

Recycling of tungsten based heavy alloy scrap

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Abstract : The recovery of tungsten from heavy alloy scrap has been explored. The oxidation of tungsten heavy alloy using oxygen and its subsequent reduction with hydrogen was studied. The oxidation behaviour of the scrap was investigated by simultaneous TG/DTA. Oxidation studies showed a weight gain of 26% and the enthalpy of oxidation was found to be -625 kJ/mol of tungsten. The X-ray diffraction of the oxidized powder has shown the formation of WO_3 , Fe_2WO_6 and $NiWO_4$ phases. The reduction of the oxidized material in hydrogen atmosphere at 1000°C yielded a pure tungsten phase in powder form with an approximate weight loss of 25%.

Keywords: Tungsten alloy, Thermal analysis, Oxidation-Reduction, Recycling

INTRODUCTION

Amongst the tungsten based scrap, the two major sources that are being generated continuously are cemented tungsten carbide (CTC) scrap which is widely used in the hard metal industry for the manufacturing of cutting tools, drilling tools and high wear resistant parts and the liquid phase sintered W-Fe-Ni or W-Ni-Cu heavy alloy kinetic energy penetrators which are used in the armament industry. The tungsten heavy alloys offers the concurrent properties of high density, relatively good corrosion resistance, high mechanical properties and high hardness. This combined set of properties has caused these alloys to be used as components in inertial systems, electrical contacts, boring bars, radiation shielding and kinetic energy penetrators^[1].

Tungsten heavy alloys typically contain 90-97% W in a binder consisting of some combination of Ni, Fe, Cu and traces of other alloying elements. This composition has a density in the range of 17.1 to 18.6 g/cm³ [1]. With an appropriate thermo-mechanical processing such alloys are capable of yielding ultimate tensile strengths in excess of 1500 MPa while retaining good ductility. Alloys within the 90-93% W compositional range are viewed as ideal for kinetic energy penetration as they offer the greatest number of options in fabrication with the retention of properties critical for good ballistic performance.

These alloys are typically produced by a liquid phase sintering process from either co-reduced oxides and/or blended elemental powders in a reduced atmosphere. The W-Fe-Ni is a classic system for liquid phase sintering. Prior studies on these alloys have been established that maximum alloy ductility is realized with a nickel-iron binder ratio of 7:3 respectively, and virtually all current commercial W-Fe-Ni heavy alloy formulations employ this ratio^[1].

The scrap that is generated during the manufacture of these alloys is of three types namely powder scrap, machining scrap and defective penetrators. Out of these three, the rejected penetrators are a major source of the scrap. Generation, of such scrap in India is approximately 150 tonnes per year and requires to be recycled^[2]. Therefore, studies were

conducted to produce the heavy alloy in powder from the defective penetrator rods by oxidizing a piece of rod in oxygen atmosphere and then reducing the oxidized heavy alloy powder in hydrogen atmosphere. This paper reports the observed oxidation-reduction behaviour of the scrap using thermal analysis, X-ray diffraction and scanning electron microscopy.

In developing the various metal oxidation theories, it has generally been assumed that the rate of growth of oxide layer is conducted by the transport of one or more charged species across the layer and the movement of these charged species is brought about by the joint action of a chemical and electrostatic potential gradient¹³. The overall oxidation reaction of any metal can be expressed as:



The oxidation of Ni-Cr-10W ternary alloy was previously studied by Espevik et al¹⁴, where oxidation was conducted in the presence of air at 1200°C and has resulted in the formation of NiO, NiWO₄ and NiCr₂O₄ phases. The studies conducted by Aliprando and Satyanska¹⁵ on the oxidation of directionally solidified cobalt-tungsten (Co-45W) eutectic alloys have shown the formation of CoO and CoWO₄ phases, when oxidized at 750°C for 1000 min in the presence of pure oxygen. In their study, the weight gain of pure Co and pure W were found to be higher compared with that of the Co-45W alloy at all the three different temperatures studied. This could be due to the formation of intermetallic compounds between Co and W, which are not readily oxidized. They have also reported that the oxidized product was always found to consist of an yellow WO₃ outer layer with an inner oxide layer of blue W₂₀O₅₈. The studies conducted by Espevik et al¹⁶, on the oxidation of Co-Cr-W alloys have shown that increasing the tungsten content from 3 to 10 wt% results in an increase in the oxidation resistance of the alloy in the temperature range of 1000-1250°C in air. The formation of CoWO₄ beneath Cr₂O₃ layer was noticed in this investigation. From these studies it is evident that whenever binary or ternary alloys were oxidized, the formation of intermetallic compounds inhibit the complete oxidation of the alloy.

