

Tungsten Direct Recovery from W-Cu Alloy Scrap by Selective Digestion via FeCl₃ Aqueous Solution

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Received December 30, 2012; Revised February 03, 2013; Accepted February 28, 2013

Abstract Tungsten alloys are the subject of many recycling studies due to the scarcity of the tungsten sources and environmental considerations to reuse metal scraps. In the current investigation, direct recovery of tungsten from W-10.5 wt.% powder metallurgy parts were performed by FeCl₃ selective digestion of copper binder. The experiments were performed at different salt concentrations, times of digestion, pH values, temperatures and scrap particle sizes. The copper was effectively driven out from W-Cu scrap with increase in FeCl₃ concentration. FeCl₃ to scrap weight ratio of 2/1 at room temperature for 24 h, yielded 97% copper removal and tungsten recovery was raised to 75.2%. Complete removal of copper was occurred at elevated temperature accompanied with acidic conditions. However the tungsten direct recovery efficiency fall as low as 50%. XRD analysis indicated the formation of tungsten oxide while turnings attacked by FeCl₃. Tungsten oxide corroded at high temperatures and low pH values and reduced tungsten recovery.

Keywords: tungsten-copper scrap, direct recovery, FeCl₃ aqueous solution

1. Introduction

Tungsten and its alloys are one of the highly applicable refractory metals and finds extensive applications such as incandescent lamp filaments, heating elements in high temperature furnaces, electronic heaters, X-ray emission tubes and TIG welding electrodes [1,2,3]. Tungsten is mostly extracted from wolframite ((Fe, Mn)WO₄) and scheelite (CaWO₄) minerals. But, the scarcity of the tungsten sources and environmental considerations oblige us to reuse tungsten scraps [4,5]. Nowadays, about one third of the total demand for tungsten in the world is supplied from scrap [6]. The main advantage of using secondary sources (scrap) is that they are high-grade raw materials [6,7]. As compared to scheelite and wolframite concentrates of 7-60 wt.% W, the grade of tungsten-bearing scrap is in the range of 40-95 wt.% W [6]. Furthermore, the least valuable scraps, like low-grade grinding sludge, contain about 15 times more tungsten than the average ore and are normally free from impurities such as vanadium that makes the extraction process intricate. Most scrap materials are even richer in tungsten than ore concentration [6],[8,9,10]. So, extensive works have been carried out on recycling of tungsten-bearing scrap [11,12,13,14].

Lassner and Schubert [6] classified tungsten recycling methods into the following four groups: hydrometallurgy, melting metallurgy, direct recycling, and semi-direct recycling. In hydrometallurgical recycling, chemical methods are used to reclaim tungsten from scrap. Generally, alkali leaching of oxidized scrap is carried out

in an autoclave at temperature of 180-200°C and in the presence of sodium hydroxide or sodium carbonate [15,16]. This processing route results in APT formation that is indistinguishable from those produced from ore concentrates. In melting metallurgical recycling, scrap is used as a source of tungsten in the production of alloys, such as steels, stellites, or superalloys; cast or menstroom tungsten carbide; or ferrotungsten or tungsten melting base [17]. In direct recycling, the scrap is disaggregated into a powder by chemical and/or physical means without changing its original composition [6,18]. In semi-direct recycling, one component of the scrap is dissolved chemically, which allowed the scrap to be broken down by physical means [6,19].

The oxidation-reduction process is a preferred method for recycling tungsten heavy metal alloy turnings and powders. In this direct recycling process, the scrap is oxidized by heating it in air to a temperature of about 800 °C, milled and screened, reduce with hydrogen at a temperature of 900 °C to 1,000 °C, screen and blend, and then mix with virgin heavy metal alloy powder to make a ready-to-press powder for the production of new products [6]. Electrolysis, which uses the scrap as an anode in an electrolytic solution, could be used to dissolve the tungsten from tungsten scrap prior to chemical processing [20]. Leach-milling and leaching with an iron chloride solution to dissolve copper, nickel, and iron selectively are other possible methods for recycling heavy metal alloy scrap [6].

