

Original Article

Electrochemical Behavior of Tungsten Carbide-Cobalt Alloy using Molten Hydroxide as Electrolyte under Low Temperature

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Abstract

Tungsten carbide-cobalt alloys (WC-Cos), which are used to cutting tools, consist mainly of tungsten carbide and cobalt with minor elements including chromium, tantalum, nickel and possess excellent hardness, heat resistance, and chemical resistance. Recycle of WC-Cos requires a large amount of energy and chemicals to leach tungsten. We previously showed that tungsten in WC-COs can be leached by potentiostatic electrolysis at -0.7 V in molten sodium hydroxide (NaOH) at 723 K, which tungsten constituted 99.7 mass% of the leached component in the molten salt. In this study, we studied the tungsten leaching at a lower temperature by using an eutectic mixture of 51.5 mol% NaOH and 49.5 mol% potassium hydroxide (KOH) as the electrolyte. Tungsten leached from the alloy at temperatures above 623 K, which was 100 K lower than the previous study. Cobalt dissolved in the molten salt, although it formed a passive layer. Chromium underwent oxidization and dissolved as a hexavalent ion below 623 K. Tantalum dissolved even without electrolysis. It was found that tungsten was leached at 623 K in this system. Highly purifying tungsten could be obtained by dissolving of the cooled molten salt in water and contacting with air to precipitate the other metal ions.

Keywords: tungsten, cobalt, tungsten carbide-cobalt alloy, molten salt electrolysis, recycle

Introduction

Tungsten carbide-cobalt alloys (WC-Cos) are used for fabricating cutting tools, and they are composed of tungsten carbide with cobalt as a binder and chromium, tantalum, and vanadium added for improving heat resistance and surface hardness of the alloy properties [1]. Tungsten and cobalt are rare elements, so WC-Cos mainly consist of rare elements. Tungsten is an important material for industrial applications, however, the recycling rate for WC-Cos in Japan is 15% or less [2]. In addition, the demand for cobalt is increasing [3] because cobalt is a key electrode material for secondary lithium ion batteries. Thus, cobalt recycling is also very important. Therefore, waste WC-Cos is an important industrial resource.

Processes for recycling WC-Cos are categorized into direct and indirect processes. In the direct recycling process, the waste material is transformed into the powder form with the same composition as the waste by either physical or chemical treatments. Direct recycling is a quality-specific process in terms of the chemical composition, tungsten carbide grain size, and foreign substance contamination. The zinc method is a low-energy-consumption process to separate WC from cobalt for WC-Cos recycling [4], and it is commercially employed in Japan. The indirect process involves the chemical modification of the intermediate products and the final product are tungsten compounds ammonium paratungstate (ATP) or tungsten oxide (WO_3). The indirect process involves an oxidation process combined with a purification process. The oxidation process can be one of many types, including thermal oxidation [5-6], chemical oxidation [7-8], mechanochemical oxidation [9], and electrochemical processes [10-12]. We have previously reported the recovery of tungsten from WC-Cos using molten NaOH electrolysis at 723 K [13], it showed that tungsten in WC-COs can be leached by potentiostatic electrolysis at -0.7 V in molten sodium hydroxide (NaOH) at 723 K, which tungsten constituted 99.7 mass% of the leached component in the molten salt.

In the present study, we focused on leaching tungsten from WC-Cos via electrolysis using a molten eutectic mixture of NaOH and KOH at a low temperature compared with previous study for reduction of energy consumption and investigated the electrochemical oxidation behavior of each element in the alloy.

MATERIALS AND METHODS

Experimental conditions

The experimental equipment is shown in Fig. 1. The electrolysis potential was controlled using a potentiostat (HZ-5000; Hokuto Denko). The eutectic mixture of 51.5 mol% NaOH (Nakalai tesque) and 49.5 mol% KOH (Nakalai tesque) was used as the electrolyte. The temperature in the furnace was controlled from 523 K to 723 K. An alumina crucible (SSA-S; Nikkato corporation) was used as the electrolysis reactor. All experiments were performed in an argon atmosphere. The cathode was a nickel wire. The anode was the WC-Cos or its elements, which are tungsten, cobalt, chromium and tantalum, and The purity of these metals is more than 99%. The elemental composition of the WC-Cos alloy is shown in Table 1. The reference electrode was a platinum coil, Potential was calibrated with reference to generate oxygen gas, oxygen gas was generated from 0.0 V in anodic polarization analysis on platinum coil as working electrode. The scanning rate of for anodic polarization analysis was 5 mV s^{-1} from the rest potential.

