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Recycling of tungsten carbide scrap metal: A review of recycling methods and future prospects

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ABSTRACT

Tungsten's unique properties and the excellent cutting and wear resistance properties of its carbides have made it a strategic commodity of high importance globally. Cemented carbides, used for the production of tools and components for metal cutting, rock drilling and wear resistance applications, are highly employed in the manufacturing, petrochemical, construction, gas drilling and mining sectors. These materials, with a typical tungsten content of about 40–95 wt%, become available for recycling and re-use when scrapped.

Cemented carbide recycling methods are classified into three categories: (1) direct, (2) indirect and (3) semi-direct. The direct methods have advantages of high recoveries, good quality powders' production and good grain size control. These methods, however, suffer from incomplete separation of metal carbides from the binding material, require specialized costly equipment and are energy intensive. Indirect methods have the advantage of producing 'virgin Ammonium para tungstate (APT)', the most important precursor for tungsten intermediate products such as tungsten trioxide, tungsten blue oxide, tungstic acid and ammonium metatungstate. These methods, however, have a shortcoming of long reaction times and use several conversion steps. The semi-direct methods have the advantage of being low on energy requirement and environmental impact. However, these methods have a disadvantage of slow process kinetics.

Statistics show that tungsten-based scrap will become an increasingly important source of raw material for the worldwide tungsten industry. Thus the future prospects of recycling will require optimization of current recycling methods, as well as the possible development of new ones with special emphasis on conversion and energy costs, purity of the scrap metal, recovery of all valuable constituents, as well as diminished environmental impact. In this paper, a review of current research efforts and various methods of scrap recovery, future prospects and sustainability of the tungsten industry, are presented.

1. Introduction

Among the many applications tungsten is known for, its most important use today is in the production of tungsten carbide, also referred to as cemented carbide or hardmetal (Sandvik, 2016; Exner, 1979). The main constituent in this composite material is tungsten monocarbide (WC), which has hardness close to that of diamond (ITIA, 2010). Other transition metal carbides such as TiC, TaC, Cr_3C_2 and/or Mo_2C are often added to hardmetals for specific industrial applications. These brittle, refractory carbide phases are combined with a tough binder metal, most often cobalt, in some cases nickel or other metals from the iron group to form cemented carbides (Trent, 1946; Exner, 1979). Characterized by high strength and hardness with a moderate toughness, cemented carbides provide an optimal solution as tools and components for metal cutting, rock drilling and wear resistance applications. They are widely utilized in the manufacturing, mining, construction, gas and oil sectors. Cemented carbide, typically containing 40–95% tungsten, is the most metallic of the carbides, and by far the most important hard phase (Lassner and Schubert, 1999; ITIA, 2010).

Over the years, cemented carbides have proven their superiority over super hard materials in certain high-tech tooling and engineering applications. The super hard materials namely diamond, the hardest of all, followed by Cubic Boron Nitride (CBN), polycrystalline Diamond (PCD) and ceramics (Al_2O_3, SiC, SIALON etc.) all have very low toughness and are thus prone to brittle fracture (Sandvik, 2016). Cemented carbides, on the other hand, have a unique combination of high hardness and good toughness and thus, constitute the most versatile hard materials group for engineering and tooling applications (Exner, 1979; Sandvik, 2016).

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Tungsten's high melting point, high density, good corrosion resistance, good thermal and electrical conductivity properties of its alloys, and the excellent cutting and wear resistance properties of its carbides serve to provide important end-use products (Smith, 1942; Shield, 2000). These qualities, coupled with tungsten's essential applications in industry, aerospace and military, have made tungsten a strategic commodity of worldwide importance (Smith, 1942; SMEAG, 2016; Shield, 2000). As a finite resource, however, the sustainability of tungsten over the long term is of prime concern to all end-users. It is essential, therefore, that as the concept of sustainable development gains ever-increasing importance in the world's future, more efficient and economical recovery and re-use of the world's finite resources of tungsten be achieved (Smith, 1942; Lassner and Schubert, 1999). This paper presents a critical review of tungsten carbide recycling. The paper begins with a review of tungsten resources and processing, followed by a review of the various recovery techniques, future prospects and sustainability of the tungsten carbide industry, and ends with tungsten-related trends and issues.

2. Tungsten resources and processing

Tungsten, a rare and hard metal produced mainly from natural resources is globally low in abundance. The earth's crust accounts for less than 0.0001% tungsten whereas aluminium, in comparison, makes up about 8% (Sandvik Hyperion, 2016; Shield, 2000). Further, world tungsten resources are geographically widespread but unevenly distributed across the globe. Tungsten world production and reserves is displayed in Table 1. In terms of tungsten reserves, China ranks first in the world. It holds more than 54.3% of the world's tungsten deposits and is the major producer (83.6%) of primary tungsten. The next largest tungsten reserves are in Canada at 8.3% and Russia 7.1%, followed by the USA 4.0%, Bolivia 1.5%, Austria 0.3%, Portugal 0.1% and then 24.4% combined in other countries (Kimball, 2014).

