

Anodic dissolution behaviour of tungsten carbide scraps in ammoniacal media

^aN. S. Randhawa, Prvan Kumar Katiyar^b, J. Hait^a, R. K. Jana^a, K. K. Singh^b and T. R. Mankhand^b

^aMetal Extraction & Forming Division, CSIR-NML, Jamshedpur-831007

^bDepartment of Metallurgical Engineering, IIT(BHU), Varanasi-221005

Abstract

In the present paper, potentiodynamic studies of WC scrap have been carried out as these studies give better idea about the anodic dissolution behaviour of the scrap material for their recycling to recover metal values. However, it has been seen that anodic passivation retards the dissolution of the scrap and adversely affects the recovery of metals. To minimise the passivity and to increase the anodic dissolution, some chemicals are often used as additives. Two different electrolytes namely hydrochloric acid and aqueous ammonia at varying concentrations had been employed for the above studies. The additives citric acid and oxalic acid were added to the acidic electrolyte whereas ammonium chloride, ammonium carbonate, ammonium sulphate were added in different concentration to the ammoniacal electrolyte. The studies revealed that 2% citric acid in 1N HCl was the optimum to achieve maximum anodic dissolution (current) of WC scrap. On the other hand, 2% NH₄Cl was found suitable to obtain maximum anodic dissolution (current) in the ammoniacal (1N) medium. The potentiodynamic studies were followed by the actual electrodisolution experiments in an electrolytic cell with the help of a rectifier. The W and Co were recovered as tungsten oxide and metallic chips, respectively.

Keywords: Cobalt; Electrodisolution; Potentiodynamic studies; Tungsten carbide scrap; Tungsten oxide;

1. Introduction

Cemented tungsten carbides (WC) are composite material produced by powder metallurgy method of liquid phase sintering. Cemented tungsten carbide is composed of hard tungsten carbide particles dispersed into a tough metallic matrix (Co). These materials find many applications for their combined high hardness and toughness [1]. Tungsten carbide materials are widely used in cutting tools, drilling tools, machining tools and wear resistant parts [2]. Scraps of WC tool bits and its components are used as secondary resource of W and Co.

When the tungsten carbide tools and components are scrapped, they are collected with a view to recovering the W and Co [3]. Statistics revealed that the recovered tungsten carbide comprises of about 20% to 30% of the total supply, lowering the raw material cost by about 15% to 50% [4]. A number of methods are used to process WC scrap. These processes involve either hydro or pyrometallurgical or a combination of them to recover the valuable metal (W, Co). Among the several methods available in literature for processing of WC tool bit scraps, electrochemical method has been emerged as an attractive method as it is a single step process consuming very low energy. Hydrochloric acid and ammoniacal solutions have been used as electrolytes for the effective dissolution of tungsten carbide scraps [5]. Scraps of tungsten carbide (WC) are electrolyzed to dissolve the material for recovery of the valuable metal (W, Co). However, it has been seen that anodic passivation retards the dissolution of the scrap and adversely affects the recovery of metals [6]. To reduce the passivity and to increase the anodic dissolution, some chemicals are often used as additives such as citric acid, ammonium chloride etc. The potentiodynamic studies may give better idea about the anodic dissolution behaviour of the scrap material and the role of additives during dissolution. Therefore, the aim of this work was to carry out the potentiodynamic studies for the selection of suitable electrolyte and additive for electrodisolution of WC scrap tool bit. Hydrochloric acid and ammonia solution at varying concentration are employed for this study. The additives citric acid and oxalic acid are added to the acidic electrolyte whereas ammonium chloride, ammonium carbonate and ammonium sulphate are added in different concentration to the ammonia electrolyte for achieving the maximum dissolution of WC scrap. Thereafter, some experiments on electrodisolution of WC tool bit scraps in ammoniacal medium were attempted using a rectifier.

