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Processing of tungsten alloy scrap for the recovery of tungsten metal

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ABSTRACT

Penetrators used for defence purposes are prepared by powder metallurgical technique. The material contains 90% tungsten along with other minor constituents such as iron, nickel, cobalt, chromium, aluminium etc. During the manufacturing process, three forms of scraps are generated which are : powder, turnings and defective solid. Since the major constituents of the scrap is the costly tungsten metal, attempts were made to recover the metal by four different methods which are described in this paper. Electro-leaching of turnings in a diaphragm cell using chloride electrolyte bath was tried to remove minor elements. The purity of tungsten achieved in this process was 99.9%. In the soda roasting - leaching process of powder/turning scraps, sodium tungstate of 99.85% purity was obtained with 90% yield. Attempt was also made to remove the impurities by acid leaching. 99.8% pure tungsten with 99% yield was achieved by acid leaching. Fine gravity separation and high intensity magnetic separation techniques were also adopted to enhance the tungsten value from the powder scrap, which produced the concentrate containing 96.2% tungsten.

INTRODUCTION

The penetrators used for defence purposes are produced by powder metallurgical technique. Very fine powder of tungsten, nickel, iron, cobalt, chromium, aluminium, etc. are mixed thoroughly and they are compacted. The compacted rods are sintered to produce the alloy which is machined to give the proper shape for specific applications. During the manufacturing process, three types of scraps are generated: (i) powder scrap during compaction (ii) machining scrap (turnings) and (iii) defective penetrators (solid rods). Generation of these types of scraps are appreciable amount. Moreover, good amounts of such scraps are stockpiled for a long period. The cost of the metals entrapped in the scraps are estimated to be sufficiently large. Since the major constituent of the scrap material is the costly tungsten metal (90%), it is desirable to recover this metal by suitable method. It was therefore, decided to explore the possibility of recovering tungsten from these scraps at NML, Jamshedpur. Some preliminary studies were carried out by four methods and the results obtained so far are presented in this paper.

REVIEW OF STATUS

Amongst the tungsten based scraps, there are two major sources[1] which are continuously generated and are available for recycling. One being the cemented tungsten carbide (CTC) which is widely used in the hard metal industry for manufacture of cutting tools, drilling tools and high wear resistant parts. Another source of such scrap[2] is from the armament industry - which uses its liquid phase sintered alloy (W-Ni-Fe) or (W-Ni-Cu) as armour piercing core of medium. Beside these, certain alloys are applied as pre-formed fragments in various anti-aircraft and anti-missile warheads[2]. Because of strategic importance of tungsten, cobalt and nickel metal as well as the scarcity of these metals in India, its processing becomes all the more important. As such the processing of CTC has been widely reported in the literature but information on treatment of scraps from armament industry is rarely available. Most of the techniques which have been used to recover tungsten from CTC may be classified into two broad-based groups. First involves the conversion of total tungsten into its salt[3-8] and second aims at recovery of tungsten carbide as such, which can be recycled for fabricating new tools[9-11].

Fusion with sodium nitrate to yield water soluble sodium tungstate, is a conventional Nitre method[12] of recovering tungsten from CTC. Hartline et.al. reported[13] the oxidation process which involves heating of CTC at > 600°C in presence of oxygen to oxidise WC and Co both, with provision of subsequent recovery. The process of recovering WC from CTC developed by U.S Bureau of Mines[14] is known as Molten Zinc process. The zinc process is used world-wide[15] including China[8]. 80% WC recycling in USA is done through this route, because of the short and simple flowsheet of the process. The cold stream process[16] uses a high velocity of air stream to shatter the CTC to produce fine well - distributed powder. Anodic dissolution processes involve removal of binder phase Co-W from CTC in nitric acid[17], phosphoric acid[18] and hydrochloric acid[15] media.

For the processing of turning of W-Fe-Ni alloy, similar to armament scrap, preliminary results reported[19] involves roasting, acid leaching to remove Fe and Ni and subsequent H_2 reduction to produce tungsten powder. Attempts were also made to make water soluble sodium tungstate. Electrochemical dissolution[20] of similar alloy in NaOH electrolyte was also studied. A process employing electrodialysis system[21] using NaOH to dissolve total tungsten values from different types of scraps followed by solvent extraction (SX) to produce ammonium paratungstate (APT), has been commercialised at Budapest with a capacity of 70 T/Y. It is, therefore, essential to attempt the chemical as well as electrochemical processes to produce useful product or pure tungsten powder of desired specification from armament scrap and the initial studies carried out at NML open up such possibility.