EXPERIMENTAL

The heavy alloy rods having the composition given in the Table 1 were supplied by M/s. Heavy Alloy Penetrator Project, Tiruchirapalli. High purity oxygen and hydrogen were procured from commercial sources. The oxidation behaviour was studied using a simultaneous TG/DTA (SEIKO Model No. 320) and the metallography of the sample was done on a Nikon optical microscope. The SEM studies were carried out using JOEL JSM 840A scanning electron microscope.

RESULTS AND DISCUSSION

Material characterization

The as received heavy alloy rods were cut into smaller pieces using a laboratory size silicon carbide cutting wheel. The cut alloy pieces were etched in hydrofluoric acid and after washing with dilute HCl and water, the samples were observed under the optical microscope. The microstructure has revealed spheroidal grains of tungsten embedded in iron and nickel binder, which is typical of a liquid phase sintered tungsten based heavy alloy. The microstructure obtained from one of the samples is shown in Fig. 1. Similar microstructures were also reported by Caldwell¹¹. The X-ray analysis conducted on the

received sample indicates the presence of $\gamma(\text{Fe-Ni})$ phase (Fig. 2), and this indicates that the spheroidal tungsten grains are embedded in this phase. The chemical composition of the material was also analyzed by the standard wet chemical methods and the results obtained are given in Table 1.

Table 1 : Wet chemical analysis of the heavy alloy sample

Element	Wt (%)
W	93.10
Ni	2.85
Co	0.75
Fe	3.30

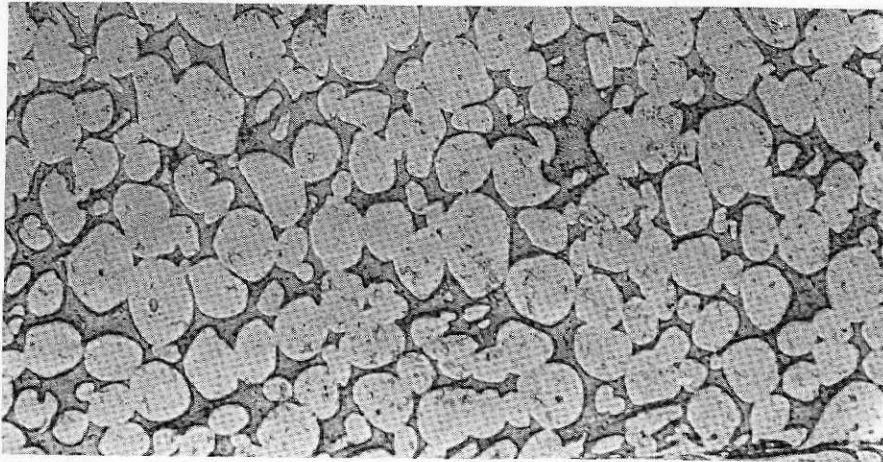


Fig. 1 : Microstructure of the tungsten heavy alloy ($\times 100$)

