

Recycling of Tungsten Alloy Swarf

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Abstract—The recycling process of Tungsten alloy (Swarf) by oxidation reduction technique have been investigated. The reduced powder was pressed under a pressure 20Kg/cm² and sintered at 1150°C in dry hydrogen atmosphere. The particle size of the recycled alloy powder was 1-3 μm and the shape was regular at a reduction temperature 800°C. The chemical composition of the recycled alloy is the same as the primary Swarf.

Keywords—Recycling, Swarf, Oxidation, Reduction.

I. INTRODUCTION

TUNGSTEN and tungsten alloy group represent a wide range of uses extending from every day uses (coil of an incandescent lamp) to component of nuclear fusion reactor or ion drive motors in space probes. The reason of this range of uses lies in the many outstanding properties of tungsten, high melting point, low vapour pressure, high atomic number, good electrical and thermal conductivity. [1,2]

Recently, the recycling of tungsten alloys techniques are economically viable and ecologically acceptable [2].

Scrap recycling is a very important factor on the supply of tungsten materials, where 1/3 of the total tungsten demand is supply by tungsten alloy scrap. Furthermore, the least valuable scrap, like low-grade grinding sludge, contains about 15 times more tungsten than the average ore. Most scrap materials are even richer in tungsten than ore concentration.[1]

The aim of this work is to produce from a heavy metal Swarf a homogenous powder by a controlled oxidation to break down the swarf, followed by a reduction process and finally pressing and sintering at certain temperature.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

This work was carried out using heavy metal (tungsten) swarf taken from cutting machine waste. Samples for study were prepared first by washing the swarf in acetone in order to remove the oil that was used as the cooling fluid in the cutting machines. After the acetone wash, the swarf was dried at room temperature for 5 hours; it was then washed several times with distilled water to remove other possible deposits, and then dried at room temperature for 5 hours.

The swarf was mounted in cold-setting resin and polished to 6μm for 10 minutes and then etched by immersing the sample in "Nital" (Nital is an acid which removes the lighter elements from the surface of the polished samples to give two or more layers on the surface to reveal the microstructures) for 30 seconds. The sample was then washed and dried in order to observe the structure in an optical microscope. Its

chemical composition tested by Energy Dispersive Spectrometer (EDS) is listed in Table I.

For XRD analysis, the sample was ground and sieved and a heavy metal powder of less than 150μm was prepared for analysis.

In the final stages after the pressing and sintering the pressed pallet was placed in a cold resin for mounting and polishing.

TABLE I
CHEMICAL COMPOSITION OF THE PRIMARY TUNGSTEN ALLOY SWARF

composition %	W	Ni	Fe	Cu	Co	Mn
Grain	100	--	--	--	--	--
Matrix	15	36	35	8	3	0.6

B. Materials Characterization

The samples were characterised using XRD and SEM. The first characterisation was of the starting material, and then subsequent characterisation was carried out after oxidation, reduction, and finally after pressing and sintering

C. Oxidation Experiments

The oxidation experiments were carried out using two types of instruments according to the required analysis. Initially, isothermal TGA was used with 20 mg of sample to study oxidation in a natural air environment. The experiment was carried out in order to determine the oxidation rate over the temperature range from 20°C to 1100°C. Subsequently, different experiments were carried out at six different temperatures with fixed holding times. The conditions used in these experiments were 750°C, 800°C, 850°C, 900°C, 950°C, and 1000°C, each with a holding time of 3 hours.

Secondly, oxidation of larger quantities (20 grams) of the tungsten alloy swarf was carried out using an electric resistance Carbolite furnace to produce larger amounts of oxide samples. The heavy metal swarf powder was oxidised in air at the same temperatures and for the same times determined from the TGA data. The sample was placed in ceramic boats in the furnace (the boats were inert at high temperatures, so did not react with other elements).

D. Reduction Experiment

The reduction experiments were carried out using a "Vecstar Furnace" with a gas supply system. The furnace had an upper operating temperature of 1600°C and could accommodate gram amounts of powder. The reduction was studied at 800°C temperature for (300mg) of oxide powder.