2. Materials and methods

2.1 Materials

Tungsten carbide tool bit scraps sample used in potentiodynamic experiment was obtained from M/s Bharat Futuristic Pvt. Ltd., Bengaluru, India. The photograph of tungsten carbide scrap sample is shown in Fig.1 The composition of WC scrap is listed in Table 1. All the electrolyte solution (HCl, NH₃) was prepared from analytical grade chemicals reagent with deionized water. Additives used were also of analytical grade. These chemicals were supplied by Merck Specialities Private Limited (Mumbai).

Table 1: Chemical composition of tungsten carbide scraps material.

Element	Weight %, by mass
W	81.23
C	5.2
Co	10.15
Fe	0.98

Al	0.062
Ti	0.005
Mo	0.0007



Fig. 1: Cemented tungsten carbide scrap

2.2 Potentiodynamic experiments method

A three electrode cell setup consisting of a working electrode (WC scrap sample), saturated calomel electrode (SCE) as a reference electrode, and a counter electrode was used for the experiments. A platinum foil served as a counter electrode whose exposed surface was 1cm^2 . The sample was connected with the help of platinum wire for power supply. The sample was coated by the resin and exposed sample surface area was only 1cm^2 .

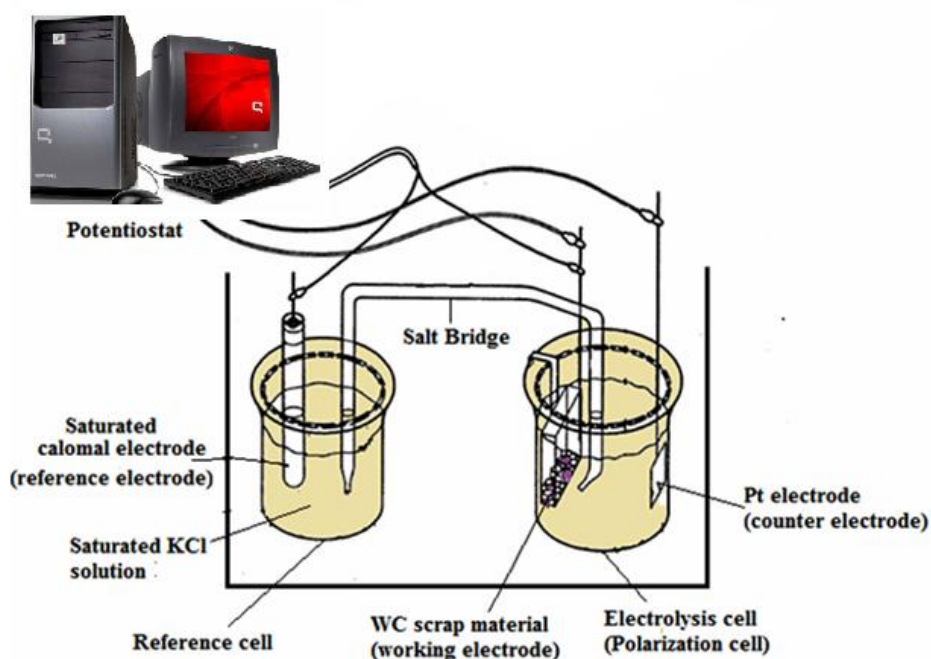


Fig. 2: Schematic diagram of cell set up for potentiodynamic studies.

The sample was ground and polished to remove the unwanted materials (Fig.1) and to produce a new surface with the help emery paper and rinsed with deionized water prior to

each experiment. Cell was made of (150 ml) glass beaker. An electrolyte solution (100 ml) was used to fill the cell for each potentiodynamic experiments. A reference electrode (SCE) was placed on other glass beaker (cell), which was filled with saturated KCl solution and both cell was connected by salt bridge. One end of the salt bridge was close to the working electrode. A schematic diagram of cell set up for potentiodynamic studies is shown in Fig.2. A Gamry EchemAnalyst Potentiostat was used for all the potentiodynamic measurements and the anodic dissolution behaviour was studied by potentiodynamic polarization curves. The scan rate was applied 5mV/s. All the potentiodynamic experiments were carried out at room temperature.

