Mathematical Correlation for Tungsten-Based Alloy Nanopowder to Determine the Relation between Temperature Time and Weight under Certain Temperatures

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Abstract: High temperature treatment of tungsten alloy of W-5wt.% TM (transition metals, TM = Ni, Fe, Cu, Co) nanopowder was run under different temperatures to cover the oxidation rate at different temperatures. The correlation was developed for certain temperatures to find an equation for the relation between time and weight. The thermal treatment was done for different quantities at certain times. The proposed equation studies the correlation between temperature, time, and weight. For each temperature, a number of points were recorded from the measured oxidation curve. The shape of the curves is well-represented in this paper. The final results will present the highest temperature, the maximum weight, and the maximum time for full oxidation at high and low temperatures.

Key words: Tungsten alloy, transition metals, nanopowder, oxidation, correlation.

1. Introduction

In physical chemistry, the transition metals show very outstanding properties. Tungsten oxide WO_3 is a very important material in some of electrical devices [1], catalyst [2], and chemical sensors [3-5]. The change in electrical conductivity is one of the characteristic properties of WO_3 which can vary from the wide semiconductor state (for WO_3), to the conductor one (for WO_2).

Tungsten and the tungsten alloy group represent a wide range of uses extending from everyday uses, e.g., the coil of an incandescent lamp or the contact tip of an electrical switch or an automobile horn, to component of nuclear fusion reactors or ion drive motors in space probes. The reason for this range of use lies in the many outstanding properties of tungsten. High melting point, low vapour pressure, high atomic number, good

electrical and thermal conductivity.

In the W-O system, there are not only the stoichiometric oxides WO_3 , $WO_{2.9}$, $WO_{2.7}$, and WO_2 , but also nonstoichiometric structure that represents the ordered or partially ordered defect structures of the oxygen-rich oxide in which the central W atom is octahedrally surrounded by six oxygen atoms. In WO_3 , neighbouring octahedra are in contact only at the corners, which increases oxygen deficiency (reduction, conversion to lower oxides), common edges and surfaces are progressively formed.

The aim of this work is to produce a homogeneous powder from a heavy metal swarf for recycling. The process route envisaged was a controlled oxidation to breakdown the swarf. In the first step, the microstructure of the swarf was characterised using optical metallography, SEM (scanning electron microscope), and XRD (X-ray diffraction). This characterization was followed by oxidation to achieve the mechanical breakdown and to give a friable oxide.

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In this step, a TG (thermogravimetry) was used to determine the temperatures for oxidation and to give some idea on the kinetics of the process. Scanning electron microscope and X-ray diffraction were used to find the morphology and the type of the oxide. According to the TG results, temperatures were selected for oxide manufacture.

2. Mathematical Correlation

A data set was compiled, covering the effect of oxidation rate with respect to temperature (750 °C to 1,000 °C) and the time taken for full oxidation [6].

Figs. 1-6 illustrate that, for a range of temperatures, the oxidation rate follows a similar pattern but that, if a different quantity of swarf were used, the rate could become dependent on both time and temperature.

To calculate a fitting equation for the oxidation curves, a data fit for all temperatures is shown in Figs. 1-6, where in all figures time is in minutes and weight is in mg for all of the oxidation curves. Also, a calculation for unknown parameters (A , B , C factors, and $\bar{t}$) has been performed to complete all of the parameters in the equation.

Fig. 1 Curve fit for oxidation at 750 °C.

Fig. 3 Curve fit for oxidation at 850 °C.

Fig. 2 Curve fit for oxidation at 800 °C.

Fig. 4 Curve fit for oxidation at 900 °C.

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Fig. 5 Curve fit for oxidation at 950 °C.

Fig. 6 Curve fit for oxidation at 1,000 °C.