Analytical method

Following electrolysis, the WC-Cos, cooled molten salt, and residual materials were separately dissolved. A mixed acid solution containing 8 mass% hydrofluoric acid and 12 mass% nitric acid was used for dissolving, the WC-Cos and residual materials, respectively. The elemental composition was analyzed by inductively coupled plasma optical emission spectroscopy (ICP, Optima 3300 DV; Perkin Elmer Japan). The materials were identified by X-ray diffraction (XRD, RINT2500TTR; Rigaku). Surface morphologies and elemental contents were analyzed by scanning electron microscopy combined with energy dispersive X-ray analysis (SEM-EDX, JSM-6330F & JED-2140GS; JEOL). The solid carbon content was determined using a carbon-sulfur analyzer (EMIA-540; Shimadzu).

The current efficiency of the WC-Cos, C_{eff} , was calculated for the expected reaction:



$$C_{\text{eff}} = \frac{z_{\text{W}} \times n \times F}{Q} \times 100,$$

where z_{W} is the atomic charge of tungsten(-), n is the molar amount of leached tungsten(mol), F is the Faraday constant(C/mol), and Q is the quantity of electricity (C).

RESULTS AND DISCUSSION

Anodic polarization curves of component elements of WC-Cos

The anodic polarization curve of tungsten was similar for electrolytes NaOH, KOH, and the eutectic mixture of 51.5 mol% NaOH and 49.5 mol% KOH at 723 K (data not shown), indicating that the electrochemical behavior was not significantly influenced by the type of cation in the electrolyte.

The anodic polarization curves of tungsten in the eutectic mixture of 51.5 mol% NaOH and 49.5 mol% KOH are shown in Fig. 2. The current increased at approximately -1.0 V at 723 and 673 K, and two peaks were observed around -0.9 and -0.4 V at 573 and 523 K in anodic polarization curves, respectively. The peaks indicate the formation of a passive layer in electrochemistry, suggesting the formation of a passive tungsten layer at 573 and 523 K. And white material was observed on the anode surface after anodic polarization analysis. Tungsten oxidizes and dissolves as tungstate ion (WO_4^{2-}) in the electrolyte after forming WO_3 and WO_2 . The difference in the free energy between WO_3 and WO_2 is less than 5%. Therefore, the oxidization of WO_2 to WO_3 proceeds smoothly. From the results of this study, the current increases at 623 K and higher; this indicates that tungsten oxides diffuse into the electrolyte for stable electrolysis. The tungsten oxides increase the melting point of the electrolyte. The diffusion rate decreases with decreasing melting point. Tungsten oxides, which were prepared by anodic polarization analysis from anode material, accumulate around the anode surface. Therefore, potassium tungstate and/or sodium tungstate were deposited on the anode surface and formed passive layer.

The anodic polarization curves of cobalt are shown in Fig. 3. The current peaks were observed around -0.9 and -0.5 V using the cobalt metal anode. This result is similar to that of our previous study, cobalt was oxidized to cobalt oxide (CoO) around -0.8 V, and CoO converted to cobalt oxide (Co_2O_3) at approximately -0.4 V. This was confirmed from XRD analysis data for each condition. However, the second peak became broader with decreasing temperature.

The anodic polarization curves of chromium are shown in Fig. 4. Chromium was oxidized to hexavalent chromium at 623 K and 523 K. This was confirmed from potentiostatic electrolysis at -0.4 V and -0.1 V, and the calculated current efficiency and the color of the electrolyte established the oxidation reaction of chromium. Chromium(III) oxide (Cr_2O_3) was observed at 723 K, because hexavalent chromium reduced to Cr_2O_3 at 523 K or above. It was shown that Cr_2O_3 was produced via hexavalent chromium. The current density decreased from around -0.2 V at 623 K and 523 K; this suggested that a passive layer, which is composed of Cr_2O_3 , formed on the anode surface as a result of decomposition of the hexavalent chromium without an electrochemical reaction. The difference in the current density between 623 K and 523 K was attributed to the diffusion around the anode surface.

