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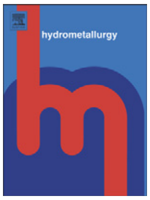

Dissolution behavior of cobalt from WC–Co hard metal scraps by oxidation and wet milling process

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ABSTRACT

Wet milling was fundamentally investigated as a process for dissolution of Co from WC–Co hard metal scrap in this study. The development of a relatively fast and low acid-concentration recycling method of Co from WC–Co hard metal scrap is significant, considering the rare and uneven deposition of Co worldwide. WC–Co scraps were fully oxidized, resulting in a mixture of WO_3 and $CoWO_4$. $CoWO_4$ was readily decomposed to produce soluble $CoSO_4$ and insoluble tungstic acid in sulfuric acid solution of pH 2 or less. Dissolution conditions such as the concentration, temperature, and stirring rate of the solution were varied to determine changes in Co dissolution efficiency with dissolution time. Adding 2 vol.% hydrogen peroxide to the solution augmented the Co dissolution rate considerably. Co dissolution by disruption of the tungstic acid layer via wet milling in 1 M sulfuric acid solution with hydrogen peroxide was four times faster than simple chemical dissolution of Co in 1 M sulfuric acid solution. Wet milling is a time-efficient process to recycle Co from WC–Co scraps which uses a relatively low concentration acid solution.

1. Introduction

WC–Co hard metals have been used for machining tools which require a high degree of wear resistance, mechanical strength, and toughness for proper performance (Brookes, 1996). W and Co are rare metals that have very limited deposits worldwide. There have been many efforts to recycle discarded parts and tools made of WC–Co hard metal. Recycling methods of WC–Co scraps can be divided into direct and indirect processes. Direct recycling methods include the cold stream process and the Zn process. Hard scraps of WC–Co are pulverized using jet milling in the cold stream process, while in the Zn process, WC–Co scraps are immersed in molten Zn bath to selectively react Co with Zn, producing porous scrap residue which can be easily milled. Recovered Co-containing carbide powders are sintered for manufacturing hard metal tools. Indirect recycling methods such as chlorination, oxidation–alkaline leaching, and oxidation–reduction are composed of sequential steps of dry and wet processes. However, most of the conventional recycling processes, whether they are direct or indirect, restore WC–Co hard metal scraps to a mixed powder of WC particles and Co binder.

Selective elemental recovery of W and Co from hard metal scrap has been investigated based on hydrometallurgy or hydrothermal treatment methods. The melt bath technique was introduced to convert W scrap to WC powder (Venkateswaran et al., 1996). Selective removal of Co binder from WC–Co scraps has been attempted using an additive-involving acid solution (Lin et al., 1996), inorganic acid leachants (Gurmen, 2005; Malyshev and Hab, 2004, 2007), an acetic acid solution (Edtmaier et al., 2005), aqua regia treatment (Kim et al., 2010; Lee et al., 2011) and a hydrothermal extraction process (Kojima et al., 2005). Electrochemical recovery of W and Co, using hard metal scrap as an anode material in nitric acid solution, has also been reported (Madhavi Latha and Venkatachalam, 1989). The molten Sn process has been proposed to replace the Zn process to selectively recover W or WC by forming a Sn–Co intermetallic compound (Kamada and Nakamura, 2001). Researchers reported that the oxidation of WC or WC–Co scraps as a preliminary treatment to selective acid leaching is effective in increasing the dissolution or leaching rate of W or Co (Andersson and Bergstrom, 2000; Jia et al., 2011). However, they focused mostly on the separation of W from scraps, and, moreover, argued that Co is oxidized to CoO during scrap oxidation.