One important composite among other tungsten compounds is tungsten-copper (W-Cu) alloy. In this alloy, hardness, strength, and wear resistance of tungsten are combined with excellent electrical and thermal

conductivity copper [6]. So, they are widely used in circuit breakers, as heat sinks in high power microelectronic devices, heavy-duty electronic contacts, arcing resistant electrodes and deviator plates for fusion reactors [1,21,22,23]. However, powder metallurgy is the only practical procedure to produce high quality parts, due to low mutual solubility of tungsten and copper, high differences between their melting points and densities, and high wetting angle of liquid copper on tungsten [6].

W-Cu alloys that lose their property in service or fail to keep desired function can be referred to "scrap". As the resulting product of W-Cu alloy is composed of distinct particles of one metal dispersed in a matrix of the other one (the microstructure is rather a metal matrix composite than a true alloy) [24] and the constituents can be restored easily.

In this study, we developed a new recovery method for tungsten reclamation of W-10 wt.% Cu scrap by selective dissolution of copper content in ferric chloride. Because the chemistry of tungsten is substantially different from most other metals, including the formation of insoluble species under acidic conditions, it would not be severely affected under acidic conditions [6]. Chemical treatment routes first require that the scrap to be converted to a finely-divided state in which chemical dissolution can proceed at a suitable rate. Subsequently, powder scrap was dissolved in a solution of concentrated FeCl_3 at different conditions to obtain the best tungsten recovery efficiency.

2. Materials and Methods

The W-Cu powder metallurgy scrap of current study were prepared from samples of a previous independent investigation [25]. This alloy contains 10.5 wt.% copper. FeCl_3 , HCl, HNO_3 , H_2SO_4 and HF purchased from Merck (Germany) and used in as-received condition without further purification. First of all, some quantity of W-Cu scrap was cut into small turnings with a cutting tool machine. Afterward, the obtained powders were separated according to their size by means of 500 μm and 100 μm sieves. Subsequently, the turnings with sizes greater than 500 μm were loaded into a high energy ball mill (Pulversiette6- Fritsch) using stainless steel container and balls, with the ball-to-powder weight ratio of 16:1. The milling prolonged 3 hours at 450rpm rotational speed.

The selective digestion process was performed in a glass container at atmosphere pressure. The glass reactor was equipped with a reflux to keep the solvent volume constant for examinations at higher temperatures. Prepared solutions were stirred via a mechanical stirrer with polytetrafluoroethylene (PTFE) handle. Before the recovery process began, scrap was washed with diluted acid nitric solution to remove any contaminant introduced from machining procedure.

Various experimental procedures were executed to evaluate the efficiency of selective FeCl_3 digestion process for tungsten recovery:

1. Time of recovery process was varied from 4h up to 48h for FeCl_3 /tungsten alloy scrap (denoted as W) weight ratio of 1/1 and 2/1.

2. Experiments were operated at various FeCl_3 /W weight ratios from 1/2 up to 10/1.

3. The pH of the recovery process adjusted to 0.5, 1, 1.5 and 2 employing HCl for 2/1 and 5/1 FeCl_3 /W weight ratios.

4. Temperature of the examinations was changed from room conditions to 100°C at pH of 2 and 0.5.

5. Scrap turnings with size of about 1-2mm and two different powder size of <500 μm and <100 μm were exposed to 2/1 and 5/1 FeCl_3 /W weight ratios.

Chemical analysis with atomic absorption spectroscopy (AA, Avanta GBC Scientific) was conducted to measure the concentration of W-Cu alloy scrap comprising and dissolved materials. A specific amount of solution was mixed with $\text{HF}/\text{H}_2\text{SO}_4/\text{HNO}_3$ to appropriately measure the dissolved tungsten content. Remaining copper was also examined with spectroscopy evaluation of residue material.

Electron microscopy (SEM, XL30 Philips) and laser particle size analyzing (Mastersizer 2000 Malvern) for particle size distribution were performed for characterization of powder size evolution. X-ray diffractometry (XRD 300 Unisantis) was done with the aim of residue phase detection.