The anodic polarization curves of tantalum are shown in Fig. 5. The current flowed from -1.4 V to more than 0 V, which is the oxidation generation potential at 723 K and 623 K. This shows that the current is not affected by a change in the potential. A peak was observed around -1.2 V at 723 K and 623 K, and it indicated the formation of tantalum oxide. From the result of potentiostatic electrolysis at -0.7 V, the tantalum oxide was determined to be tantalum pentoxide (Ta_2O_5). The value of the current remained constant with increasing potential from -0.7 V, indicating that tantalum as Ta_2O_5 dissolved in the molten hydroxide without electrolysis. However, an electrochemical reaction of tantalum was not observed at 523 K. The current for the oxidation of tantalum decreased with an increase in the electrolyte temperature, so tantalum was dissolved at the oxidation potential of electrolysis.

Anodic polarization curves of WC-Cos

The anodic polarization curves of the WC-Cos are shown in Fig.6. The anodic polarization curve of the WC-Cos is similar to that of tungsten without Co at 623 K. The peak from -1.0 V to -0.8 V was similar to that corresponding to the formation of CoO. The current density peaked at -0.7 V, and decreased with increasing frequency of anodic polarization analysis cycles as shown in Fig. 7. Further, the form of the anodic polarization curve of the alloy changed from that resembling the cobalt curve to that resembling the tungsten curve. This shows that the surface of the cobalt phase in the alloy was oxidized during the anodic polarization analysis. The oxidized cobalt did not influence the electrochemical reaction, so the peak located around -0.7 V decreased with the frequency of cycles of the anodic polarization analysis (Fig.7).

Tungsten was oxidized with a decrease in the metallic cobalt phase content although the surface of the WC-Cos is mostly composed of tungsten carbide [14].It was shown that the oxidation of cobalt in the alloy was dominant over that of tungsten at 623 K. Further, it suggested that a large amount of electrical charge is suitable for selective leaching of tungsten from the WC-Cos.

Oxidation of WC-Co using electrolysis at 623 K

The current density behavior of potentiostatic electrolysis at -0.7 V, -0.6 V, and -0.5 V is shown in Fig.8; the electrical charge was 5,000 C. The electrochemical behaviors were similar from -0.7 V to -0.5 V. In the early period around 10 s, the current density decreased with time. The current density was similar to the anodic polarization curve of initial analysis, which is shown in Fig.8; this current was used for cobalt oxidation. The current density was stable from 10 to 1,000 s,

tungsten was oxidized and dissolved readily. After 1,000 s, the current density varied with a change in the surface area of the WC-Cos with decomposition.

The composition of the molten salt after electrolysis at 623 K and composition of the electrolyzed WC-Cos are shown in Tables 1 and 2, respectively. The current efficiency (C_{eff}) was calculated from the elemental compositions. The composition of tungsten in molten salt increased, while that of cobalt decreased with an increase in the electrolysis potential. The XRD pattern of the sediments in molten salts and these of electrode after electrolysis are shown in Figs. 9 and 10, respectively. We expect the peaks of cobalt to be disappeared with electrolysis, because it oxidized into low crystallinity oxides. This is supported by the XRD of sediments, which showed only weak reflections of CoO and Co₂O₃. In our previous study, cobalt was not leached into the molten NaOH at 723 K, and the reaction material was tricobalt tetroxide (Co₃O₄) around this potential. CoO and Co₂O₃ were generated in this study, and these dissolved in the molten hydroxide. The dissolving of cobalt in the molten hydroxide was confirmed by the deposition of cobalt on the cathode. Chromium was slightly dissolved in the molten salt. The amount of dissolved chromium increased with an increase in the potential, as a result of anodic polarization. Tantalum dissolved without any electrochemical reaction, and the increase in the tantalum content at -0.7 V was affected by the total dissolved amount of each elements. Although cobalt, chromium, and tantalum were also dissolved in the molten salt after electrolysis, they can be precipitated and separated by dissolving the molten salt in water and contacting with air.

