \qquad (13)$$

$$M(COOH)_2 \longrightarrow MO + CO + CO_2 + H_2 \qquad (14)$$

Now

$$K_{11} = \frac{[M][H_2O][CO][CO_2]}{[M(COOH)_2]}$$

$$K_{12} = \frac{[M][H_2][CO_2]^2}{[M(COOH)_2]}$$

$$K_{13} = \frac{[MO][H_2O][CO]^2}{[M(COOH)_2]}$$

while

$$K_{14} = \frac{[MO][H_2][CO][CO_2]}{[M(COOH)_2]}$$

For

$$2\ CO + O_2 = 2\ CO_2$$

and

$$2\ M + O_2 = 2\ MO$$

it has already been shown that

$$\left(\frac{K_4}{K_3}\right)^{1/2} = \frac{[MO][CO]}{[M][CO_2]}$$

[see eqns. (5) and (6)].

From reactions given in eqns. (11) and (13) it also follows that

$$\frac{K_{11}}{K_{13}} = \frac{[MO][CO]}{[M][CO_2]} = \left(\frac{K_4}{K_3}\right)^{1/2}$$

and from reactions given in eqns. (12) and (14) it similarly follows that

$$\frac{K_{12}}{K_{14}} = \frac{[MO][CO]}{[M][CO_2]} = \left(\frac{K_4}{K_3}\right)^{1/2}$$

These are exactly the same conditions which determine whether an oxalate will decompose to a metal or an oxide, and inspection of the Ellingham free energy diagrams for the variation of the free energy of formation of various oxides with temperature again provides the answer.

This prompts speculation that other oxysalts can be treated in the same manner. The indications are that it is possible but there are difficulties. Thus for acetates we have

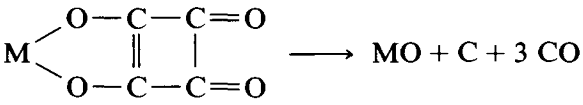
$$M(CH_3COO)_2 \longrightarrow MO + (CH_3)_2CO + CO_2$$

and

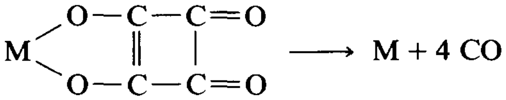
$$M(CH_3COO)_2 \longrightarrow M + CH_3COOH + CO_2 + C + H_2$$

This case would be amenable to thermodynamic treatment, but side reactions in these and higher carboxylic acids causes a degree of carbon formation which can be quite severe, and there is also the possibility that carbides might be formed. This might not interfere with the generality of these predictions based on thermodynamics.

Another series of oxysalts which might be considered are the squarates. Here we have ideally



or



(where M is a divalent metal as an example).

In practice the sequence is not so simple, as carbon and suboxides of carbon have been reported [8–10]. Nickel squarate, however, is reported to decompose with the production of the metal and the evolution of carbon monoxide [11]. In some of these squarate decompositions substantial quantities of carbon dioxide are reported, however unlikely this would appear on initial inspection of the structure of squarates. There are therefore limits to the extent to which the above treatments can be applied.

KINETICS

The kinetic aspects of the degradation of an oxysalt to a metal possess no fundamental features different from those of any other study on the decomposition of oxysalts. However, it must be borne in mind that the product metal can oxidize in the presence of air, and that there is a vast difference in density between the solid products and the solid reactant oxysalt. This would tend to distort the geometry upon which many of the kinetic mechanisms are based, leading to shifts from one mechanism to another. The inference is usually that nucleation proceeds from the formation of a reaction interface, and that in many cases nucleation at the surface is preferred, followed by the formation of a reaction interface which advances through the crystal matrix. The geometric considerations imply that in these models the majority of the reaction process is rate deceleratory with respect to time, and this limits the number of relationships which have to be tested. A normalization process, usually by normalizing at fraction decomposed (α) equal to 0.5, then allows the available models to be further restricted in number [12]. An alternative is to utilize this reduced time method but to linearize the data by comparing $\alpha_{\text{theoretical}}$ with $\alpha_{\text{experimental}}$ [13]. There are other methods for linearizing the data for comparison purposes, and they have been discussed elsewhere [14]. These comments apply to the classical method of obtaining kinetic data from a series of isothermal plots of α against time (t), identifying the α–t relationship and calculation of the specific reaction rate constant $[k(T)]$ at each temperature. A plot of ln $k(T)$ against $1/T$ then allows the formal calculation of ln $k(\infty)$ and activation energy (E) values. If the study covers a wide temperature range there is the possibility of different kinetic mechanisms being found, due to abrupt changes in the mode of diffusion (see next section). The extreme variation between solid reactant oxysalt and metal product means that a drastic change in reaction geometry and specific reaction rate per unit area of interface could occur in isothermal experiments. The identification of a second reaction mechanism at some later stage in the reaction might pose a problem, particularly with the time scale. Thus, if the kinetic expression is for example of the form