The furnace was heated to the required temperature at the rate of 300°C/hour. The product was removed for characterization by x-ray diffraction and scanning electron

microscopy and for subsequent processing to give a sintered product.

E. Pressing and Sintering

The reduced powder was pressed into compacts using a pressure of 20 Kg/cm² in a single cylindrical die of 3.5 mm.

The compacted sample was then sintered in the same furnace used for reduction. The sintering was carried out in hydrogen gas in order to prevent the re-oxidation of the tungsten and at the same flow rate as that used for the reduction. The temperature was raised gradually at a rate of 300°C/hr to the sintering temperature. When the sintering process is completed the sample removed to be analysed in the scanning electron microscopy.

III. RESULTS AND DISCUSSION

A. Oxidation

Scanning electron micrographs show that the swarf was a composite material, with a grain size of 10 to 20 µm. Fig. 1 shows that the tungsten grains account for more than 95% of the composite swarf in the view. XRD analysis verified the EDS analysis and showed a diffraction pattern containing peaks that could be clearly related to the tungsten grains and a collection of other peaks associated with the Fe-Ni-Cu matrix alloy.

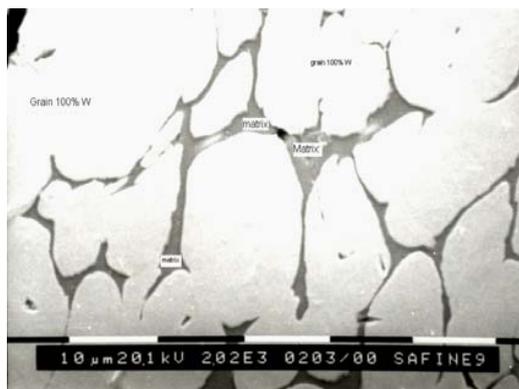


Fig. 1 Micrograph of tungsten swarf material showing tungsten grains embedded in a matrix material

The TGA data, typical examples of which are shown in Figs. 2 and 3, showed the progress of the oxidation of 20 mg samples of the swarf. The initial run using TGA, Fig. 2, was carried out to determine the temperature range over which the W-alloy oxidation took place. Subsequent TGA analyses determined the rate of oxidation at different temperatures within the range determined previously for the oxidation of the alloy.

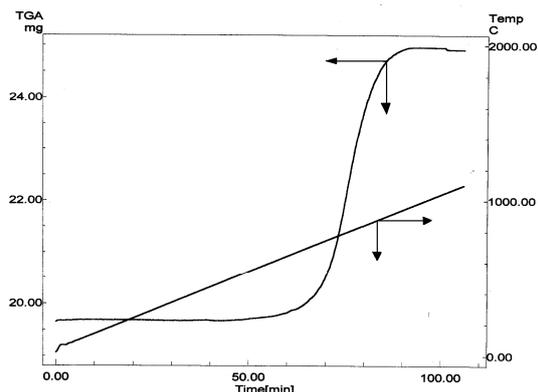


Fig. 2 Oxidation of tungsten alloy swarf in air over the temperature range from 20°C to 1100°C

It shows the trace obtained during first experiment, which was carried out over the temperature range from 20°C to 1100°C in 100 minutes. It can be observed that the oxidation process started at about 560°C (50 minutes after the start of the test). The oxidation was observed through measurement of the increase in the mass of the sample whilst being heated, since the W reacts with oxygen to form tungsten oxide. Fig. 2 shows that rapid oxidation occurs around 700°C to 870°C after 65 minutes, and the sample is fully oxidized at 960°C after 92 minutes. In order to determine the best oxidation rate, six different isothermal experiments were carried out at 750°C, 800°C, 850°C, 900°C, 950°C and 1000°C. Five temperatures were chosen in the fast oxidation region (700°C to 950°C) and the last one in the fully oxidized region in order to determine the best oxidation rate as a function of temperature.

