



# The influence of $\text{Cl}^-$ on the electrochemical dissolution of cobalt white alloy containing high silicon in a sulfuric acid solution



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## ABSTRACT

Investigations were conducted on the electrochemical dissolution of cobalt white alloy and the anodic passivation in a sulfuric acid solution. The galvanostatic and potentiodynamic experiments were carried out using PARSTAT 2273. The composition and structure changes of alloy anodes were analyzed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS) and X-ray Diffraction (XRD). The metal contents in the electrolyte were measured by Atomic Absorption Spectrophotometry (AAS). The results showed that the cobalt white alloy was composed of the Co–Fe alloy matrix phase and the Cu alloy precipitate phase. This multiphase alloy did not dissolve uniformly and was subjected to anodic passivation due to the high silicon content. The passivation occurred due to the generation of colloidal  $\text{SiO}_2$ , which covered the anode surface and hindered the dissolution of the alloy. However, the polarization curves indicate that  $\text{Cl}^-$  could accelerate the electrochemical dissolution of cobalt white alloy.  $\text{Cl}^-$  could be preferentially adsorbed on the anode surface and undermine the  $\text{SiO}_2$  coating and the passive film on the alloy surface.  $\text{NH}_4\text{Cl}$  significantly increased the dissolution rate of the Co–Fe alloy phase by 4–6 times and improved the anode current efficiency by 27.83%. The electrochemical dissolution was selective, which facilitated the separation of valuable metals. Fe and Co were dissolved into the electrolyte while Cu deposited on the cathode. The anode current efficiency in the electroleaching process was 54.6%. The calculated recoveries of Co and Fe were respectively 100.77% and 98.56% after 22 h of electroleaching, indicating that the Co–Fe alloy phase was preferentially dissolved.

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## 1. Introduction

With the development of rechargeable batteries and functional alloy materials, cobalt is increasingly demanded for commercial, industrial, and military use. Cobalt is mostly recovered by hydrometallurgical processes from oxide ores, sulfide deposits, concentrates, wastes, and by-products (Cooper and Michaylov, 1997). Some amount of cobalt is also found in nonferrous scrap, metallic alloys, and certain intermediate products from the metallurgical process (Burzynska et al., 2008). Cobalt white alloy containing cobalt as high as 42% is obtained from cobalt oxide concentrates processed by electric reduction furnaces. This kind of alloy has become an important form of cobalt resource exported by Africa (Bai, 2007).

Intensive studies have been performed on the dissolution of cobalt-containing alloys to extract cobalt. Whyte et al. (1977) studied the sulfuric acid leaching of Cu–Co–Fe alloy which was produced from the copper slag by an electric-arc reduction furnace. Anand et al. (1983) applied a pressure leaching process to the converter slag in sulfuric acid and extracted 90% Cu, 95% Ni and Co. Acma (1997) investigated the effect of sulfur content on cobalt dissolution behavior during the sulfuric acid leaching of a metallic matte. Xia et al. (2010) leached the white alloy in hydrochloric acid with  $\text{H}_2\text{O}_2$  as an oxidant, which was less poisonous and more effective than chlorine and sodium hypochlorite. Cobalt-containing alloys and scraps can also be processed by ammoniacal leaching. For the alloys containing cobalt and iron, ammoniacal leaching can remove iron during the dissolution step (Das and Anand, 1995), but cobalt ions could be adsorbed onto hematite (Osseo-Asare and Fuerstenau, 1980) or co-precipitate with iron (Han et al., 1982). Osseo-Asare et al. (1983) investigated the electrochemical behavior of Fe–Co alloy in the  $\text{NH}_3\text{--H}_2\text{O--CO}_3$  system and implied that a passive layer of iron oxides could be formed to inhibit cobalt dissolution at high anodic overpotentials. Burzynska et al. (2004a,b) studied the influence of phase structures on the anodic dissolution of synthetic Cu–Co–Fe alloys in sulfuric acid and ammoniacal solutions and reported

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that the electrochemical dissolution was selective without anodic passivation.