3. Results and discussion

3.1 Potentiodynamic studies in HCl medium

Initially, potentiodynamic studies were carried out in hydrochloric acid medium with and without additive. The polarization curve in HCl medium without any additive is shown in Fig. 3. It is evident from the anodic polarization curve that after reaching a current of 744.2 mA at 3.1 V, there is no further increase of the current value, which signified that no further anodic dissolution took place or in other words the sample was passivated.

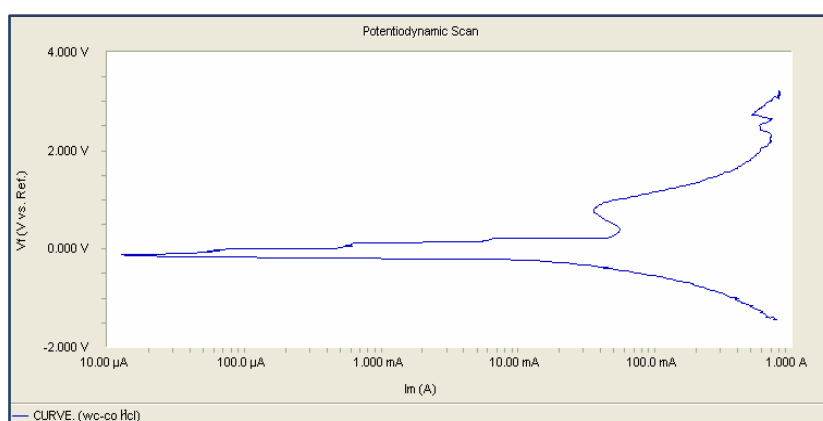


Fig. 3: Potentiodynamic curve obtained with 1N HCl without additive.

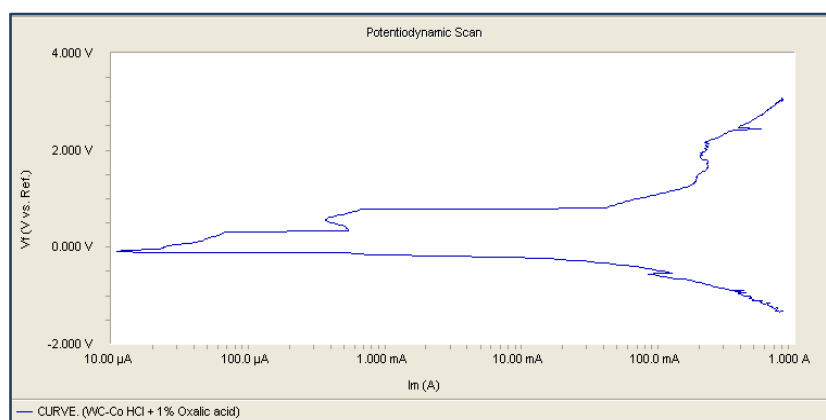


Fig. 4: Potentiodynamic curve for WC scrap in 1N HCl + 1% Oxalic acid.

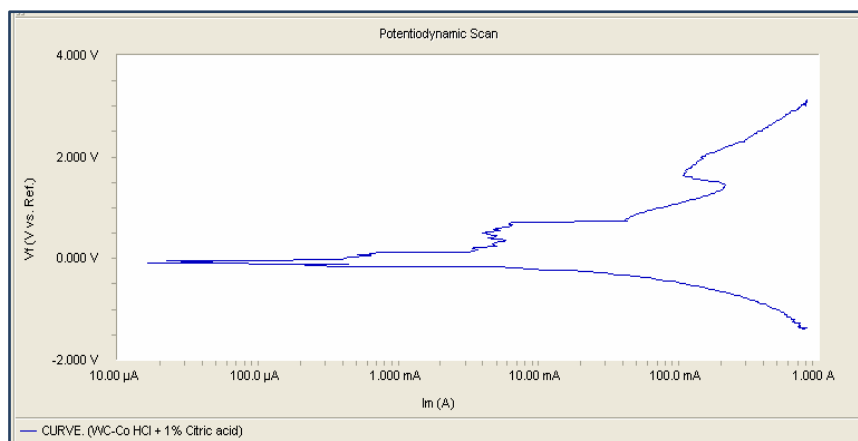


Fig. 5: Potentiodynamic curve for WC scrap in 1N HCl + 1% citric acid.