CONCLUSION

Tungsten was leached from the WC-Cos into eutectic NaOH-KOH molten hydroxide, by employing electrolysis. The electrolyte temperature affected the leaching behavior of each element in the WC-Cos. Tungsten was leached from WC-Cos at above 623 K, which was 100 K lower than the previous study. The influence of the electrolysis potential on tungsten leaching is smaller than that of temperature at 623 K and higher. The anodic polarization curve of cobalt shows the formation of a passive layer on the surface, although cobalt was dissolved in the molten salt with electrolysis at 623 K. The reaction materials on the cobalt surface were CoO and Co₂O₃. The chromium was oxidized to Cr₂O₃ and dissolved as hexavalent ions below 623 K without electrolysis. The leaching amount of tungsten and chromium from the alloy increased with the electrolysis potential. Tantalum was dissolved without electrolysis. It was shown that tungsten was leached at 623 K. Cobalt was dissolved with tungsten at 623 K, however, it is able to remove by post process as wet refining process. In the future, electrochemical process is expected to use for separation of tungsten from WC-Cos.

Acknowledgments

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Caption list

Table 1 Composition of WC-Cos

Table 2 Composition of the molten salt after electrolysis at 623 K

Table 3 Composition of the electrolyzed WC-Cos at 623 K

Fig.1 Illustration of equipment used for molten salt electrolysis

Fig.2 Anodic polarization curves of tungsten

Fig.3 Anodic polarization curves of cobalt

Fig.4 Anodic polarization curves of chromium

Fig.5 Anodic polarization curves of tantalum

Fig.6 Anodic polarization curves of WC-Cos

Fig.7 Current density behavior of potentiostatic electrolysis at -0.7 V, -0.6 V and -0.5 V

Fig.8 Influence of frequency for anodic polarization curve of WC-Co at 623 K

Fig.9 XRD pattern of sediment in molten salts after electrolysis at -0.7 V, -0.6 V, and -0.5 V

Fig.10 XRD pattern of electrode after electrolysis at -0.7 V, -0.6 V, and -0.5 V

Table 1 composition of WC-Cos

	W (%)	Co (%)	Cr (%)	Ta (%)	C (%)
Raw material	38.0	18.7	1.5	0.7	41.1

Table 2 composition of the molten salt after electrolysis at 623 K

Potential (V)	W (%)	Co (%)	Cr (%)	Ta (%)	C _{eff} (%)
-0.7	82.7	15.3	0.1	1.9	63.6
-0.6	86.6	12.5	0.2	0.7	66.3
-0.5	88.6	10.9	0.5	<0.1	69.1

Table 3 composition of the electrolyzed WC-Cos at 623 K

Potential (V)	W (%)	Co (%)	Cr (%)	Ta (%)	C (%)
-0.7	42.3	19.2	1.6	0.5	36.4
-0.6	42.1	19.2	1.5	0.4	36.8
-0.5	40.1	18.9	1.4	0.4	39.1

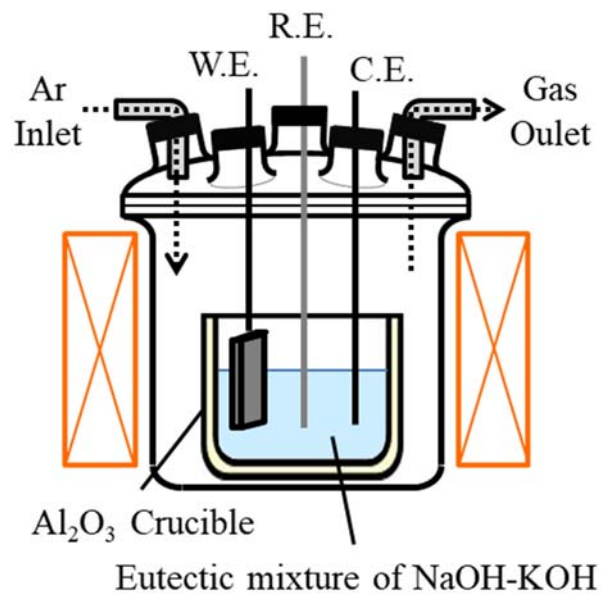


Fig.1 Illustration of equipment used for molten salt electrolysis.