However, valuable metals like Co and Fe are not easily extracted from the cobalt white alloy by leaching due to the high content of silicon, irrespective of acid leaching (Mutamba et al., 2001) or ammoniacal leaching (Burzynska et al., 2004b). In order to remove silicon or destroy its erosion-resisting structure, some pretreatments can be applied before leaching like slag roasting (Peng et al., 2007) and mechanical activation (Bryukvin et al., 1995). In contrast, electrochemical dissolution (Kim et al., 2006) is a simple, selective and environmentally friendly method to process the cobalt white alloy, in which an external voltage is imposed on the alloy to facilitate the anodic dissolution of the metals with no oxidants or pretreatments necessary.

The problem with an electrochemical dissolution method is that the anodic passivation was observed in the electroleaching process because of the high silicon content in cobalt white alloy. Some research showed that the passivation could be eliminated by adding certain additives into the electrolyte (Li, 2008; Zhang and Chen, 2008), but few were concerned with a deeper understanding of the passivation mechanism in electrochemical dissolution. In corrosion, it has been studied for decades that  $\text{Cl}^-$  could induce pitting corrosion in steel or alloys (Landolt, 2007); therefore,  $\text{Cl}^-$  is expected to have a similar effect on the electrochemical dissolution.

The present paper was focused on the electrochemical dissolution of cobalt white alloy in a sulfuric acid solution. A mechanism of anodic passivation was proposed based on the experimental results. The effect of  $\text{Cl}^-$  on the electrochemical dissolution was discussed using the Gouy–Chapman–Stern–Grahame model of the electrical double layer theory (Gileadi et al., 1975). The recovery of valuable metals through electroleaching is also presented.

## 2. Experimental

### 2.1. Material preparation and characterization

The original material is a cobalt white alloy powder from South Africa. The chemical composition of the alloy (Table 1) was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

In order to carry out the electrochemical dissolution process in a feasible and convenient manner, the cobalt white alloy powder was melted in an induction furnace at 1450 °C for one hour. Then the alloy ingots were cut into two sizes of cylindrical specimens with dimensions of  $R5 \times 10$  mm and  $R25 \times 10$  mm. The alloy structure was examined by means of an optical microscope (Neophot 32) and SEM (JEOL-6301F) with EDS.

### 2.2. Electrochemical dissolution and measurement

The cylindrical alloy specimens with dimensions of  $R5 \times 10$  mm were prepared for the electrochemical dissolution experiments. Measurements were conducted under galvanostatic conditions with the anodic current density around 300 A/m<sup>2</sup>. The alloy anode was leached in 150 mL sulfuric acid solution with 1.8 mol/L  $\text{H}_2\text{SO}_4$  at 25 °C. The initial pH was calculated to be  $-0.22$  by the equilibrium model in the software HCh (Shvarov, 2008). A square platinum plate ( $10 \times 10 \times 2$  mm) was used as the cathode. The electrodes were submerged vertically in the solution, parallel to each other with a spacing of 3 cm. Because all the surfaces were coated with epoxy resin except one base of the alloy cylinder, the working surface was the

**Table 1**

The chemical composition of cobalt white alloy.

Element	Co	Fe	Cu	Si	P	S
wt.%	36.98	30.88	11.98	10.91	1.21	0.07

**Table 2**

Standard electrode potential  $E^\circ$  and equilibrium constant  $K$  (25 °C) (Bard and Faulkner, 2001; Hayes and Algje, 1993).