RESEARCH & DEVELOPMENT ACTIVITIES AT NML FORE RECOVERY OF TUNGSTEN FROM TUNGSTEN ALLOY SCRAP

Penetrator scraps were obtained from M/s Heavy Alloy Penetrator Project, Tiruchirapalli, Tamilnadu. The composition of scrap and specification of tungsten metal powder to be achieved is given in the table below :

Element	Average composition of scrap(%)	Purity of W powder required(%)	Element	Average composition of scrap(%)	Purity of W powder required(%)
W	90.0	99.9	Ni	6.33	*
Fe	3.69	0.08	Al	0.03	0.02
Mo	0.20	0.05	Ca	0.04	0.04
Co	0.19	0.02	Na	0.03	0.03
Cu	0.02	0.02	C	0.05	0.04
Zn	0.01	*	Mg	0.01	0.01
Mn	0.02	0.01	S	0.01	*
Cr	0.03	0.03	O_2	1.00	0.75

* Others: 0.01 % max.

Four routes were attempted to recover tungsten from the above scrap materials. These are briefly described in the following sections.

(i) Electro-leaching of turnings from solid rods

In this process, anodic dissolution of impurities from the turnings using acidic electrolytic bath was carried out. The trials were based on the principle that metals having more negative standard electrode potential can be dissolved easily leaving behind nobler metals at anode. The electrode reactions and standard electrode potentials of some of the elements present in the alloy turnings are shown in the following table.

Electrode Reaction	Standard Electrode Potentials
$Al \longrightarrow Al^{3+} + 3e^-$	-1.66
$Zn \longrightarrow Zn^{2+} + 2e^-$	-0.76
$Cr \longrightarrow Cr^{3+} + 3e^-$	-0.74
$Fe \longrightarrow Fe^{2+} + 2e^-$	-0.44
$Co \longrightarrow Co^{2+} + 2e^-$	-0.27
$Ni \longrightarrow Ni^{2+} + 2e^-$	-0.25
$Mo \longrightarrow Mo^{3+} + 2e^-$	-0.20
$W + 3H_2O \longrightarrow WO_3 + 6H^- + 6e^-$	-0.09

From the above data it can be seen that most of impurities have more electro negative potential than tungsten. Therefore, removal of impurities is feasible by anodic dissolution method. Another important parameter in the electro-dissolution process is the choice of proper electrolyte. For this, potentiodynamic studies with different electrolytes were carried out and finally one electrolyte was chosen. The turnings in a graphite cloth or nylon cloth bag was used as anode. Titanium plates were as cathode. The highest purity of tungsten metal achieved in this process was 99.91%.

(ii) Soda roasting and leaching of turnings/powder

Soda roasting process was used for the selective recovery of tungsten from the turning/powder. The material was roasted with sodium carbonate and sodium nitrate at temperature 750°C for 4 hours in a furnace. Tungsten forms sodium tungstate which is leached with water at 60°C to dissolve sodium tungstate leaving impurities in the residue. Tungsten was then precipitated as tungstic acid with the addition of acid in the leached solution. The recovery and purity of tungsten were 90% and 99.85% respectively.

(iii) Impurity removal from powder scrap by acid leaching

Attempts were made to explore the possibility to remove the impurities from powder scrap by acid treatment. The process involves curing the scrap with acid solution at ambient temperature and subsequent separation of unreacted tungsten by filtration. The impurities are removed in the leached solution. The residue containing the tungsten value is washed repeatedly. It has been seen that 99.8% pure tungsten with 99% yield can be achieved in this process.

(iv) Physical beneficiation of powder scrap

An attempt was made to enhance the tungsten value in the powder scrap by adopting (i) fine gravity separation, (ii) wet high intensity magnetic separation technique and (iii) combination of both the above techniques. Fine gravity separation techniques did not give much enhancement of the tungsten value. However, wet magnetic separation technique at 1700 Gauss intensity gave a concentrate with 96.20% tungsten with about 62.0% recovery.

CONCLUSION

Four processes based on the electrochemical, chemical and physical separation methods have been tried at NML. The results are encouraging. Once the technical viabilities of these processes to treat this particular alloy are further established on the bench scale at NML, a process may be scaled-up for techno-economic evaluation. The physical beneficiation process adopted for powder materials is expected to be a quite cost effective technique and can be safely applied for the floor sweep materials.

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