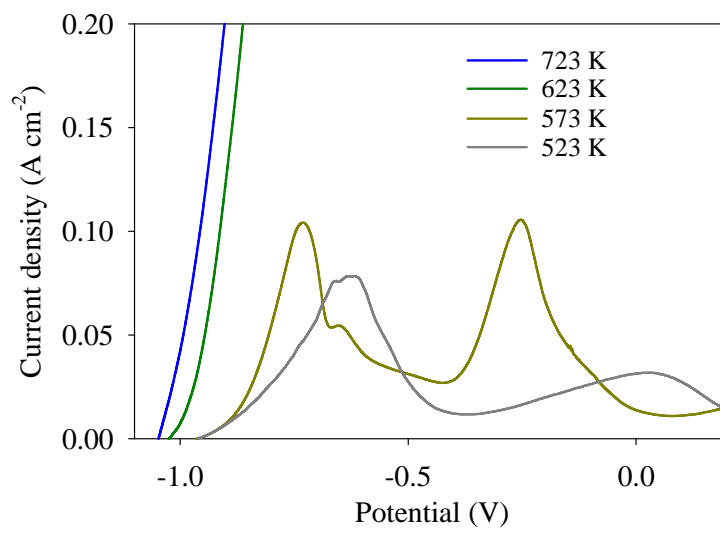


Fig.2 Anodic polarization curves of tungsten

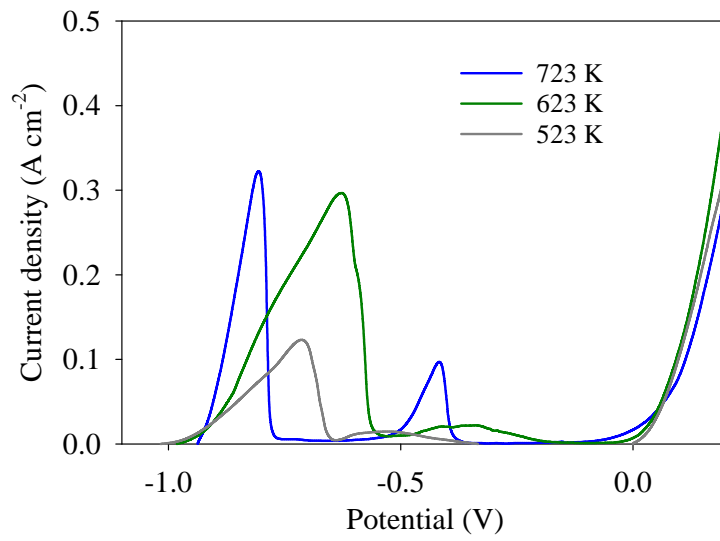


Fig.3 Anodic polarization curves of cobalt

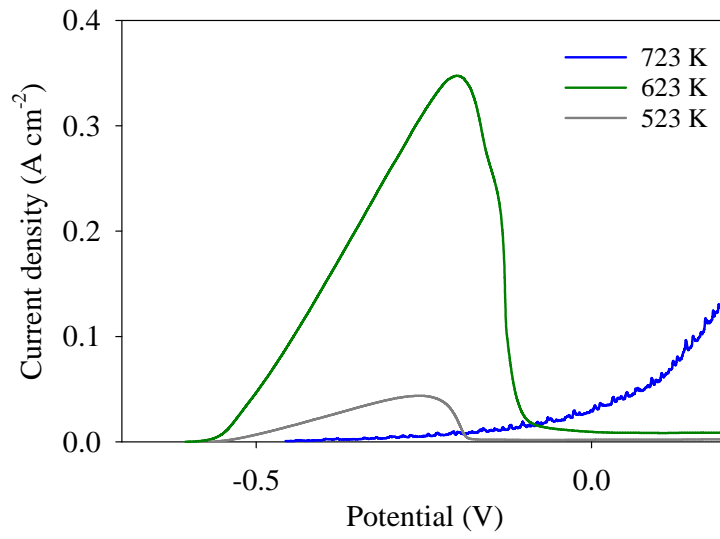


Fig.4 Anodic polarization curves of chromium

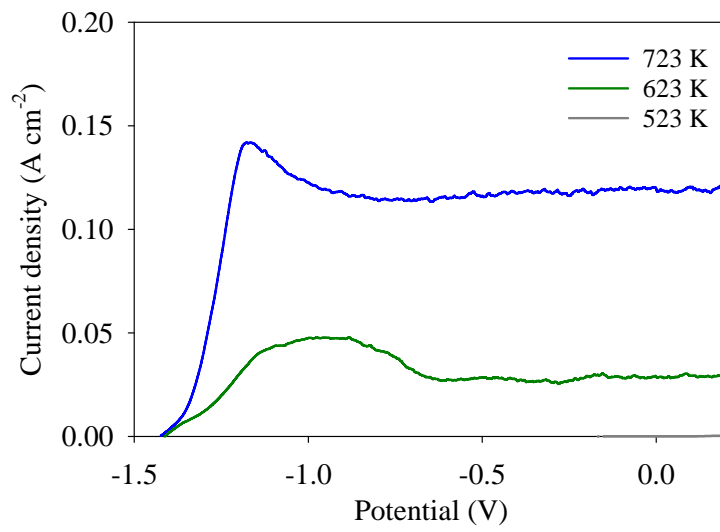


