An overview on different processes for recovery of valuable metals from tungsten carbide scrap.

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Abstract

Cemented tungsten carbide material has been widely used in the hard metal industry for the manufacture of cutting tools, drilling tools, mining and machining tools and high wear resistant parts. When these tool bits and components are scrapped, they are collected and processed for recycling following appropriate methods. Tungsten and cobalt both are strategic rare metals and the cost of these metals entrapped in these scraps is estimated to be very high. Therefore, WC scraps have been considered as an important secondary resource of cobalt and tungsten metals. Recycling of hard materials like tungsten carbide scrap require specialised techniques. This paper presents a review of the different processes reported so far to recover valuable metals (W, Co) from cemented tungsten carbide scrap materials. Recycling techniques following either hydro or pyrometallurgical or a combination of them to recover the valuable metals (W, Co) are discussed. Thermal oxidation in presence of air/oxygen generates friable oxides of metals contained in tungsten carbide hard material, which is either leached in acid/alkali to produce tungsten oxide or subjected to reduction by hydrogen to produce tungsten powder. Direct leaching of tungsten scrap in concentrated acid/alkali solutions has also been investigated and different value added materials like ammonium para tungstate, tungstic acid etc are produced in the subsequent processing of leach liquor. The electrochemical route has emerged as an attractive method as it is a single step dissolution process consuming very low energy. However, passivation has been reported to slow down the dissolution rate and hence, some additives have also been tried for continuous dissolution. The environmental and economical aspects of some of the important processes have also been highlighted in this paper.

Keywords: Tungsten carbide scrap; pyro-hydrometallurgical methods; electrochemical processing; tungsten; cobalt.

1. Introduction

Tungsten carbide is a fine gray solid powder, often used to make tools and drill bits by powder metallurgy method via liquid phase sintering process. Tungsten carbide, also referred to as a composite material, is composed of hard tungsten carbide (WC) in soft binder (Fe, Co, Ni) matrix. Tungsten carbide powder (WC), generally ranging in proportion between 70%-97% of the total weight, is mixed with a binder metal (Yih and Wnag, 1979). The high solubility of WC in a cobalt matrix at high temperature with excellent wetting properties makes a structure with little porosity. The resultant cemented carbide has high strength, toughness and hardness. Scraps are WC tools material and its components can be considered as secondary resource of W and Co. Therefore, recycling of tungsten carbide scrap material is a good secondary material to recover the valuable metals. A number of methods have been used in processing of WC scrap. These processes involve either hydro or pyrometallurgical or a combination of them to recover the valuable metals (Yih and Wang, 1979). Statistics reveal that the recovered tungsten carbide comprises of about 20% to 30% of the total supply, lowering the raw material cost by about 15% to 50% (Kieffer etal., 1981). Recovery processes of W and Co from scrap can be classified into two groups (Kieffer etal., 1981). The first group involves chemical modification of the WC component metals into intermediate products which are then processed to obtain pure metals. The second group involves removal of the binder medium from the matrix, leaving behind a finely divided tungsten carbide which can be recycled in fabricating new tools. Among the several methods available in literature for processing of WC scrap, selective electrolysis technique is another potential alternative which has lower energy consumption and lesser environmental impact (Kieffer etal., 1981). Selective electrolysis in electrochemical method has been studied since 1950 to recover the tungsten and cobalt metals from WC material (Latha and Venkatachalam, 1989; Paul et al., 1985; Gandhehari, 1980). Details of different techniques and associated advantages/disadvantages are discussed in this paper.

2. Sources of tungsten carbide scrap

Cemented tungsten carbide based hard material arises from different sources. Various types of tungsten scraps are generated either during manufacturing of the tungsten alloy materials or at the end of service life. During the manufacturing process, three types of scrap are generated (1) powder scrap during compaction (2) machining scrap (turnings) and (3) defective solid product. Generation of these types of scrap are appreciably larger amount (Jana et al., 1996). WC scraps are also classified on the basis of point of generation as (i) Old Scraps: These scraps referred to as end of life scrap consist of tungsten- bearing products that are no longer being used and (ii) New Scraps: These are the scraps that are generated during the processing of tungsten concentrates or scrap to make tungsten metal powder, tungsten containing chemical generated during the fabrication of tungsten products, carbide material from tungsten containing material (Shedd, 2000).

(a) Cutting tool bits. (b) Ammunition and other scraps.

Fig. 3: Various types of WC scraps.

Cemented carbide scrap include metal cutting tool such as burs, drill bits, form cutters, gun drills, saw tips, threading and grooving tools etc (Shedd, 2000). Tungsten carbide scrap also comes from wear-resistant parts, mining bits, jet nozzles and super alloy scrap which is used in high temperature applications such as turbine blades, jet nozzles etc.