$$\alpha = kt^n$$

where k is the specific reaction rate and n is an integer in the latter part of the reaction, then it should be written as

$$\alpha = k(t + t_0)^n$$

where t_0 is the corrected value of t the time, when

$$\alpha^{1/n} = k^{1/n}(t + t_0)$$

and

$$\left(\frac{\alpha}{k}\right)^{1/n} = t + t_0$$

also

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nk^{1/n}\alpha^{(1-1/n)}$$

or

$$\log \frac{\mathrm{d}\alpha}{\mathrm{d}t} = (1 - 1/n) \log \alpha + \text{constant}$$

Thus plotting log $(\mathrm{d}\alpha/\mathrm{d}t)$ against log α gives a slope of $(1 - 1/n)$ from which n can be calculated. From a plot of $\mathrm{d}\alpha/\mathrm{d}t$ against $\alpha^{(1-1/n)}$ the value of k can be determined from the slope. If the time scale had been correct, a plot of log α against log t would have given k and n. In other cases a faulty time scale is not important. Take the first order decay law as an example: for plotting purposes this is best expressed as

$$\log (1 - \alpha) = \text{const.} - kt$$

A faulty time scale clearly does not affect the determination of k.

The preparation of a metal by the thermal decomposition of an oxysalt clearly leads to the production of a powdered product at temperatures which are below the melting point of the metal. Furthermore, as the metal can be produced in fine particulate form, it has potential use as a catalyst, as a reactive chemical, or in metallurgy can be formed to give shapes of controlled porosity. The lower the temperature of formation, the less cost is involved in any manufacturing process.

Some features of textural and surface chemistry have to be considered. The metal product receiving heat treatment will undergo sintering, a process defined here as an increase in particle size with a decrease in surface area. This sintering process is a function both of temperature and time. Isothermal heating runs show that the decrease in surface area occurs towards an equilibrium value determined by the initial physical condition of the metal (i.e. its texture and surface area) and the temperature of the experiment. The process of sintering can be considered as a growth in particle size brought about by diffusion. One can assume a constant rate of growth per unit area under isothermal conditions, when the sintering process becomes a contracting interface per unit mass of material involving coalescence of adjacent particles with a decrease in their number. If the basic process of diffusion remains the same, then the Arrhenius equation can be applied to calculate an activation energy associated with sintering. However, the sintering process occurs over a wide range of temperatures so the possibility exists that the process of diffusion alters and the two processes considered here are surface diffusion changing to volume diffusion.

In fact, the three following processes may be distinguished [15]

(1) Adhesion between particles, which leads to seized joints at points of contact.

(2) Surface diffusion, in which the coalescence of particles occurs by movement of metal atoms along the surface.

(3) Bulk diffusion, in which further coalescence is brought about by diffusion of the metal atoms through the bulk material.

These phenomena occur in the order listed above as the temperature is increased. It has been suggested that the various mechanisms become operative at defined temperatures which can be expressed as a fraction of the melting point in degrees kelvin. Thus if $\alpha = T/T_m$, where T_m = melting point in K, then surface diffusion occurs in the range $\alpha = 0.33$–0.45, whilst bulk diffusion takes place beyond $\alpha = 0.5$, often called the Tammann temperature [16]. Adhesion between joints takes place at much lower temperatures. Table 1 indicates the ranges of temperature where surface and bulk diffusion may be expected for a series of metals.

In the region where surface diffusion takes place (and the possibility for

TABLE 1

Temperature range (°C) for surface and bulk diffusion based on equations given in text for various metals