The calculation for the unknown parameters has been done by MAPLE (multi-paradigm programming language) program, and is presented as:

For As,

$$y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}} + \frac{1}{200} e^{(13f - 1.7f^2 - 2.9)}$$

$$f = \frac{x}{250} - 3$$

$$Y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}} + \frac{1}{200} e^{\left(\frac{13x}{250} - 39 - 1.7 \left(\frac{x}{250} - 3 \right)^2 - 2.9 \left(\frac{x}{250} - 3 \right)^3 \right)} \quad A1 = 85.4$$

$$B1 = 60.4$$

$$C1 = 0.15$$

$$D1 = 880$$

$$85.4 - \frac{60.4}{1 + 0.471116580210^{-57} e^{(0.15x)}} + 0.132445610610^9 e^{(-0.2204000000x)} e^{(0.0003904000000x^2)} e^{(-0.185600000010^{-6}x^3)}$$

For Bs,

$$y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}}$$

$$f = \frac{x}{250} - 3$$

$$Y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}}$$

$$A1 = 22$$

$$B1 = 17$$

$$C1 = 0.065$$

$$D1 = 900$$

$$Y = 22 - \frac{17}{1 + 0.392439585810^{-25} e^{(0.065x)}}$$

For Cs,

$$y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}} - \frac{1}{2000} e^{(11.1f - 4.4f^2)}$$

$$f = \frac{x}{250} - 3$$

$$Y = A1 - \frac{B1}{1 + e^{(C1(x-D1))}} - \frac{1}{2000} e^{[0.044400000000x - 33.3 - 4.4(\frac{x}{250} - 3)^2]}$$

$$A1 = 0.585$$

$$B1 = 0.415$$

$$C1 = 0.2$$

$$D1 = 880$$

$$0.585 - \frac{0.415}{1 + 0.366582041110^{-76} e^{(0.2x)}} - 0.109371022810^{-34} e^{(0.1500000000x)} e^{(0.00007040000000x^2)}$$

For Ds = $\bar{t}$,

$$y = A1 - \frac{B1}{1 + e^{(-C1(x-D1))}} + \frac{1}{200} e^{(10.5f - 3f^4)}$$

$$f = \frac{x}{250} - 3$$

$$Y = A1 - \frac{B1}{1 + e^{(-C1(x-D1))}} - \frac{1}{200} e^{[0.042000000000x - 31.5 - 3(\frac{x}{250} - 3)^4]}$$

$$A1 = 76$$

$$B1 = 40.5$$

$$C1 = 0.2$$

$$D1 = 880$$

$$76 - \frac{40.5}{1 + 0.272790231910^{77} e^{(-0.2x)}} + 0.305586892310^{-121} e^{(1.338000000x)} e^{\left(\frac{-3x^4}{3906250000}\right)} e^{\left(\frac{9x^3}{3906250}\right)} e^{\left(\frac{-81x^2}{31250}\right)}$$

For each temperature, a number of points were recorded from the measured oxidation curve. The shape of the curves is well represented by the following equation:

$$W = A - \frac{B}{1 - \exp C \times (t - \bar{t})}$$

where, W is the mass of the alloy (g), t is the heating time (min), A is the maximum mass of alloy produced at full oxidation (g), C is a factor related to the rate of mass change in the sample at 50% tungsten to tungsten oxide conversion, and $\bar{t}$ is the oxidation time (min) that corresponds to 50% conversion. B , given by A

minus the initial mass of tungsten, is equal to $0.26 M_i$, where, M_i is the initial mass found by

$$B = A - M_i$$

where, $\frac{M_i}{A} = \frac{79}{100}$ as shown in Table 1.

$$A = \frac{M_i}{0.79} = 1.26M_i$$

$$B = A - M_i = 1.26M_i - M_i = 0.26M_i$$

The experimental values obtained for A , B , C , and $\bar{t}$ are shown in Table 1. An increase in the alloy mass is observed during the oxidation process, which is expressed as:

$$\frac{A \times B}{A}$$

These data show that the mass percent is between 78.73% at 950 °C and 84.55% at 900 °C. Furthermore, the oxidation time at 900 °C is a minimum of 38 min. As presented in Figs.7 and 8, they give the maximum C factor of 0.5.

From the first equation,

$$W = 1.26M_i - \frac{0.26M_i}{1 - \exp C \times (t - \bar{t})}$$

$$W = M_i \times \frac{1.26(1 - \exp C \times (t - \bar{t})) - 0.26}{1 - \exp C \times (t - \bar{t})}$$

$$W = M_i \times \frac{1.26\{(1 - \exp C(t - \bar{t})) - 1\} + 1}{1 - \exp C(t - \bar{t})}$$

$$W = M_i \times \frac{\{(1 - \exp C(t - \bar{t})) - 1\} + 0.79}{1 - \exp C(t - \bar{t})}$$

$$W = M_i \times \frac{0.79 - \exp C(t - \bar{t})}{1 - \exp C(t - \bar{t})}$$

$$W = M_i \times \frac{1 - 0.26 \exp C(t - \bar{t})}{1 - \exp C(t - \bar{t})}$$

And finally,

$$W = M_i \left(\frac{1 - 0.26 \exp(t - \bar{t})}{1 - \exp(-c(t - \bar{t}))} \right)$$

Using MAPLE program methods, the previous mathematical equation was obtained for the weight vs. temperature relationship, according to Table 1.