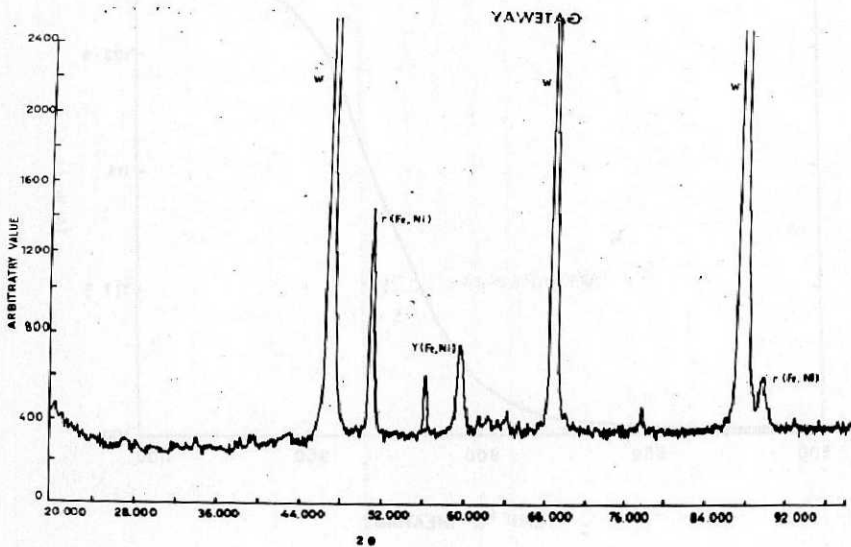


Fig. 2 : X-ray diffractogram of the as received tungsten heavy alloy

Oxidation studies

The oxidation mechanism of the heavy alloy scrap using TG/DTA by placing a piece of alloy in a flowing stream of oxygen. The experimental conditions adapted during the thermal analysis study are given in Table 2.

Table 2 : Experimental conditions adapted for the TG/DTA studies

Sample Weight (Initial)	63.174 mg
Sample Weight (Final)	79.60 mg
Reference Material	$\alpha\text{-Al}_2\text{O}_3$
Furnace Atmosphere	O ₂ , 400 ml/min
Thermocouples	Pt-13% Rh
Heating Rate	5°C/min

The oxidation reaction was found to commence around 700°C and was completed around 1000°C and the weight gain of the material was found to be 26%. The thermogravimetry and the DTA results are shown in Figs. 3 and 4 respectively, where the enthalpy of oxidation was obtained from the peak area of the DTA curve using the expression^[7]:

$$\Delta H^\circ = K \times \text{Peak Area} \quad \dots (2)$$

where,

K = Instrument constant in Amperes (Determined from calibration experiments conducted by melting pure melts)