The anodic dissolution curve of the sample in HCl medium with additives such as citric acid and oxalic acid are shown in Fig. 4 and 5, respectively. It can be seen from Fig. 5 that with the addition of 1% citric acid in the electrolyte there was no significant change in maximum anodic current while in the case of 1% oxalic acid addition (Fig. 5), the maximum anodic current rather decreased (650 mA) somewhat. During the potentiodynamic studies, it was observed that lot of chlorine evolution took place at the anodic site and the connecting material to hold the sample was corroded. The same chlorine evolution and corrosion problem was observed during one actual experiment in an electrochemical cell with the help of a rectifier. Further only very small amount of cobalt was deposited at the cathode and some amount of disintegrated tool bit material was observed lying at the bottom of the electrolytic cell. The precipitated material at the bottom was perhaps undissolved WC loosened by the dissolution of cobalt metal from the cemented WC matrix.

3.2 Potentiodynamic studies in ammoniacal medium

Since the electrolytic dissolution of tool bit material in the hydrochloric acid medium created pollution and corrosion problem, it was decided to examine the dissolution behavior of the WC tool bit material in the ammoniacal medium with/without additive.

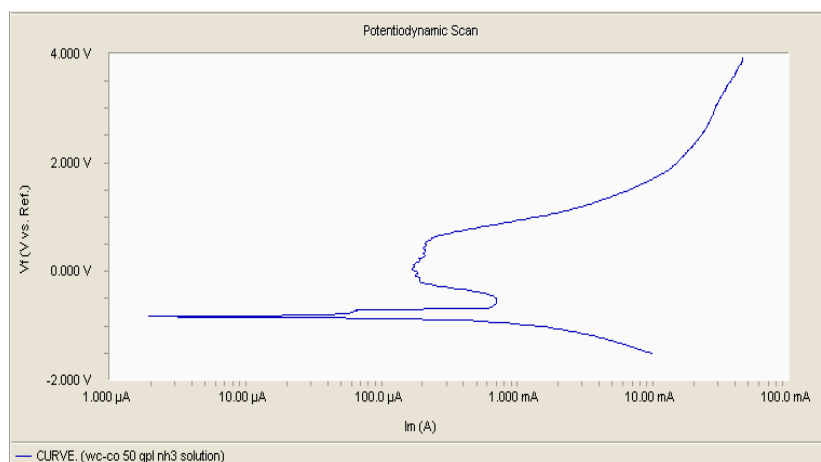


Fig. 6: Potentiodynamic curve for WC scrap in 50 g/L ammonia electrolyte.

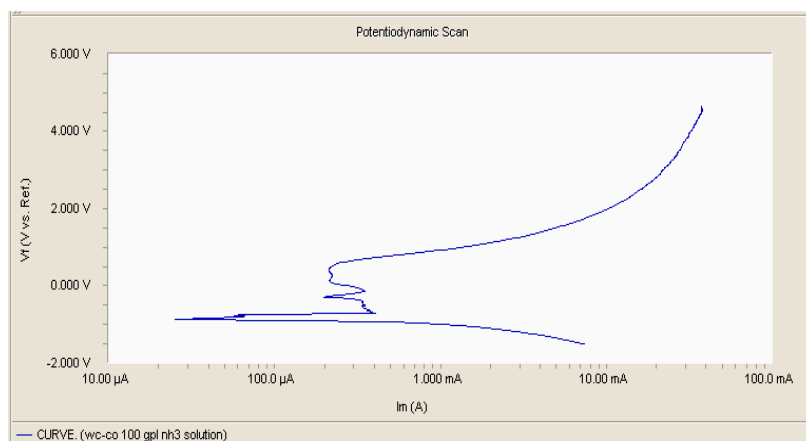


Fig. 7: Potentiodynamic curve for WC scrap in 100 g/L ammonia electrolyte.