3. Recycling of tungsten carbide scrap

A considerable amount of R&D work has been carried out on the processing of tungsten-bearing scrap. Some of the important processes are described below:

3.1 Zinc Melt Process

Historically, this process has its origin in a patent awarded to Powder Alloys Ltd (Moore, 1946). This patent discloses the fact that molten zinc rapidly alloyed with cobalt binder and embrittle the cemented carbide. However, as mentioned in this patent, both the zinc and cobalt were removed by treatments with hydrochloric acid, and only tungsten carbide was reused directly. Removal of the zinc from Zn-Co alloy by distillation was invented by

Barnard et al. (1971). In this process, the product contains all of the original cobalt and may be re-entered without further treatment after grinding. Venkateswaran et al. (1996) also tried the melt bath technique to convert the scrap to WC powder by selectively dissolving Co in molten Zn. Zinc melts process involves removal of the binder medium from the matrix, leaving behind a finely divided tungsten carbide which can be recycled in fabricating new tools. However, high energy consumption and high installation cost are the main drawbacks of this process.

3.2 Cold Stream Process

In the cold stream process scrap material of cemented carbide is heated above 600- 700^{o}C and the cold stream air is forced to the heated carbide scarp. Due to the action of forced air, scrap materials are disintegrated or broken in small pieces (Lin et al., 1995). Oxygen and Nitrogen gas are used to minimize the contamination.

3.3 Hydrometallurgical route

In hydrometallurgical route cemented tungsten carbides are immersed in to leachant to dissolve the matrix or binder material so as to leave a residue of the tungsten carbide. The residue of carbide material is ground and powder material is reused for the preparation of cement carbides. The advantage of this process is that metal carbide can be directly produced and the number of operations involved is less, which is helpful to save energy. Attempts have also been made for selective removal of Co binder from WC–Co scrap for recycling by leaching with various acid solutions with additives. Table 1 summarizes the work carried out following the hydrometallurgical route with/without pyrometallurgical pretreatments for the recovery of valuable metals from WC scrap.

3.4 Chlorination method

In this process, scrap of cemented carbide material is subjected to chlorination at high temperature in a chlorine atmosphere where metal chlorides are formed. This is followed by mechanical reduction operation for producing tungsten carbide powder material (Jonsson, 1971; Takahashi, 1958).

Table 1: Hydrometallurgical processes for recovery of valuable metals from WC scrap.

Sl. No	Types of Scraps	Leaching agent	Temp.	Recovery/product	References
1	WC-Co Scraps of hard	Acetic acid	40-80°C	Fine Co powder	Edtmaier et al., 2005
2	Cermet scraps	HCl	110°C	WC particle became similar to that of	Kojima et al., 2005
3	Sludge containing WC	Aqua regia	100°C	99.97 % pure APT	Lee at al. 2011
4	Hard metal WC-Co	HNO_3	25°C	Metallic Co powder of 99.7 % purity	Gurman et al., 2005
5	Sintered hard carbide block	H_3PO_4	46°C	WC and Co dissolved in phosphoric acid	Shwayder, 1969
6	Cemented carbide scraps	Amine solution	60°C	Carbide in particulate form	Shwayder, 1972
7	Cemented carbide scraps	Glacial acetic acid	118°C	WC powder	Macinnis et al., 1976
8	Cemented carbide scraps	HCl	140-195°C	W metal	Reilly et al., 1983
9	Scrap of cemented	H_2SO_4	160-330°C	W metal	Vanderpool et al. 1884
10	Scrap of cemented	HCl	55-85°C	W	Farrell et al., 1985
11	Metal carbide scrap	NaOH	120°C	WC	Kinstle at al., 2002

3.5 Oxidation method

In oxidation- leaching method, scrap of cemented tungsten carbide is first heated above the melting point of cobalt, which causes the swelling and a porous mass is obtained on cooling. The porous metal carbide scraps are then subjected to mechanical reduction to produce a fine powder of tungsten carbide. Gu et al. (2012) proposed an attractive process based on thermal oxidation followed by leaching and electrowinning. However, high energy requirement in the thermal oxidation of tungsten carbide scrap at 900^{o}C demands very high electric energy. Some of the research work carried out for a processing of WC scrap following thermal oxidation followed by hydrometallurgical treatment is given in Table 2.

Table 2: Thermal oxidation methods for treatment of WC scrap with/ without combination of other techniques.

Sl. No	Types of Scraps	Temp.	Follow up process	References
1	Hard metal and Heavy metal WC alloys	900°C	W recovered using molten salt mixture of hydroxide and sodium sulphate. Yield of W from digestion 91.5%.	Lohse, 1999
2	Sintered masses of WC	1800 °C	HCl leaching	Trapp et al., 1949
3	Sintered tungsten carbide	704-1093 °C	HCl leaching	Avery et al., 1995
4	Sintered hard carbide masses	825-850 °C	NaOH leaching	Maclnnis et al., 1975
5	Super alloy scrap	1515 °C	HCl leaching	Rosof, 1979
6	Cemented tungsten carbide	825-850 °C	Leaching with NaOH.	Martin et al., 1981
7	Cemented tungsten carbide	825 °C	Oxidized product digested in 20-40% alkali metal hydroxide to form alkali metal tungstate.	Quatrini, 1981
8	Tungsten containing materials	680-700 °C	Oxidation with sodium nitrate and leached with $CaCl_2$ and form crystalline calcium tungstate. Tungstic acid formed by 80-180 gpl HCl leaching.	Fruchter et al., 1986
9	Tungsten carbide	600-1050 °C	Dissolution in solution of NaOH followed by spray drying to form precursor compound.	Seegopal et al., 2003
10	Hard metal carbide scrap	850-1020 °C	Oxidation in rotary tube furnace followed by milling with graphite powder in ball mill for subsequent sintering.	Joost et al., 2008
11	Sintered masses of WC	1600-1800 °C	High temperature oxidation process.	Avery, 1995
12	Cemented tungsten carbide	760-871 °C	Oxidised product carburized and sintered to form cemented WC.	Hartline et al., 1976
13	Tungsten carbide alloy	400-1000 °C	Oxidised product subjected to carbothermic reduction (800-1400°C) to produce WC.	Arumugavelu, 2012