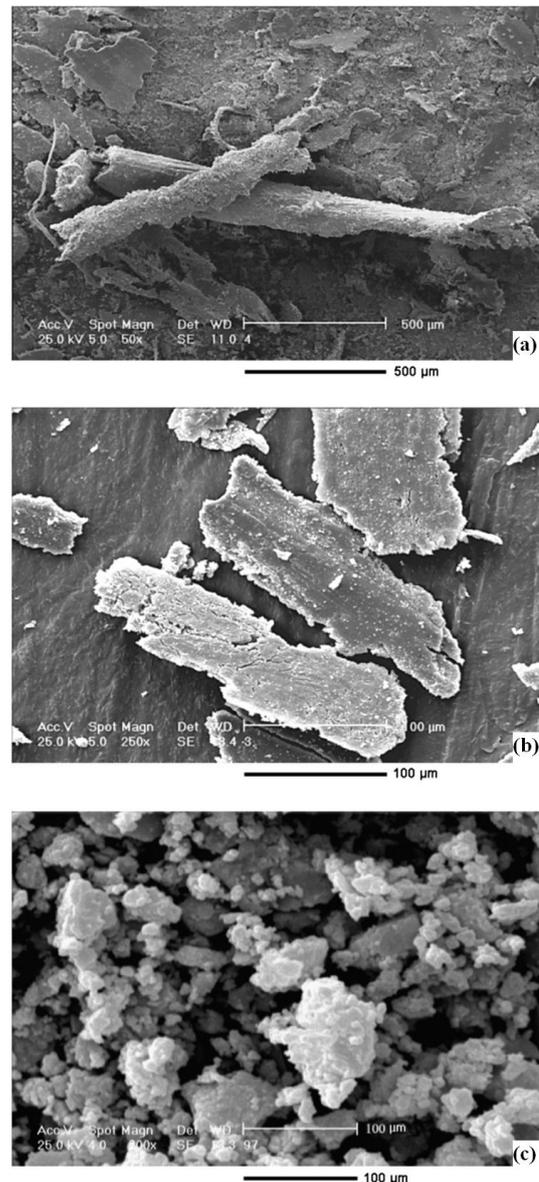


Figure 1. SEM micrographs of (a) original turnings obtained from cutting machine, (b) turnings screened with 500 μm sieve, (c) ball-milled powder.

3. Results and Discussion

Figure 1 shows electron microscopy images of the scrap in different stages of powder preparation. As can be seen in Figure 1 a, the turnings initially had great size. The turnings passed the 500 μ m screening are demonstrated in Figure 1 b and exhibited flattened shape. Ball-milling of these scraps resulted in much smaller particles (Figure 1 c). We used 500 μ m sieved turnings as the main precursor in this study. Nevertheless, original turnings and the ball-milled powders were further investigated to assess the particle size effect on recovery process. Particle size results of these particles are presented in Figure 2.

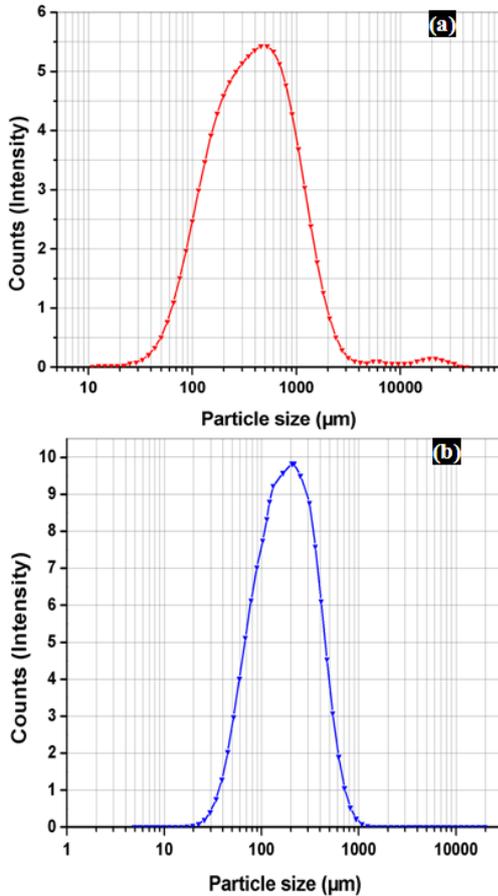


Figure 2. particle size analysis of (a) turnings screened with 500 μ m sieve, (b) ball-milled powders used as scrap in this study.