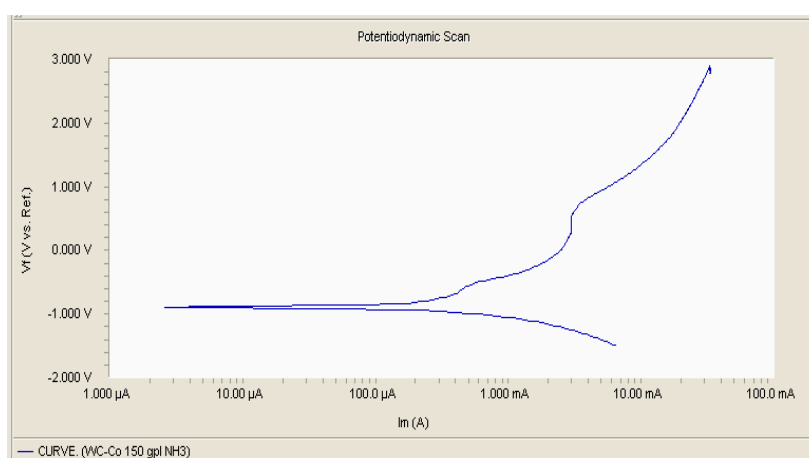


Fig. 8: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte.

Initially, potentiodynamic studies in ammoniacal medium was carried out at different concentration of ammoniacal solution. Figs. 6, 7 and 8 show the polarization behavior of tool bit material with 50, 100 and 150 g/L of ammonia, respectively. It can be seen from these figures that maximum anodic current before passivation were 42.28, 37.76 and 32.82 mA respectively at 3.9, 4.5 and 2.9 V, respectively. It can be seen that there was no significant changes in the maximum anodic current values. However, since 150 g/L ammoniacal solution required the lower voltage (2.9V) for reaching the maximum anodic current; further studies with addition of different additives such as ammonium chloride, ammonium sulphate and ammonium carbonate at this concentration of ammonia were carried out. The polarization curves with 1% ammonium chloride, 1% Ammonium sulphate and 1% ammonium carbonate as additive in 150 g/L ammoniacal solution are shown in Figs. 9, 10 and 11, respectively.

It can be seen that with the addition of ammonium chloride highest anodic current of 443.7 mA (Fig. 9) was achieved, whereas, with the ammonium sulphate and ammonium carbonate additions (Fig. 10 and Fig. 11), these values were 352.4 mA and 294.4 mA, respectively.

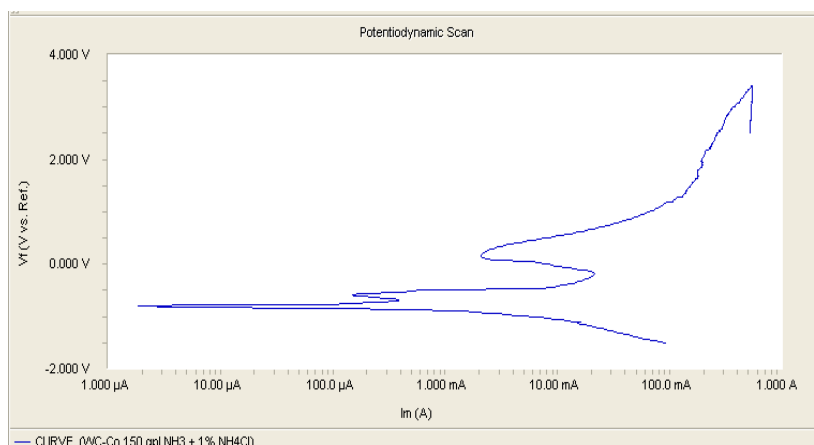


Fig. 9: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte containing 1% NH_4Cl .