Tungsten mining is predominantly an underground operation while open pit mining is done only in exceptional cases. The mines are typically not very large and are limited by the size of the ore bodies. Rarely, more than 2000 tonnes of ore per day is produced (Lassner and Schubert, 1999). In recent times, however, tungsten mines such as the Masan Resources Nui Phao mine in Vietnam, established in 2013 and currently in operation, has higher production rates of up to about 5, 500 tonnes of ore per day (Mining Atlas, 2018). Located in Thai Nguyen Province in northern Vietnam, Nui Phao is the world's largest tungsten mine with tungsten reserves estimated at 66 million tonnes containing 0.21 wt% tungsten trioxide (WO_3) (Mining Global, 2016).

Naturally occurring tungsten ores and the chief primary source of tungsten in the world such as Scheelite, wolframite, ferberite or hübnerite contain about 0.1–5% WO_3 (ITIA, 2012; Bhosale et al., 1990). On the other hand, ore concentrates traded internationally require 65–75% WO_3 (ITIA, 2017a). Therefore, the mining of a huge ore tonnage is required in order to gain a small amount of tungsten and a very huge amount of gangue material must be separated in order to reach the international requirement of concentrate grade. For this reason, ore dressing plants are always located in close proximity to the mine to save on transportation costs. The gangue material separated from the concentrates is normally disposed of as tailings.

2.1. Tungsten extraction from primary resources

The initial leaching step of getting tungsten into solution is based on the use of aqueous media such as acids and alkalis. Modern processing methods dissolve scheelite and wolframite concentrates by an alkaline pressure digestion, using either soda ash (Na_2Co_3) or a concentrated sodium hydroxide (NaOH) solution (ITIA, 2017b; Lassner and Schubert, 1999). The sodium tungstate solution obtained is then purified by using techniques such as ion exchange or solvent extraction before it is converted into an ammonium tungstate solution ($(NH_4)_2WO_4$).

When subjected to crystallisation at 100 °C, ammonium tungstate forms high purity Ammonium-Paratungstate (APT), the most important intermediate product almost exclusively used as a precursor for tungsten products, with the formula $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$. Under oxidizing conditions, APT, when subjected to a number of decomposition reactions, produces WO_3 (Fig. 1). Finally, a hydrogen reduction of WO_3 produces a pure metallic ready-to-use tungsten powder. The tungsten extraction process requires several conversion steps, several reagents and costly specialized equipment in order to ensure efficient and successful recovery of the metal.

Wolframite concentrates can also be smelted directly with charcoal or coke in an electric arc furnace to produce ferrotungsten (FeW) that is used as an alloying material in steel production (ITIA, 2017b).

2.2. Primary uses of tungsten

Tungsten, in its pure metallic form, can be used to manufacture products or it may be combined with other elements to form composite materials such as cemented carbides, metal alloys and various types of steels. Table 2 shows the primary uses of tungsten for various products such as cemented carbides, mill products, steels and alloys. Cemented carbide tools are the workhorses for the shaping of metals, alloys, wood, composites, plastics and ceramics, as well as for the mining and construction industries. Tungsten mill products are either tungsten

Table 1
Tungsten World Mine Production and Reserves in tonnes (Kimball, 2014, 2015, 2016, 2017).

	Mine Production				Reserves			
Country	2013	2014	2015	2016	2013	2014	2015	2016
USA	NA	NA	NA	NA	140,000	140,000	NA	NA
Australia	320	NA	NA	NA	NA	160,000	NA	NA
Austria	850	870	861	860	10,000	10,000	10,000	10,000
Bolivia	1250	1250	1460	1400	53,000	53,000	NA	NA
Canada	2130	2340	1680	NA	290,000	290,000	290,000	290,000
China	68,000	71,000	73,000	71,000	1,900,000	1,900,000	1,900,000	1,900,000
Congo (Kinshasa)	830	NA	NA	NA	NA	NA	NA	NA
Portugal	692	671	474	570	4200	4200	4200	2700
Russia	3600	2800	2600	2600	250,000	250,000	250,000	83,000
Rwanda	730	1000	850	770	NA	NA	NA	NA
Spain	NA	800	835	800	NA	NA	32,000	32,000
UK	NA	NA	150	700	NA	NA	51,000	51,000
Vietnam	1660	4000	5600	6000	NA	870,00	100,000	95,000
Other Countries	1290	2060	1910	1700	852,800	360,000	670,000	680,000
World Total	81,352	86,791	89,420	86,400	3,500,000	3,254,200	3,307,200	3,143,700

NA: Not available