Figure 3 illustrates the time effect on tungsten recovery. It is clearly observed that copper content of the alloy decreases with increasing recovery time and $FeCl_3$ digestion brings about greater attack at much longer times. On the other hand, in comparison with 1/1 $FeCl_3/W$, recovery with 2/1 $FeCl_3/W$ solution higher concentration of $FeCl_3$ solely cannot promote copper digestion, even at 24 h recovery. In contrast, more tungsten quantities up to 13.5 wt.% was dissolved in 10/1 solution.

We conducted the recovery process with $FeCl_3$ solution at various pH values. As demonstrated in Figure 5, the helpfulness of acidic conditions on driving out the copper from W-Cu alloy scrap is inevitable. But it should be noted that examinations at low pH may lead to superior tungsten digestion that reduces recovery efficiency to about 65%. The effect of (more salt concentration) yielded better results. While after 48h of digestion, copper content of the alloy diminishes to 2.1 wt.% in 1/1 $FeCl_3/W$ ratio,

this value is as low as 1.3 wt.% for 2/1 ratio. Similarly, more tungsten amount dissolved in concentrated solution. Recovery process results for different $FeCl_3/W$ weight ratios under 24h room temperature digestions are reflected in Figure 4. It revealed that higher $FeCl_3$ to tungsten scrap ratio for copper drainage is not significant at pH=0.5 in a way that the involving copper of residue for both cases becomes as low as ~0.3 wt.%. pH effect on tungsten recovery is more evident at higher temperatures. As Figure 6 displays, for $FeCl_3/W$ of 2/1 increasing test temperature at pH=0.5 resulted in overall removal of copper from W-Cu alloy scrap. Temperature effect on tungsten recovery at pH value of 2 ($FeCl_3$ solution with no HCl) is negligible. Acidic $FeCl_3$ digestion after 24h examination at 100 $^{\circ}C$ causes tungsten dissolution of about 50 wt.%.