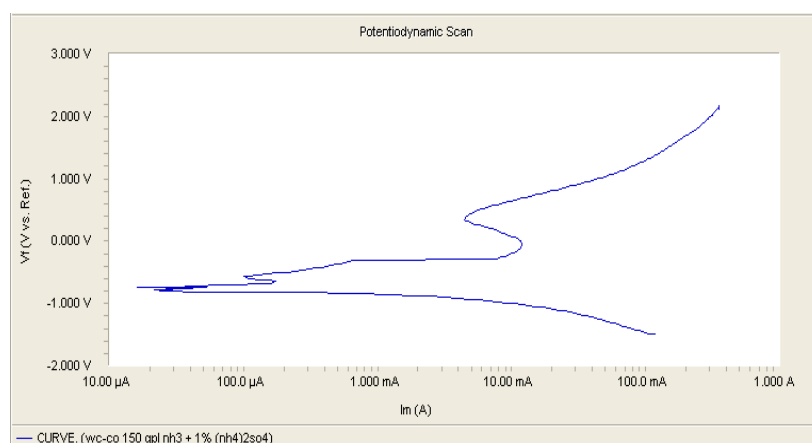


Fig. 10: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte containing 1% $(\text{NH}_4)_2\text{SO}_4$.

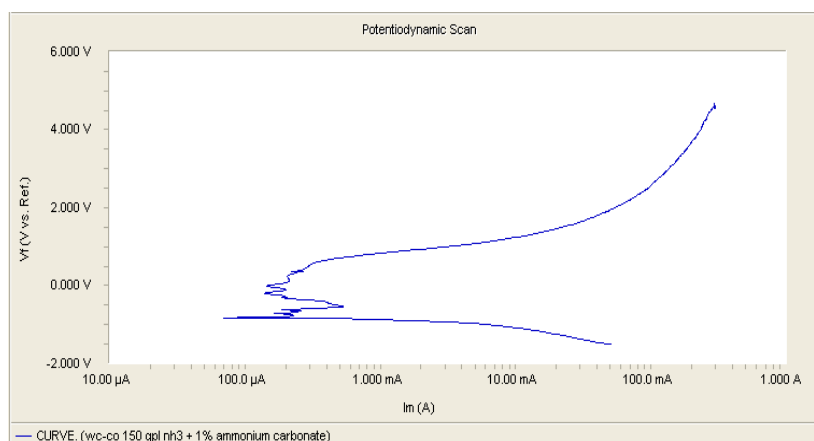


Fig. 11: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte containing 1% $(\text{NH}_4)_2\text{CO}_3$.

Further, it was noticed that open circuit potential (OCP) was found to be -795 mV with ammonium chloride addition compare to -779.1 mV and -719.2 mV in the case of ammonium sulphate and ammonium carbonate additions, respectively. This substantiates that

ammonium chloride addition is more effective for the anodic dissolution of the tool bit material. Two S-type portions were observed in the anodic polarization curve with ammonium chloride. This is perhaps due to dissolution followed by passivation of some elements one by one in the tool bit material. Since the standard dissolution potential of W (0.09 V) is lower than that of Co (0.28 V), W perhaps, dissolved first and then anode becomes passivated and on reaching the required higher potential value, the Co dissolution started. To determine the mechanism of tool bit material dissolution, the cyclic polarization studies of the sample was carried out in 150 g/L ammoniacal solution with 1% ammonium chloride addition. The results of which are shown in Fig. 12, it can be seen that between the forward and reverse polarization curves, two loops were formed. These loops probably indicate the pitting mechanism of anodic dissolution of tool bit material.