ΔH° = Change in Enthalpy

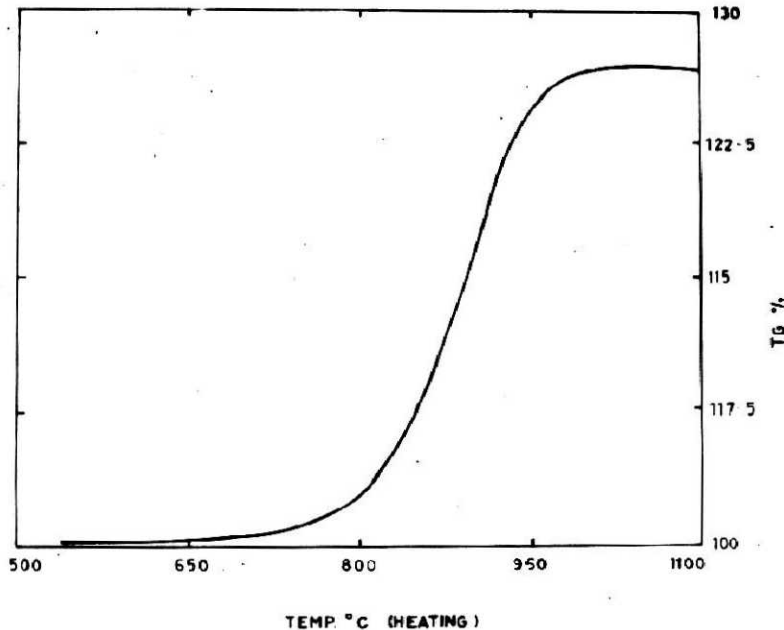


Fig. 3: Weight gain obtained during the oxidation of the tungsten heavy alloy

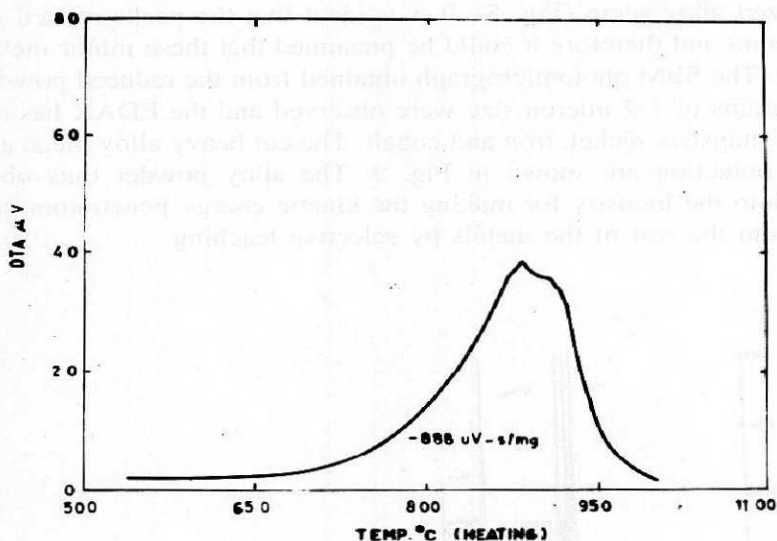


Fig. 4 : The DTA peak and its area obtained during the oxidation of the heavy alloy

The peak area measured by the instrument was found to be $-888 \mu\text{v.s/mg}$ from which the enthalpy of reaction was calculated to be -625 kJ/mole . The details of the calculations are given in the Appendix. The enthalpy of formation of the WO_3 phase given in the literature is -825 kJ/mole at 900°C ^[8]. Determination of the enthalpy of reaction by differential thermal analysis is associated with some uncertainties due to the uncertainties involved in the determination of the instrument constant K . The theoretical weight gain for the complete oxidation of W to WO_3 corresponds to 26.1% and this close agreement between the theoretical and experimental values indicates complete oxidation of tungsten to tungsten trioxide.

The oxidation of the heavy alloy sample was also carried out in a laboratory size tube furnace by placing 20g of the material into it in the presence of oxygen at a flow rate of 600 ml/min at 1000°C for 4h. Under these conditions the oxidized material was found to contain WO_3 , Fe_2WO_6 and NiWO_4 phases determined by conducting the X-ray diffraction analysis, which is shown in Fig. 5. The formation of NiWO_4 phase was reported previously by Espevik et al^[4] and the combination of WO_3 and $\text{W}_{20}\text{O}_{58}$ phases were reported by Aliprando and Satyanska^[5]. In the latter case, oxidation was conducted over a longer period of time, which is little over 15 h. The oxidized heavy alloy scrap collected in the powder form was observed under SEM where the formation of WO_3 grains were revealed (Fig. 6). The material is found to detach along the grain boundaries and one would expect the formation of iron and nickel tungstates along these boundaries.

Reduction studies

The powder obtained from the oxidation of the heavy alloy was subjected to reduction in a tube furnace at 1000°C in the presence of H_2 for 1 h, and the weight loss after reduction was found to be close to 25%. The reduced powder was collected and subjected to XRD, which has indicated the formation of W as shown in Fig. 7. The minor phases of iron, nickel and cobalt were not detected by XRD and by comparing this with the XRD obtained

from the oxidized alloy scrap (Fig. 5), it is evident that the peaks related to NiWO_4 and Fe_2WO_6 are absent and therefore it could be presumed that these minor metals are in their elemental form. The SEM photomicrograph obtained from the reduced powder is shown in Fig. 8, where grains of 1-2 micron size were observed and the EDAX has also confirmed the presence of tungsten, nickel, iron and cobalt. The cut heavy alloy piece and the powder obtained after reduction are shown in Fig. 9. The alloy powder thus obtained can be recycled back into the industry for making the kinetic energy penetrators or tungsten can be separated from the rest of the metals by selective leaching.