Fig.5 Anodic polarization curves of tantalum

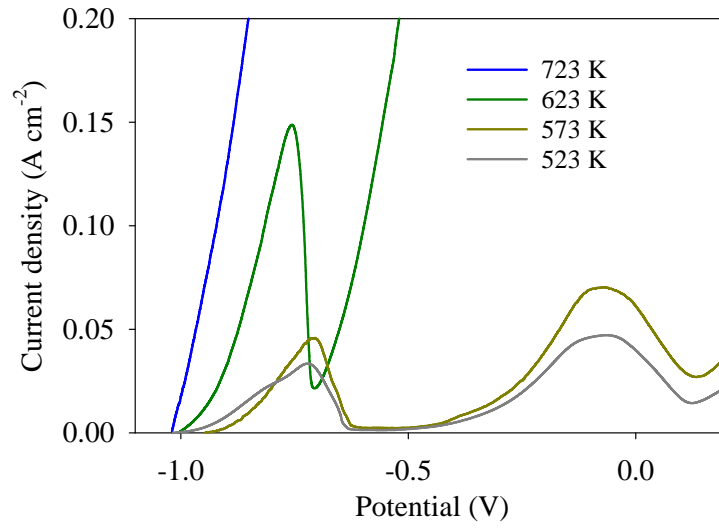


Fig.6 Anodic polarization curves of WC-Cos

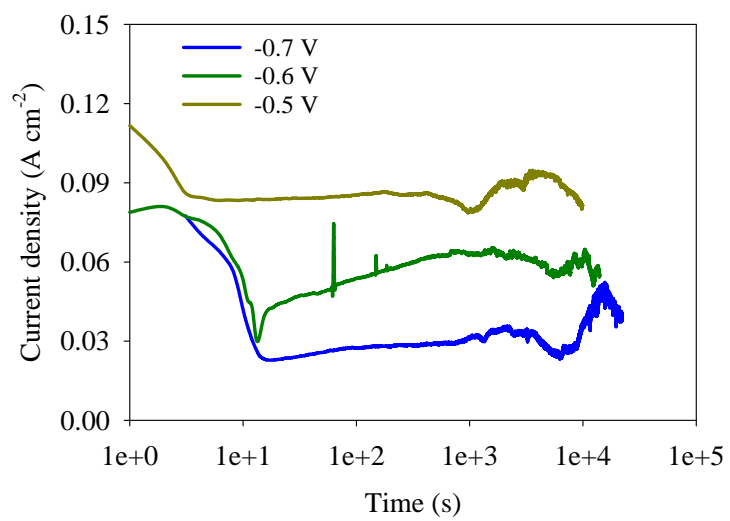


Fig.7 Current density behavior of potentiostatic electrolysis at -0.7 V, -0.6 V and -0.5 V