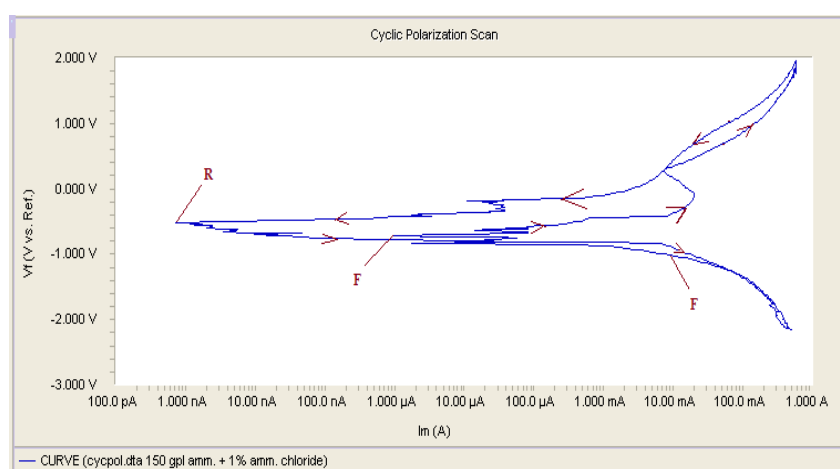


Fig. 12: Cyclic polarization scan for WC scrap in 150 g/L ammoniacal electrolyte containing 1% NH_4Cl ; the forward and reverse scan curve are indicated as 'F' and 'R', respectively.



Fig. 13: Microscopic image of pits formed in WC scrap after cyclic polarization scan in 150 g/L ammoniacal electrolyte containing 1% NH_4Cl .

A photograph of the reacted surface of tool bit material after polarization was taken with a metallurgical microscope. The same is shown in Fig. 13. It was seen that a number of pits were formed on the surface of the sample. It signified that dissolution of the anodic materials occurred from the unpassivated deep pit sites of the material. With the encouraging results of anodic polarization studies of tool bit material with the ammonium chloride additive, further studies on the anodic dissolution behavior of the material with higher amount of ammonium chloride addition in the ammoniacal solution were carried out. The polarization curves with 5% and 10% ammonium chloride additions are shown in Fig. 14 and Fig. 15, respectively.

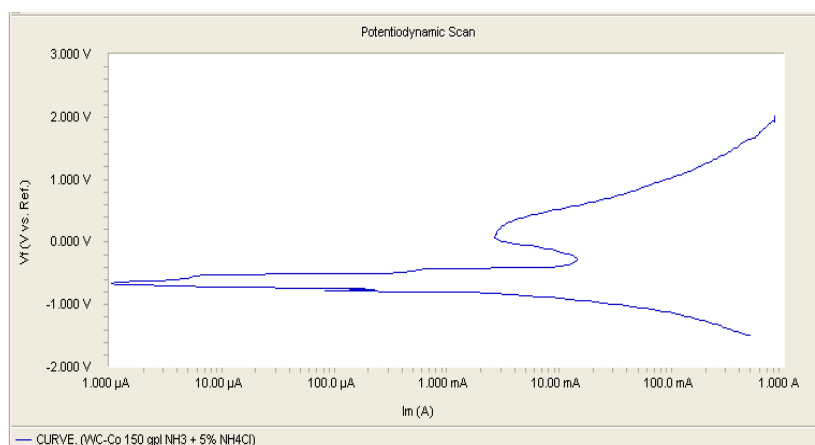


Fig. 14: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte containing 5% NH_4Cl .

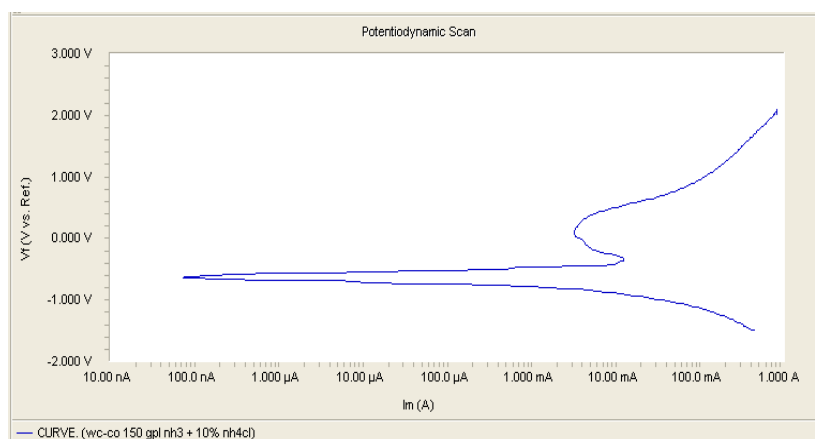


Fig. 15: Potentiodynamic curve for WC scrap in 150 g/L ammonia electrolyte containing 10% NH_4Cl .