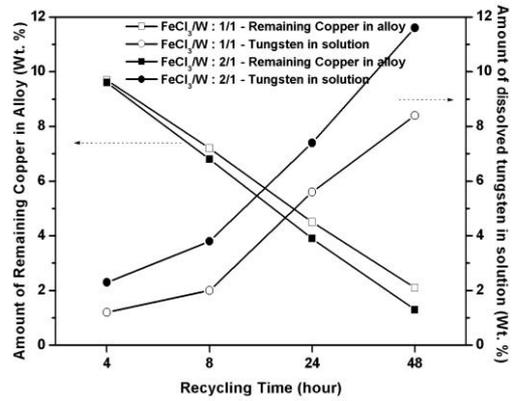


Figure 3. Effect of time evolution on tungsten recovery

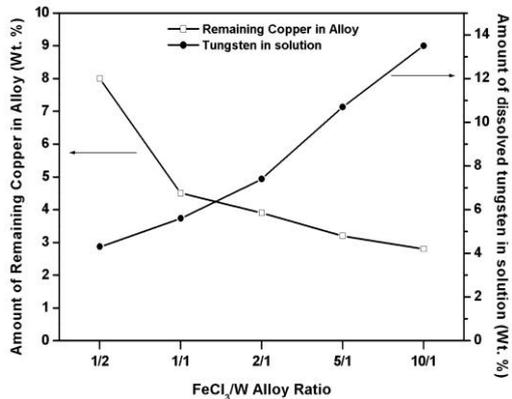


Figure 4. $FeCl_3/W$ effect on recovery process

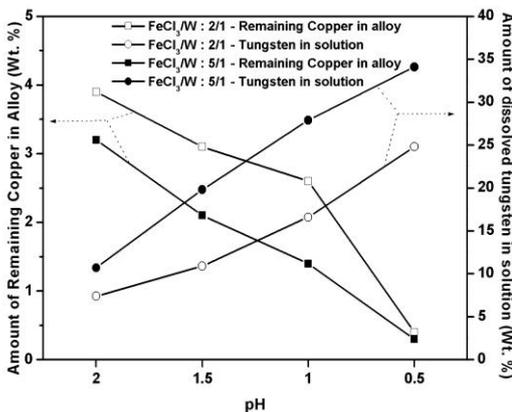


Figure 5. Recovery of tungsten with $FeCl_3$ solution at different pH values

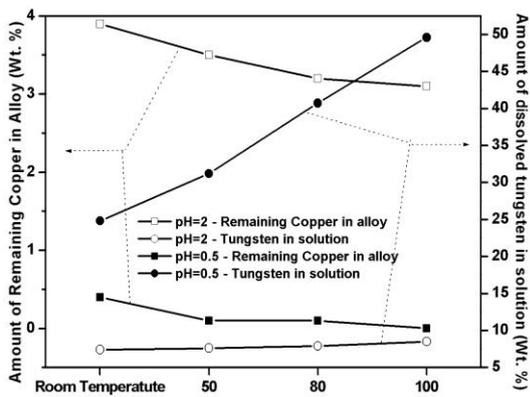


Figure 6. The effect of temperature for tungsten recovery with FeCl₃/W of 2/1 at different pH

Figure 7 demonstrates the effect of scrap particle size on tungsten recovery (24h room temperature digestion at pH=2). As previously described, ball-milled turnings were undergone FeCl₃ digestion to evaluate the particle size effect. Related size of these particles is exhibited in Figure 2b. We discovered that under constant FeCl₃/W conditions, copper dissolution increases with particle size lowering and tungsten recovery efficiency diminishes at the same time. It seems that higher exposure of FeCl₃ to alloying constituents has raised the copper removal. However, up to 1.5 wt.% copper still remains in the residue that makes clear that particle decrement cannot provide suitable conditions for complete copper elimination.

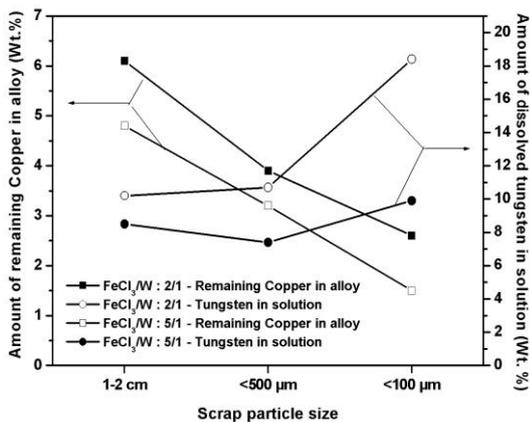


Figure 7. Removal of copper content in scraps with various particle size

It is anticipated that ferric chloride can dissolve transition metal components. So, copper is corroded by FeCl₃ solution. In the recovery some factors were introduced to enhance the copper salvation; salt concentration, temperature, pH and particle size. Noteworthy to say that, all these parameters may cause higher attack to tungsten.

XRD patterns of the digested samples are gathered in Figure 8. It is clearly observed that FeCl₃ attack in aqueous solution gave rise to tungsten oxide formation. We know that tungsten oxide is slightly solvable in aqueous media [6]. Accordingly, lower efficiency of direct tungsten recovery can be attributed to the development of tungsten oxide in the scrap structures. On the other hand, acidic conditions and high temperature dissolution may disintegrate this phase and leave lesser solid tungsten in

the residue. On the contrary, since with particle size degradation the tungsten affinity stay unchanged, no meaningful alterations were produced.