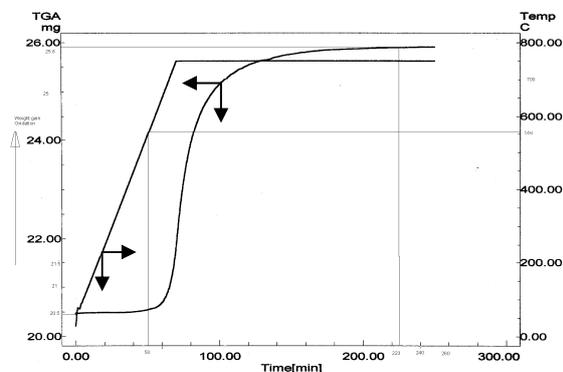


Fig. 3 Oxidation of tungsten alloy swarf in air at 750°C for 3 hours

Fig. 3 shows the oxidation of the W-alloy at 750°C over a period of three hours during which the mass changed from 20.4 mg to 25.8 mg. The results show that the oxidation starts after 50 minutes at 550°C. Above 220 minutes the alloy was fully oxidised with a mass difference of 5.4 mg in 170 minutes.

At 800°C the mass changed rapidly from 20.4 mg to 25.9 mg in 70 minutes, then the alloy was fully oxidised after 72 minutes with a maximum mass change of 5.5 mg. In the

experiment at 850°C it was found that the weight increased rapidly from 20.4 mg to 25.9 mg in slightly less than 70 minutes. The full mass change was 5.5 mg.

If the tungsten mass in the swarf is taken to be 95%, the oxidation of the tungsten part of the sample would have given a mass gain of 4.8 mg. The Fe/Ni/Cu alloy matrix would have oxidised to give the respective tungstates and a mass gain of 0.5 mg, thus giving a total mass gain of 5.3 mg. In these experiments it was observed that the oxidation starts at temperature of 550°C with full oxidation occurring at the different temperatures but taking different times as shown in Table II.

TABLE II
TIME TAKEN TO FULLY OXIDIZE SAMPLE OF THEN TUNGSTEN SWARF AT DIFFERENT TEMPERATURES

Temperature (°C)	Time to oxidise 20mg (minutes)	Time to oxidise 80 mg (minutes)
750	170	-
800	72	-
850	68	-
900	-	60
950	-	31
1000	-	29

At 750°C it was observed that the alloy took a longer time to fully oxidized [3, 4], while at the higher temperatures the oxidation was faster. However, at the higher temperatures the oxide was less friable and appeared to have a larger particle size, shown in Fig. 4. Hence larger amounts of powder (20 grams) were oxidised at 800°C, 900°C, 950°C, and 1000°C for three hours in the furnace.

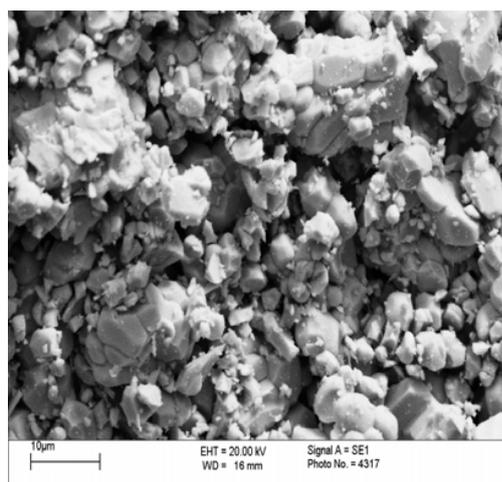


Fig. 4 SEM micrograph of the oxide after oxidation at 1000° C

Fig. 5 shows the XRD spectrum of the oxidised specimen produced at 900°C. The only peaks observed on this figure are associated with the oxide materials WO_3 , Mn_2O_3 and Fe_2O_3 , which confirmed the full oxidation of the sample. It was observed that at all temperatures the samples yielded similar results, i.e. tungsten oxide and the other metals tungstates. The tungsten content was more than 95% in the starting alloy and the matrix which comprised the remaining 5% contained 15 % of W and 85% of the other alloying elements. On this basis it is not surprising that evidence for some oxidised products could not be found as the oxides were likely to be present at a level lower than the detection limit of XRD.