It can be seen that maximum anodic current with 5% ammonium chloride addition was 819.1 mA at 1.97 V (Fig. 14) compared to 543.7 mA at 3.41 V (Fig. 15) with 1% ammonium chloride. This signifies that much higher anodic current was obtained with lower energy consumption (lower potential value) with increasing ammonium chloride addition from 1% to 5%. However, it was seen that further increase of ammonium chloride addition to 10% did not increase the maximum anodic current (Fig. 15). Therefore, for the pitting studies a cyclic

polarization study was carried out with the 5% ammonium chloride addition in 150 g/L ammonia solution, which is shown in Fig. 16. Here also two distinct loops between the forward and reverse polarization curves were observed signifying the pitting mechanism of anodic dissolution of the material.

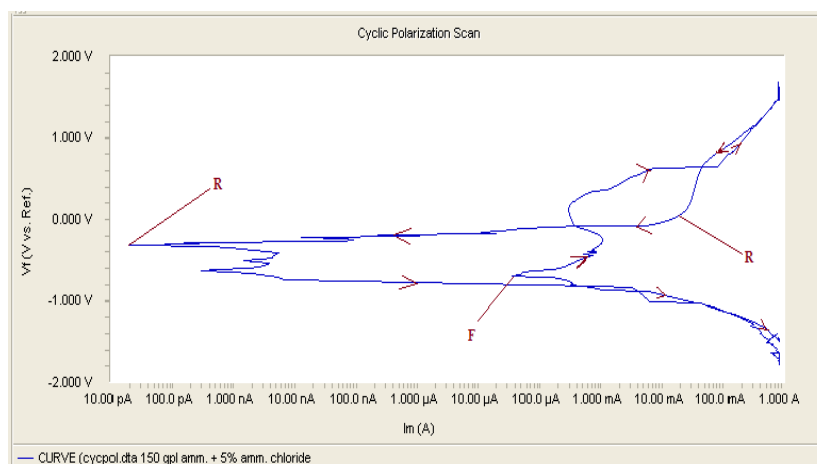


Fig. 16: Cyclic polarization scan for WC scrap in 150 g/L ammoniacal electrolyte containing 5% NH_4Cl ; the forward and reverse scan curve are indicated as 'F' and 'R', respectively.

3.3 Electrodisolution of WC scrap

Optimum conditions obtained from potentiodynamic studies were successfully applied for electrodisolution of WC scrap in water cooled electrolytic cell varying potential and time. The cobalt was recovered as metal deposited over cathode during the electrodisolution experiments whereas tungsten was recovered as tungsten oxide by calcination of tungstic acid produced by addition of HCl into the ammoniacal electrolyte after the electrodisolution experiments.

4. Conclusion

Potentiodynamic studies of WC scrap were carried out in HCl and ammoniacal electrolytes followed by electrodisolution of WC scrap in ammoniacal medium. Polarization studies in HCl electrolyte gave rise to maximum anodic current density (to signify the anodic dissolution reaction) of 744.2 mA/cm^2 at 3.1 V. On increasing the potential beyond 3.1 V the WC material passivated. The addition of additives like citric acid and oxalic acid in HCl did not increase the anodic current. Further, evolution of Cl_2 gas and corrosion of connecting material were observed during the polarization studies in HCl. During the polarization studies in ammoniacal electrolyte, anodic current density was not very high, which however, increased significantly with addition of ammonium chloride, ammonium sulphate or ammonium carbonate. Maximum anodic current density was obtained with 150 g/L ammonia and 5% ammonium chloride (819.1 mA/cm^2). These conditions were further applied for electrodisolution studies of WC scraps and cobalt was recovered as metal deposited over

cathode. The ammoniacal electrolyte was further treated with HCl to recover tungsten as tungsten oxide. Thus, electrodisolution studies of WC scrap with the help of potentiodynamic polarisation carried out in present work would be very helpful in the development of an alternative process for recycling of WC scrap to recover tungsten and cobalt metals.

5. Acknowledgements

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6. References

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