Metal	Melting point	Surface diffusion (occurs above temperature indicated and below temperature indicated in adjacent column)	Bulk diffusion (occurs above temperature indicated)
Aluminum	660.2	35	194
Barium	725	56	226
Beryllium	1278	239	503
Calcium	842	95	558
Cerium	795	79	261
Chromium	1890	441	809
Cobalt	1495	301	611
Copper	1083	174	405
Gold	1063	168	395
Iron	1535	324	631
Magnesium	651	32	189
Manganese	1244	228	486
Nickel	1453	297	590
Silver	961	134	344
Strontium	769	71	248

volume diffusion), the variation in surface area due to diffusion may be written as [17,18]

$$\frac{\mathrm{d}S_t}{\mathrm{d}t} = -k_s(S_t - S_i)$$

for an isothermal experiment, where S_t is the surface area at any time t, S_i is the surface area at $t = \infty$, when the rate has diminished to zero, and k_s is a rate constant. Hence

$$\ln(S_t - S_i) = k_s t + \text{const.}$$

In application to particulate metal systems, it is probably best to follow the sintering by noting the particle size. However, if the particle radius is initially large, then there is merit in quoting sintering data in terms of the alteration of particle size or the increase in size in the junctions between the particles. To make comparisons between data quoted in terms of particle size and data quoted in terms of surface area, the relationship $D = 6/Sp$ can be used, where D is the equivalent particle diameter, S is the surface area and p is the metal density.

PRODUCTION OF ACTIVE METAL POWDERS BY THERMAL DECOMPOSITION

By active metal powders we mean metal powders with high surface area. If we consider the general case of thermal decomposition of an oxysalt going to a metal, this can be represented as

$$A(s) \longrightarrow M(s) + \text{gaseous products}$$

Here A(s) is a suitable oxysalt and M(s) is metal product. One should note that the reaction interface is seldom the surface area measured by gas adsorption, and the two are quite distinct. The mean alteration in property is the change in volume that occurs due to differences in density between the oxysalt and the product metal. This causes a distortion of the geometrical system and finally a break-up of particles under the strain imposed upon them by this process. This break-up of the particles means that the particle radius will diminish with an increase in the number of particles in the system, resulting in an observed increase in specific surface area s determined by adsorption. This is opposed by the sintering processes discussed in the previous section. The net result is an increase in surface area on heat treatment followed by a diminution (see Fig. 4). The maximum surface area coincides with the situation where the strain cannot be contained within the original lattice structure. It does not necessarily coincide with the completion of the chemical reaction [19]. The treatment correlating the kinetics with this kind of change in the surface area has been set out in general terms [17] but is cited here for a specific kinetic behavior [18]. It needs to be substantiated with more experimental studies.

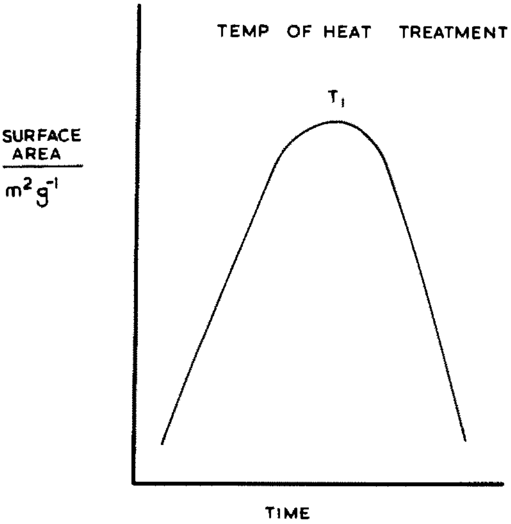


Fig. 4. General behavior pattern of surface area of metal powders formed by heat treatment of oxysalts.

Let the surface area due to the activation, S_a, be proportional to the fraction decomposed, i.e.

$$S_a = k_1\alpha$$

Suppose in the decomposition the contracting sphere equation which holds is of the type

$$1 - (1 - \alpha)^{1/3} = k_2t$$

which rearranges to

$$\alpha = 1 - (1 - k_2t)^3$$

Then

$$S_a = k_1\left[1 - (1 - k_2t)^3\right]$$

Differentiating gives

$$\frac{\mathrm{d}S_a}{\mathrm{d}t} = 3k_1k_2(1 - k_2t)^2$$

Let the sintering be described by

$$\frac{\mathrm{d}S_a}{\mathrm{d}t} = -k_4S$$

The contracting sphere equation is used here because most metal powders produced by thermal decomposition of oxysalts are spherical in shape.

The overall rate of change of surface area is then

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 3\ k_1k_2(1 - k_2t)^2 - k_4S = A(1 - Bt)^2 - CS$$

where A, B and C are substituted for the various functions of k to simplify the expression. Rearrangement gives

$$\frac{\mathrm{d}S}{\mathrm{d}t} + CS = A(1 - Bt)^2$$

The corresponding expression after integration takes the form

$$S = A'\left[E - Ft + Gt^2\right] + \text{const.}$$

where A', E, F and G are substituted for various functions of k to simplify the expression.