In this research, we propose the selective dissolution of Co from oxidized WC–Co hard metal tool tip scraps by an efficient wet milling process in sulfuric acid solution. Previously, we fundamentally studied the thermal oxidation behavior of WC–Co scrap to determine the preferential oxide phases and oxidation mechanism of WC and Co (Gu et al., 2012). Our results regarding the oxidation of WC–Co scrap corresponded to previous reports concerning the nature of oxidized phases of WC–Co hard metal at high temperatures (Basu and Sarin, 1996; Bhaumik et al., 1992; Casas et al., 2001; Lofaj and Kaganovskii, 1995; Voitovich et al., 1996). Based on the current understanding of WC–Co oxidation, in the present research we investigated the dissolution behavior of Co from oxidized WC–Co according to various dissolution conditions such as concentration, dissolution time, temperature,

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and stirring rate in the sulfuric acid solution. The effect of hydrogen peroxide addition on Co dissolution efficiency was also examined. Lastly, wet milling of oxidized WC–Co is suggested to dissolve Co efficiently by combining the optimized dissolution process with mechanical ball milling.

2. Experimental

2.1. Oxidation of WC–Co scrap

WC–Co scrap samples from insert-tip-type cutting tools were provided by an industry after sufficient usage, when they became useless for cutting metals or alloys. The chemical composition of the WC–Co insert tip scrap was WC–9% Co-less than 0.5% TiNbC. The WC–Co insert tip scrap samples were covered with a CrAlN coating, which increases the wear-resistance and hardness of WC–Co insert tips. WC–Co scrap samples were isothermally maintained in an oxygen atmosphere at 900 °C for 3 h after heating from room temperature at a rate of 5 °C-min^{-1}. The oxygen flow rate was 180 ml-s^{-1}.

2.2. Co dissolution in sulfuric acid

Oxidized WC–Co samples were ground to powder using a ball mill machine. The particle size of oxidized WC–Co powder was in the range of 2 to 3 μm in diameter. Sulfuric acid solutions of 1 to 9 M were used to selectively dissolve Co from oxidized WC–Co powder. One gram of the powder was added to 200 ml of sulfuric acid solution. After each Co dissolution operation, solutions were passed through filter paper with 1-μm diameter pores to screen undissolved oxide residue. 10 ml of the solution was then diluted with 90 ml of distilled water before measuring Co content by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPS-7000, Shimadzu). The temperature of sulfuric acid solution was maintained constant in the range of 20 to 70 °C during dissolution experiments using a constant-temperature bath. The top of the solution-containing flask was covered with a plastic paraffin film to avoid increases in sulfate concentration caused by water evaporation. The sulfuric acid solution containing oxidized WC–Co powder was stirred at rates of 0 to 200 rpm using a Teflon-coated magnetic bar on a magnetic stirrer to investigate the effect of solution agitation on Co dissolution efficiency at room temperature. The addition of 2 vol.% hydrogen peroxide to 1 M sulfuric acid solution was also tested with varying dissolution time at room temperature without agitating the solution.

2.3. Co dissolution by wet milling

A 30-cm diameter plastic jar, which was filled with three 1-l capacity glass bottles with a 4-cm diameter opening, was mounted on two roller bars of the ball mill machine. All empty space remaining in the plastic jar after placing the three glass bottles was filled with styrofoam pellets. Alumina balls 5 mm in diameter were inserted into the glass bottles with 1 g unground oxide sample and 200 ml sulfuric acid solution. The weight of the alumina balls was varied from 50 to 200 g to investigate the mechanical effect on Co dissolution efficiency. The neck of the glass bottles was closed with an acid-resistant rubber stopper. A small hole was drilled at the center of the rubber stopper for the emission of oxygen or hydrogen gas during dissolution. The rotation speed of the roller bars was 200 rpm. The concentration of the sulfuric acid solution was varied from 1 to 9 M. 2 vol.% hydrogen peroxide was added to the solution.

2.4. Analysis of solid and aqueous specimens

The appearance of unoxidized and oxidized WC–Co scrap samples was examined using optical microscopy images, and microstructures were viewed using a field emission scanning electron microscope (FESEM; Quanta 200, FEI). Chemical phases of both unoxidized and oxidized samples of WC–Co scrap were identified using an X-ray diffractometer (XRD; D/MAX-IIIC, Rigaku) with Cu Kα radiation ($\lambda = 0.154$ nm). ICP-AES was used to measure the precise content of Co within the dissolved solution.