3.6 Electrochemical processes

In electrochemical process, scrap material acts as anode and graphite or stainless steel or platinum foil is used as the cathode.

Table 3: Electrochemical processing for recycling of WC scrap.

Sl. No	Types of Scraps	Electrolyte/ additive	Current density	Recovery/product	References
1	Tungsten Alloy Swarf	NaOH	250 & 450 Am^{-2}	90% tungsten dissolution.	Srinivasan et al, 1994
2	Tungsten	NaOH	2.74 A cm^{-2}	Tungstate	[83]Davydov et al., 1997
3	WC-Ni pseudo alloy	H_2SO_4	15–30 $A.dm^{-2}$	WO_3	Kuntyi et al., 2012
4	Secondary hard alloys of VK	HNO_3	3.5–17.7 $A.dm^{-2}$	WO_3	Zaichenko et al., 2010
5	WC–6%Co alloy	H_3PO_4	1.3-2.1 mA cm^{-2}	Separation of Co and WC phase	Malyshev and Grab, 2007
6	WC-6% Co alloy	H_3PO_4	-	Co and W	Ghandehari et al., 1982
7	CS6,CS14,CS20, CS22	HCl/ Citric acid	-	Co and W	Lin et al., 1996
8	WC–6% Co (VK-6)	H_3PO_4	-	Separation of Co and WC phase	Malyshev et al., 2004
9	Tungsten alloy swarf	NaOH	-	APT	Hairunnisha et al., 2007
10	Scraps of sintered metal carbide	HNO_3	-	Co and W	Kobaykawa, 1979
11	WC–6% Co alloy	H_3PO_4		Separation of Co and recover WC	Ghandehari, 1980
12	Heavy metal alloys	NH_4OH/ NH_4NO_3	-	APT	Vanderpool et al., 1981
13	Hard metal scrap	10% HNO_3	-	WO_3	Nutzel, 1982
14	Sintered metal carbide	NaOH	-	WC, disintrigate powder and Co	Vanderpool et al., 1983
15	Cemented tungstate carbide	Amm. Hydroxide/	-	APT	Vanderpool et al., 1991
16	Cemented tungsten scrap	HCl/ Chelating	-	Separation of Co and recover WC	Lin et al., 1995
17	Hard metal content 15 Wt. %	HCl	-	Co and W	Yang et al., 2011
18	Cemented carbide WC- 87%	HNO_3	-	W and Co	Latha and Venkatachalam,
19	Machine or Tool grade,	H_2SO_4	-	Tungstic acid	Paul et al., 1985
20	Tungsten carbide scrap	Aqueous ammonia	-	Co metal and WO_3	Katiyar et al., 2013

During electrolysis anode and cathode are both dip into the electrolyte solution of the cell. Dissolution of the anode (scrap) material starts on applying current. Cobalt goes into the solution and deposited on the cathode and hard metal carbide disintegrate and falls at the bottom of the cell. Hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid etc. are employed as the electrolyte for dissolution of binder material from WC scrap. In addition to the above, work has also been done to dissolve tungsten component of WC scrap in sodium hydroxide electrolyte or ammoniacal electrolyte. Some of the electrochemical processes are given in the Table 3.

Acid and alkali two different types of electrolytes were used in electrodissoltion of WC scrap and high recovery of W and Co were obtained. In acidic medium, Co is deposited on the cathode and small amount of Co also goes into the solution leaving behind the WC skeleton. Co is removed from the solution by electrowinning process. WC materials are obtained from bottem of the cell and dried in a furnace. Tungsten carbide scraps are also treated with alkali electrolyte (NaOH, NH_3) because W and Co both are highly soluble in alkali medium to form ammonium para tungstate (APT) and Co deposited on the cathode (Katiyar et al., 2013).

4. Economic and environmental aspects

Various studies have been reported for the recovery and recycling of W and Co from the waste WC scrap following pyrometallurgy, hydrometallurgy or pyro/hydrometallurgy processes. The pyrometallurgical processes have disadvantages like consumption of more energy, emission of toxic gases, which cause pollution. Economics of recycling plants depend on the quantity and quality of the recovered products and also on the flexibility of the implemented process. The selective electrochemical process has some advantages over hydrometallurgical and pyrometallurgical processes such as lesser steps, higher efficiency and lower costs of production. Electrodissolution processes are also considered suitable because of the advantages such as high recovery of metals with good purity and low emission of harmful gases.

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