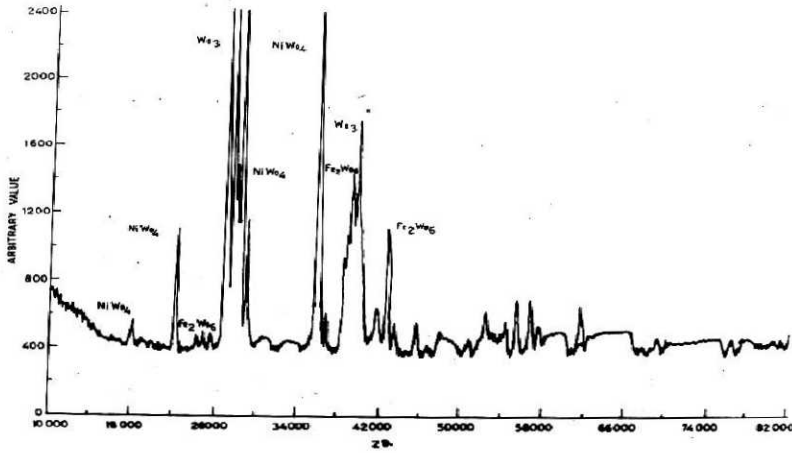


Fig. 5 : SEM photomicrograph of the oxidized tungsten heavy alloy powder

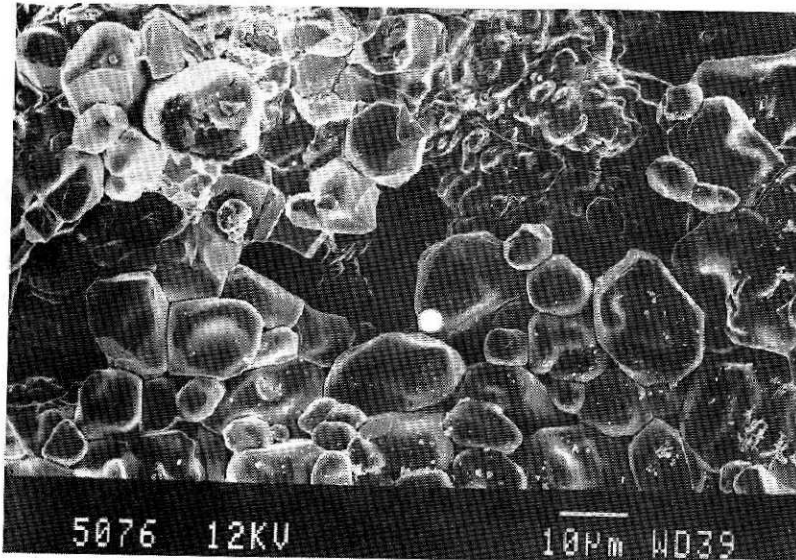


Fig. 6 : X-ray diffractogram of the oxidized tungsten heavy alloy

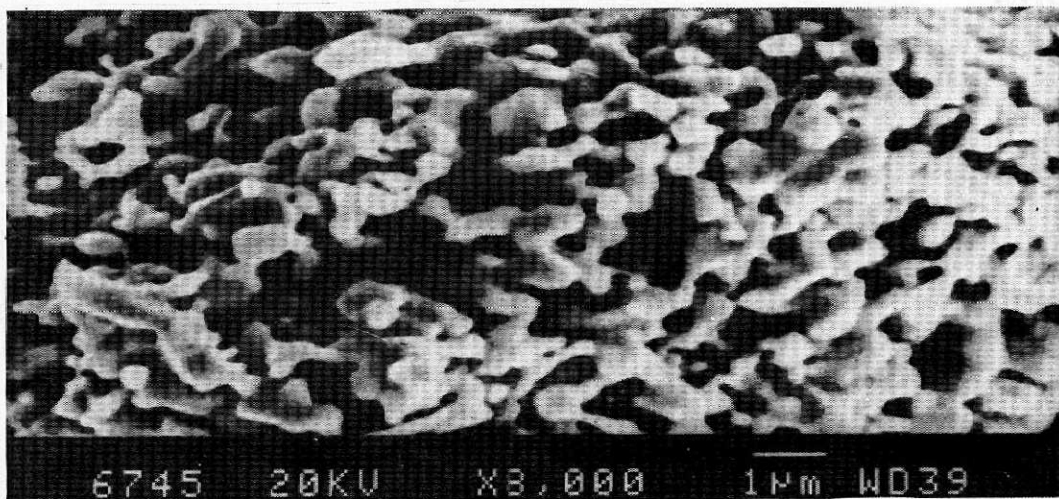


Fig. 7 : SEM Photomicrograph of the reduced powder

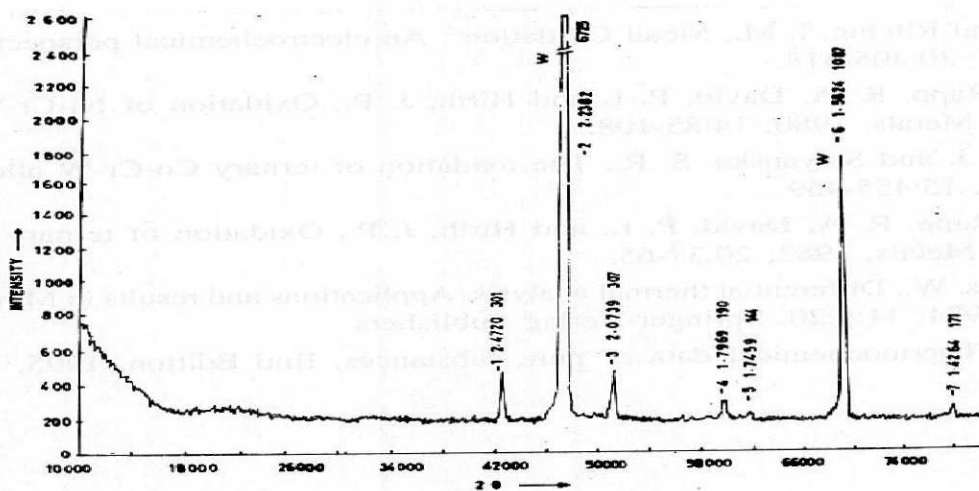


Fig. 8 : X-ray diffractogram of the reduced powder

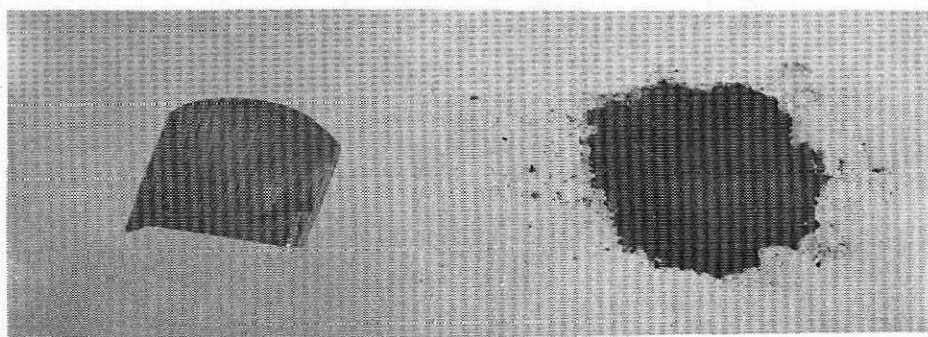


Fig. 9 : The tungsten heavy alloy before and after oxidation-reduction

CONCLUSIONS

The oxidation of W-Fe-Ni with minor amounts of cobalt was studied by thermal analysis in the presence of oxygen flow. The oxidation reaction was found to commence at around 700°C and was found to complete at around 1000°C. The weight gain corresponds to the formation of WO_3 and the enthalpy of oxidation was determined to be -625 kJ/mole of tungsten. The heavy alloy was oxidized in a tube furnace for 4 h in the presence of oxygen flow at 1000°C and the XRD obtained from this material has revealed the formation of WO_3 , Fe_2WO_6 and $NiWO_4$ phases. The oxidized fraction was subjected to reduction in the presence of hydrogen atmosphere at 1000°C for 1 h and the reduced fraction was found to contain pure tungsten metal powder along with minor fractions of iron, nickel and cobalt. This material can be recycled back into the industry as it is or tungsten can be separated from the other metallic elements by known methods such as leaching.

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APPENDIX

The calculation of the enthalpy of oxidation using equation 2 is described here. The simultaneous TG/DTA's instrument constant K is first calculated by melting pure gold in the instrument's furnace. The peak area obtained from the heat of melting of gold is found to be 18 hv.s/mg. Having known the heat of melting of gold from the literature^[8], the instrument constant K is calculated as shown below :

Molecular Weight of Gold	=	196.97 g
ΔH_m°	=	12.55 kJ/mole
	=	0.064 J/mg
Peak Area Obtained	=	18 μ v.s/mg
K	=	ΔH° /Peak Area

As Volt is equal to J/A.S where, J is Joule, A is Ampere and S is Second

K	=	3555.5 A
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This instrument constant of 3555.5 amperes is used in calculating the enthalpy of happ alloy oxidation and the step wise calculations involved are shown below:

Molecular weight of Tungsten	=	183.85 g
Peak Area Obtained	=	-888 μ v.s/mg (Fig. 4)
K	=	3556 A
ΔH°	=	K x Peak Area = -3.16 J/mg

Attributing the entire liberation of heat to the oxidation of W alone,

$$\Delta H^\circ = (-3.16 \times 183850) \div 0.93 = -624.7 \text{ J/mg}$$