3. Results and discussion

3.1. Oxidation of WC–Co hard metal tool tips

Fig. 1a shows a WC–Co hard metal tool tip discarded after use in a cutting machine. The edges of the WC–Co tool tip were seriously worn under repetitive cutting operations. Bare WC–Co surfaces were exposed by the local loss of CrAlN coating. The CrAlN coating is highly resistant to oxidation at 900 °C (Chim et al., 2009; Gu et al., 2012); thus, locally damaged edges and corners of the WC–Co tool tip can be the most vulnerable to WC–Co oxidation. The CrAlN coating is physically separated as residue during WC–Co scrap oxidation. The CrAlN residue is not added to sulfuric acid solution for Co dissolution. The microstructure of WC–Co hard metal is shown in Fig. 1b, where the bright region indicates WC particles of 1 to 3 μm diameter, while Co in the dark region binds WC particles. The XRD pattern in Fig. 1c shows the presence of TiNbC as an additive in Co binder.

The WC–Co tool tip scraps were fully oxidized in an oxygen atmosphere for 3 h at 900 °C, as shown in Fig. 1d. The WC–Co scraps were swollen by accepting oxygen, resulting in a 20% weight gain compared to the initial weight of the sample. The SEM image in Fig. 1e shows the porous microstructure of the oxidized WC–Co scrap, in which oxide particles are weakly bonded with each other such that they are easily separated under low external load. The XRD pattern of the oxidized WC–Co scrap in Fig. 1f indicates that WC–Co hard metal is transformed into a mixture of WO_3 and $CoWO_4$ phases by reacting with oxygen. TiNbC also undergoes oxidation in an oxygen atmosphere at high temperatures. However, the WC–Co scrap samples consisted of less than 0.5% TiNbC in this study, so the intensity peaks caused by oxidized TiNbC are low enough to be ignored in Fig. 1f. Possible chemical reactions of oxidizing WC–Co scrap samples were discussed in our previous publication (Gu et al., 2012).

When ICP-AES analysis of Co-containing solution was performed at 0.01 ppm resolution, Ti and Nb were not detectable, likely due to extremely low dissolution from the oxidized WC–Co scrap. In addition, intensity peaks in the XRD pattern of the oxidized WC–Co scrap in Fig. 1f do not coincide with those of $CoTiO_2$, $CoTiO_3$, Co_2TiO_4, and TiO_2, which are the possible phases formed by oxidizing Ti in the presence of W and Co. Intensity peaks of Ti-containing oxides may be hidden by XRD pattern noise because their diffraction signals were so weak, possibly on account of their very low inclusion in the oxidized WC–Co scrap.

3.2. Dissolution of powdered oxide samples in sulfuric acid

3.2.1. Effect of sulfuric acid concentration

Sulfuric acid solution has very strong acidic reactivity with most metals, similar to that exhibited by hydrochloric acid, phosphoric acid, and nitric acid. While it is possible to directly dissolve Co from WC–Co tool tip scrap using sulfuric acid, the primary goal of oxidation and ball milling of WC–Co tool tip scraps prior to the dissolution process is to considerably increase the surface of the scrap available to react with the acid solutions and to expose bare WC–Co microstructure by removing the sturdy CrAlN coating. Among oxidized phases of WC–Co, WO_3 is not reactive in acid solution, whereas $CoWO_4$ reacts with sulfuric acid according to following reaction (1).

$$CoWO_4 + H_2SO_4 \rightarrow CoSO_4 + WO_3 \bullet H_2O \quad (1)$$

Cobalt combines favorably with sulfate ion simultaneously producing tungstic acid. Tungstic acid is a hydrated form of WO_3, and is