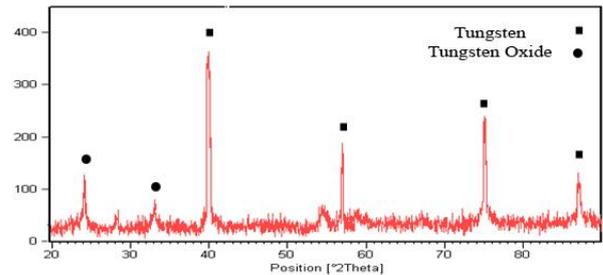
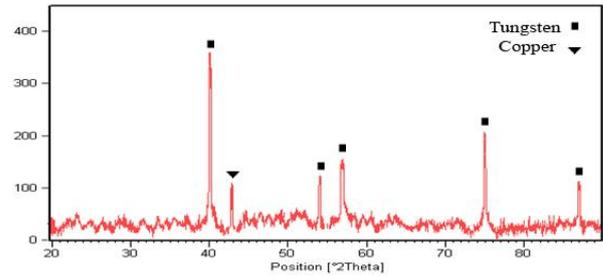


Figure 8. XRD patterns of (a) initial W-Cu alloy scrap, (b) residue after FeCl₃ digestion

Electron microscopy evaluations of residues in Figure 9 reveal that the powders possess particulate porous feature. This may be contributed to outflowing copper from the structure. Since copper act as a binder material in W-Cu alloy, copper removal may be the reason of inferior tungsten amount in residue. The supernatant can further treated to precipitate the tungsten content or iron and copper (it is investigated in a separate study) to increase tungsten recovery.

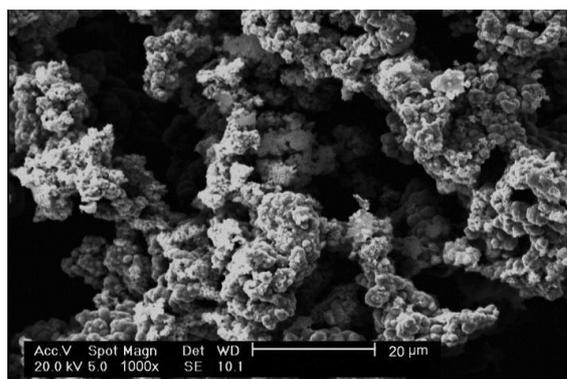
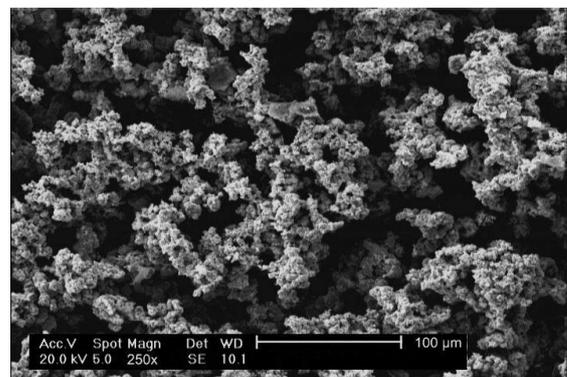


Figure 9. SEM micrographs of attacked scrap particles at two different magnifications

4. Conclusion

Tungsten recovery was conducted on the basis of selective binder removal of copper component of W-10.5 wt.% Cu by FeCl₃ solutions. First of all, W-Cu scraps were machined, sieved and acid washed to be prepared for tungsten direct recycling. The experiments were performed at different salt concentrations, times of digestion, pH values, temperatures and scrap particle sizes. The results indicated that copper can be driven out to amounts about ~0.3 wt.% with tungsten recovery of 75% by FeCl₃ digestion process at acidic condition. Examining under elevated temperature could completely remove all including copper. However, the tungsten direct recovery efficiency fall as low as 50%. Some precipitation methods can settle tungsten or accompanied dissolved ions of iron and copper in solution to enhance the efficiency of recycling process. The phase analysis results revealed that FeCl₃ attack can oxidize tungsten in aqueous media. Tungsten oxide corroded at high temperatures and low pH values and reduced tungsten recovery.

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