Element	Reduction reaction	$E^\circ$ , V(vs SHE)	logK	No.
Silicon	$\text{SiO}_{2(s)} + 4\text{H}^+_{(aq)} + 4\text{e}^- = \text{Si}_{(s)} + 2\text{H}_2\text{O}_{(l)}$	-0.860	-57.9	(1)
Iron	$\text{Fe}^{2+}_{(aq)} + 2\text{e}^- = \text{Fe}_{(s)}$	-0.440	-14.9	(2)
Cobalt	$\text{Co}^{2+}_{(aq)} + 2\text{e}^- = \text{Co}_{(s)}$	-0.277	-9.4	(3)
Hydrogen	$2\text{H}^+_{(aq)} + 2\text{e}^- = \text{H}_{2(g)}$	0.000	0.0	(4)
Copper	$\text{Cu}^{2+}_{(aq)} + 2\text{e}^- = \text{Cu}_{(s)}$	0.340	11.4	(5)
Oxygen	$0.5\text{O}_{2(g)} + 2\text{H}^+_{(aq)} + 2\text{e}^- = \text{H}_2\text{O}_{(l)}$	1.229	41.6	(6)
Chlorine	$\text{Cl}_{2(aq)} + 2\text{e}^- = 2\text{Cl}^-_{(aq)}$	1.400	47.2	(7)

base surface with a radius of 0.5 cm and an area of 0.785 cm<sup>2</sup>. The system was stirred by the magnetic stirrer at 100 RPM. Prior to each experiment, anode and cathode surfaces were polished with sandpapers and then washed with distilled water and ethanol. Before and after the tests, all electrodes were dried and weighed by an electronic scale.

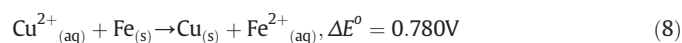
The anode potential was measured with respect to the Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> reference electrode by a PARSTAT 2273 electrochemical research station and then was converted to the Standard Hydrogen Electrode (SHE) potential. The electric charge through the circuit was calculated from the product of the constant current and the time.

During the electrochemical dissolution, solution samples were taken with the same time interval. All solution samples were analyzed for the contents of Co, Fe, and Cu by AAS. The anode surface was washed with distilled water, dried overnight at 90 °C, and then examined by SEM with EDS. Cyclic voltammetry (CV) with the scan rate of 5 mV/s was carried out to analyze the electrochemical system.

#### 2.2.1. Anodic reactions

Table 2 presents the standard electrode potentials ( $E^\circ$ ) and equilibrium constants ( $K$ ) at 25 °C (Bard and Faulkner, 2001; Hayes and Algje, 1993) of the main elements in the electrochemical dissolution system. Taking the relative electron activity into account, the equilibrium constant  $K$  shows the thermodynamic preference in an electrochemical context. According to the electrochemical series, silicon is most favorable to be oxidized and then form the thermodynamically stable  $\text{SiO}_2$  due to the low standard electrode potential and the significantly low  $K$ . As for the metallic elements, Fe and Co would be favorably oxidized compared with Cu during the anodic dissolution of cobalt white alloy. The oxidation potential for  $\text{Cl}^-$  is rather high, so  $\text{Cl}^-$  is the dominant species in the aqueous system (Baghalha et al., 2009).

On the anode surface, the generated  $\text{Cu}^{2+}$  may oxidize Co and Fe which have lower standard electrode potentials, following reactions (8) and (9). The potentials of these two reactions are positive, indicating that the reactions are thermodynamically spontaneous.



When the anode potential reaches the redox potential of oxygen, the water will be electrolyzed to release oxygen following the anodic direction of the reaction (6). This is undesirable because it will cause unstable electrochemical dissolution, low current efficiency, and unnecessary energy consumption. Anodic passivation can be observed when the anode potential is abnormally high and oxygen bubbles are produced on the anode surface.

#### 2.2.2. Cathodic reactions

According to the electrochemical series,  $\text{Cu}^{2+}$  ions in the solution would be preferentially reduced among the metallic ions and then deposit on the cathode surface, following the reaction (5). As the cathode potential decreases,  $\text{H}^+$  would be reduced to  $\text{H}_2$  on the cathode as well.

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