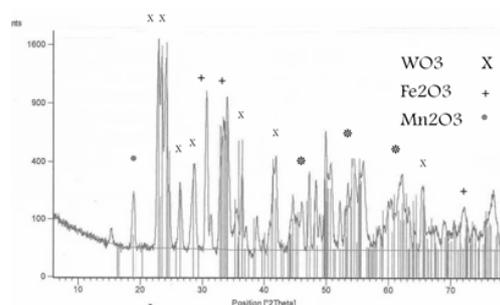


Fig. 5 XRD analysis for the tungsten alloy oxide

For all gram quantities of swarf, a 3 hour oxidation period was selected to ensure that complete oxidation occurred. The oxidation of these materials was verified by subsequent XRD analyses.

At the higher temperatures, 900°C, 950°C and 1000°C, 80 mg samples were evaluated by TGA. The mass difference was 22 milligrams, 79% of the total mass, which is the same percentage mass of the oxidised sample as in the previous lower temperature experiments, but the oxidation time is different. At 900°C, the oxidation time was 60 minutes while in 950 and 1000 it was (31 and 29 minutes respectively). The main observation in these experiments reveals that the full oxidation of the W alloy at high temperatures depends on time and temperature, and the rate of oxidation (weight gain) is constant at fully oxidation process. At higher temperatures (900°C, 950°C and 1000°C) the particle sizes are bigger, and at 1000°C not only is the oxide powder larger but the particles also have a better defined form (Fig. 5) and oxidation is faster (see Table II).

B. Reduction

The reduction experiment was carried out at 800°C for three hours in dry hydrogen atmosphere. The XRD data for a product obtained after three hours was W and a mix of Fe and Ni, and there was no evidence of any oxide in the material.

The EDS analysis data showed a tungsten peak and a very small iron peak (Fe). The quantitative analysis carried out showed 0.77% of the Fe, which is just below the claimed detection limit of the technique, and 99.23% tungsten. The Ni was not detected by EDS due to its very small concentration.

C. Pressing and Sintering

After the reduction of the oxide was completed and the XRD analysis showed the full reduction of the material, the powder was prepared for pressing and sintering. The reduced powder was pressed under a pressure of 20Kg/cm^2 using a 3.5mm single-action die.

Based on a previously published paper [5,6,7], a sintering temperature of 1150°C was used for all the compacted materials. The sample was placed in the furnace for three hours at a temperature 1150°C under a dry hydrogen atmosphere to prevent re-oxidation of the material.

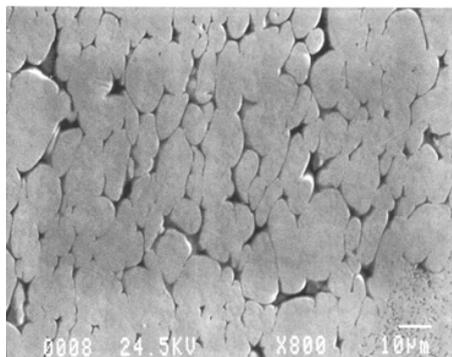


Fig. 6 Micrograph for the compacted pellet

Fig. 6 shows the compacted and sintered material obtained from the fully reduced powders. The micrograph shows that some of the grains of the tungsten have taken the same shape and size ($20\mu\text{m}$) as the un-deformed grains in the starting material Fig. 1. However, it is evident that as well as having the useful W grains present in the microstructure there seems to a rather more densified very small grained region surrounding the more round tungsten grains Fig. 6. The conclusion to be drawn here is that a massive growth and coalescence of small grains have yielded the $20\mu\text{m}$ grains during sintering.

IV. CONCLUSION

- 1) In all oxidation temperatures, the mass increasing rate was about 79% for all alloys quantities.
- 2) The lowest oxidation time and the best oxidation process was at 900°C ; At 1000°C the oxide powder particles were larger which improves the oxide powder property.
- 3) The reduction sequence can be summarized as

$$\text{WO}_3 \rightarrow \text{WO}_{2.9} \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W}.$$
- 4) The reduced powder particles consist of W, Fe, and Ni.
- 5) Some region of compacted and sintered pellet showed a microstructure that was very similar to that of the starting swarf. However, very fine grained regions were also observed.

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