Using this equation, an oxidation curve and C -factor were obtained over a temperature range of 750 °C to 1,000 °C, as shown in Figs. 7 and 8.

To find the oxidation time $\bar{t}$ from these figures, it is necessary to find the central point of the oxidation process, according to the following equation:

$$O_{\text{central}} = O_s + \frac{O_e - O_s}{2}$$

where, O_s is start of oxidation and O_e is the end of oxidation.

Finally, converting this point to axis, the oxidation time $\bar{t}$ is located.

For the C -factor, the following equation is used

$$C\text{-factor} = \frac{\frac{O_e - O_s}{t_{\text{max}} - t_{\text{min}}}}{t_{\text{max}}}$$

It is important to use a curve for the unknown in the previous equations. These unknowns are related to each factor with the temperature. Figs. 9-12 show the relation between each factor with the oxidation temperatures. These figures show that at any temperature, the unknown factors can be found easily

Table 1 Values of the equation parameters obtained at each temperature.

Factors	Temperature °C											
	750 °C		800 °C		850 °C		900 °C		950 °C		1,000 °C	
	calc.	Exp.	calc.	Exp.	calc.	Exp.	calc.	Exp.	calc.	Exp.	calc.	Exp.
A	25.9	25.8	25.9	25.9	25.7	25.7	86.1	105.2	99.2	100.2	108	97
B	5.4	5.4	5.5	5.5	5.4	5.4	13.3	22	21.1	21	22.5	20.5

C	0.2	0.25	0.2	0.25	0.2	0.3	0.5	0.25	0.3	0.38	0.2	0.2
$\bar{t}$	76	78	76	73	76	78	38	45	43	43	45	40

Fig. 7 C-factor vs. temperature.

Fig. 8 Oxidation time vs. temperature.

from the curves, and then the oxidation time can be calculated from the equation.

To demonstrate the full effect for temperature, time and weight, a three dimensional Fig. 13 is presented. The x-axis presents the temperature, the y-axis presents

the weight, and the z-axis represent the time. The blue area is for the lower temperature while the red is for higher temperatures. The red dotted lines represent the experimental temperatures.

It is noticed that at a lower temperature, the time was

longer than in the higher temperatures. It was observed that after the oxidation is completed, the remaining curve is constant which means no more weight has been added to the sample. Values for the equation

parameters obtained at each temperature are presented in Table 1.

Fig. 9 Max. mass (mg) vs. temperature (°C).

Fig. 10 Mass (mg) vs. temperature (°C).

Fig. 11 C-factor (mg/min) vs. temperature (°C).

Fig. 12 Oxidation time vs. temperature (°C).

Fig. 13 Three dimension curve fitting for the oxidation process.

In this graph, the tungsten alloy weight starts at 20 g, time at zero, and temperature from 750 °C. The time increases indirectly with weight and inversely with the temperature where at lower temperatures, the full oxidation is close to 100 min as shown in Fig. 13 and it decreases to 50 min when it reaches the higher temperature where the slope of the oxidation curve increased. This three dimensional graph is applied only for the given parameters, where at lower temperatures; the oxidation rate is totally different [7, 8].

Weight and time are related to the temperature and not to each other where the increment in the sample weight does not lead to an increase in the oxidation time if the heat was distributed uniformly over the whole sample and the sample placed in a way where the height is 2 mm or less to ensure oxygen diffusion.

Finally, Fig. 13 shows that the highest temperature was 1,000 °C, the maximum weight was 110 g, and the maximum time was 300 min while it was 90 min at full

oxidation at low temperatures.

3. Conclusions

At all temperatures, the oxidation rate (weight increase) was constant, while time decreases at higher temperatures. The time decreasing rate is reduced when the temperature increases. At 950 °C and 1,000 °C, the oxidation time was almost the same.

At a high temperature (1,000 °C), the oxide particle is getting bigger in size which improves the property of the oxide. The best oxidation process was found was at 950 °C and 1,000 °C for 60 min.

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