The effect of density changes on the texture may be seen by the following considerations [20]. The break-up of particles in the thermal decomposition to produce the larger surface area has been ascribed earlier in this text to the strain caused by these density changes. If the oxysalt consists of n particles per mole, with molar volume and molar surface area of V_1 and S_1, then

$$V_1 = \frac{M_2}{\rho_1} = \tfrac{4}{3}\pi n_1 r_1^2$$

where M_1 = gram molecular weight; ρ_1 = density; and r_1 = the average radius of the particles.

The molar surface area of the original unreacted material can be expressed by

$$S_1 = s_1 M_1 = 4\pi n_1 r_1^2$$

where s_1 = the experimental surface area in square meters per gram.

It therefore follows that

$$r_1 = \frac{3V_1}{S_1}$$

and

$$r_1 = \left(\frac{S_1}{4\pi n_1}\right)^{1/2}$$

In the thermal decomposition process to produce the metal particles, the number of particles produced can be set out at n_2 particles per mole with a molar volume and molar surface area of V_2 and S_2 respectively. Then V_2 and S_2 are given by

$$V_2 = \frac{M_2}{\rho_2} = 4/3\pi n_2 r_2^3$$

and

$$S_2 = s_2 M_2 = 4\pi n_2 r_2^2$$

where M_2 = the effective molecular weight of partially decomposed reacted material; s_2 = the experimental surface area in m^2g^{-1}; ρ_2 = density, and r_2 = average radius of the particles.

Again, it follows that

$$r_2 = \frac{3V_2}{S_2}$$

and

$$r_2 = \left(\frac{S_2}{4\pi n_2}\right)^{1/2}$$

The ratio of these two radii is given by

$$\frac{r_1}{r_2} = \frac{V_1 S_2}{V_2 S_1}$$

or

$$\frac{r_1}{r_2} = \left(\frac{S_1 n_2}{S_2 n_1}\right)^{1/2}$$

TABLE 2

Values of density for thermal decomposition of selected oxalates with value of n_2/n_1 [a]

Compound	Density [b] before decomposition	Density after decomposition	n_2/n_1
Iron(II) oxalate	2.28	5.24	1.93×10^5
Zinc oxalate	3.28	5.61	4.80×10^4
Manganese oxalate	2.43	4.86	3.87×10^2
Cobalt oxalate	3.02	6.07	9.47×10

[a] Data taken from material in D. Dollimore and D. Nicholson, J. Chem. Soc., (1962) 960.
[b] g ml^{-1}.

and

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2} \cdot \left(\frac{n_2}{n_1}\right)^{1/2}$$

If the number of particles remains the same

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2}$$

but the thermal data show that this rarely applies, and is more often $n_1 > n_1$.

If the molecular weight of the original reactant material is designated as M_1 and of the final product as M_3, then the "effective" molecular weight of the partially reacted material M_2 can be estimated by use of the relationship

$$M_2 = (1 - \alpha)M_1 + \alpha M_3$$

where α = fraction decomposed. Thus the molar surface area of the partially reacted material is given by

$$S_2 = s_2[(1 - \alpha)M_1 + \alpha M_3]$$

This allows the variation of the ratio of particles (n_2/n_1) to be followed during the course of either an isothermal decomposition or a TG experiment.

Table 2 gives density values before and after decomposition and the value of n_2/n_1.

CONCLUSIONS

It can be seen that thermal decomposition of suitable oxysalts can produce high area metal powders. In fact, the decomposition generally has to be carried out in nitrogen, because in oxygen the metal powder may be so active as to cause instantaneous oxidation at the temperature of decomposition; this type of instantaneous oxidation can be demonstrated if the sample is exposed to the air at room temperature. This can be prevented by exposing the metal powder to a very low pressure of oxygen, sufficient to allow formation of a surface layer of oxide which stabilizes the system (nickel oxalate decomposition is a good example). If mixtures of oxalates, e.g. nickel and cobalt, are used, then the end product is an intimate mixture, e.g. active cobalt and nickel powders. The process might be useful for the production of alloys below the melting points of the metals concerned. Complex oxalates might prove to be more suitable for this purpose. The treatments outlined for the general case of the decomposition of an oxysalt to a metal allow decisions to be made regarding the thermodynamic factors which make the process favorable for metal production.

It is proposed in future studies to show that the production of metal alloys with high surface area is possible from the thermal decomposition of either complex oxysalts or mixtures of oxysalts. It is necessary to establish by experiment the route of the decomposition process using thermogravimetry and the variation of surface area with the time and temperature of treatment.

The kinetic features shown in these decompositions can be related to the textural changes, and this allows likely conditions to be assigned for the production of metal powders with high activity.

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