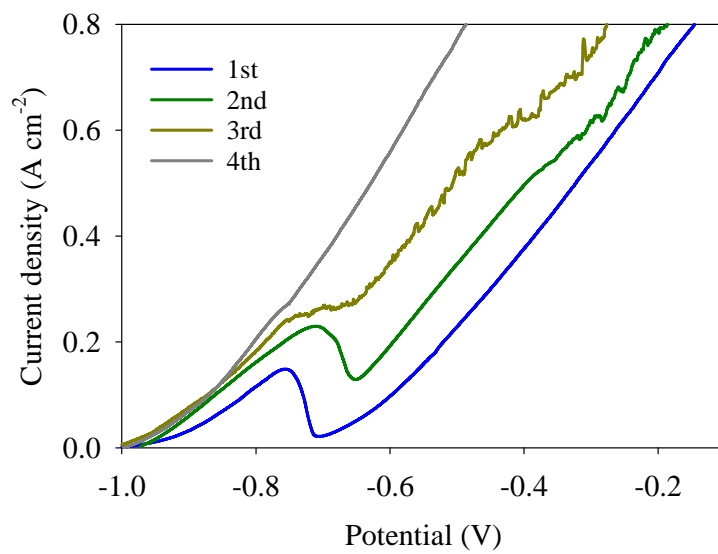


Fig.8 Influence of frequency for anodic polarization curve of WC-Co at 623 K

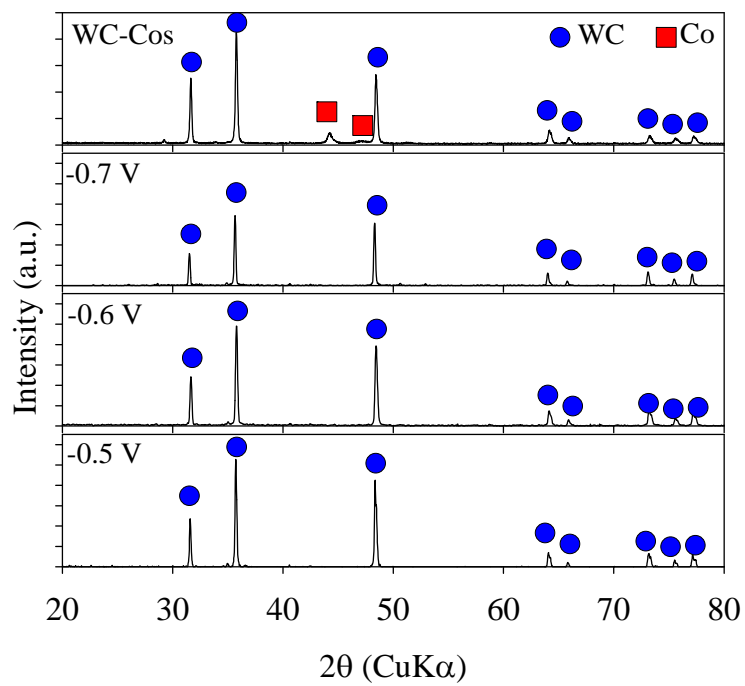


Fig.9 XRD pattern of electrode after electrolysis at -0.7 V, -0.6 V and -0.5 V

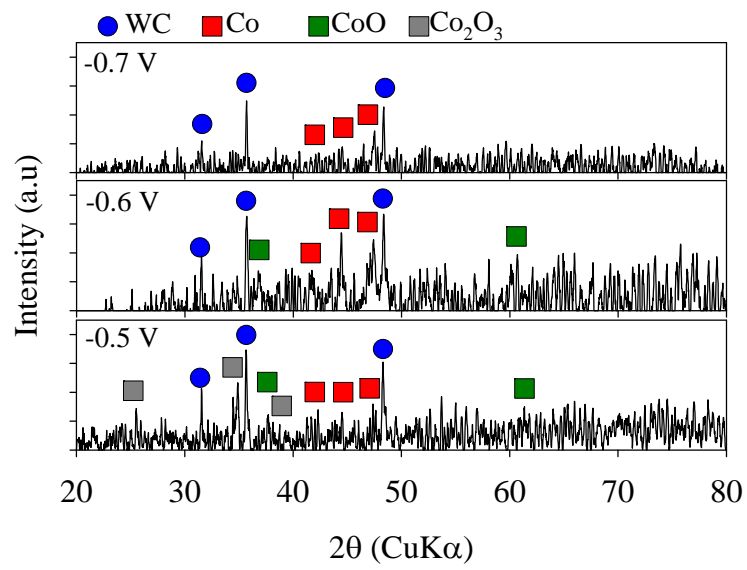


Fig.10 XRD pattern of sediment in molten salts after electrolysis at -0.7 V, -0.6 V and -0.5 V