ELECTROCHEMICAL DISSOLUTION OF NICKEL FROM A SUPERALLOY SCRAP BY ALTERNATING CURRENT

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Earlier work has shown that Ni and Pt group metals can be conveniently dissolved in acids by A.C. elctrolysis. In the investigation, the electrochemical dissolution of Ni from a nickel base superalloy scrap by A.C has been reported. HCl was used as the electrolyte. The influen of current density, HCl concentration, frequency of A.C.and time of electrolysis on the efficiency of Ni dissolution was investigated. The current efficiency for Ni dissolution initially increased with current density and subsequently decreased. Higher acid concentration resulted in increased Ni dissolution. A decrease in the Ni dissolution efficiency occurred with increasing frequency of A.C. and progress of electrolysis.

Secondary metals have been referred as man-made mine of the future raw materials. The importance of recovering valuable metals from secondary sources and scrap need not be overemphasized. The superalloy scrap forms a rich source for the recovery of valuable matals like Ni, Co, Cr Mo etc because the quality standards are very stringent, the average life-span of parts made from superalloys is limited. Thus a lot of scrap is generated. The amount of scrap generated is increasing because of the increasing number of applications of superalloys.

The peculiarity of superalloy scrap is that unlike iron and steel scrap,it cannot be reused to make a new superalloy, as this process of reuse would tend to alter the properties of the superalloy. So there is an acute problem of disposal and reclaimation of superalloy scrap.

Both pyro and hydrometallurgical methods have been used for the treatment of superalloy scrap. Vacuum melting and modifications of the process have been done. The recovery of Cr from a superalloy scrap by selective oxidation - reduction technique has been attempted. By selective oxidation, Cr goes into a chromium rich slag while Ni and Co are retained in the metallic phase. After separation, the molten slag phase could be reduced by a variety of means.

Chemical recovery of superalloy scrap has been extensively studied by U.S.Bureau of Mines[2]. Superalloy in the form of turnings, borings and grindings were used. Massive alloys were not used for chemical recovery because dissolution will pose problems. The dissolution was carried out at 90-100°C using acidic chloride solutions. The dissolution increased with acidity of the solution. The metals contained in the leach liquor were separated by a series of operations involving carbon adsorption, solvent extraction and selective precipitation.

From a review of the literature, it is seen that electrochemical methods have not been applied in the recovery of valuable metals from superalloy scrap. However A.C. dissolution has been studied with some metals. Electrodissolution and corrosion of metals by A.C. has recently been reviewed[3].

The disssolution of Pt group metals [4] and Ni[5-7] which are normally difficult is made possible by A.C. electrolysis. The dissolution of Ni in HCl and H_2SO_4 has been reported earlier [5-7]. The dissolution of Ni has been found to be influenced by the concentration of acid, current density, frequency of A.C. and time of electrolysis. Since it has been found that Ni can be dissolved by A.C. electrolysis, in this investigation an attempt has been made to study the dissolution of Ni from a Ni base superalloy scrap by A.C. electrolysis.

EXPERIMENTAL

Superalloy turbine blades (Russian origin) were used in this study. An analysis of the sample by XRF revealed the following percentages of the various elements.

Ni-74.5,Cr-19.34,Co-0.67,P-0.005,C-0.075, S-0.0052, Si-0.42, Ti-2.58,Mn - 0.12, Al-1.3 and Fe- 1

Two pieces were cut from the blade and used as electrodes. The exposed area of each electrode was 3 cm x 3 cm. An inter electrode distance

of 3 cm was used. A 250 ml glass beaker served as the electrolytic cell, the volume of electrolyte used being 150 ml. A magnetic stirrer was used for agitation of the electrolyte.

An audio and ultrasonic frequency signal generator (Type 3-33, USSR make) with a frequency range of 20-20,000 Hz was used. The current was measured by a digital multimeter.

HCl was used as the electrolyte in all the experiments. Each experiment was carried out for 30 minutes. At the end of each experiment, the solution was analysed for nickel. All the experiments were carried out at room temperature (30° C). The influence of (i) Conc. of HCl (ii) Current density (iii) frequency of A.C. (iv) time of electrolysis was studied on the current efficiency of Ni dissolution.

Apart from these experiments on A.C. dissolution, one experiment was also carried out to study whether there is any chemical dissolution without the passage of a current and also with direct current for electrolysis.

The current efficiency under A.C. conditions is calculated as follows: The part of the alternating current which is actually utilized in the electrolysis is the average value or d.c. equivalent, denoted as I_{avg}. This can be calculated from the relation

$$I_{avg} = 2\sqrt{2}/\pi \; I_{rms}$$

Where I_{rms} is the current indicated by the A.C. ammeter. If Q is the quantity of electricity (where $Q = I_{avg} \times t$ and t is the time of electrolysis) used for the electrolysis, then the weight of the metal that would dissolve theoretically at 100% efficiency is

$$m' = Q/F \cdot Aw/n$$

Where F = Faraday

Aw = Atomic wt. of metal

n = number of electrons involved in the dissolution reaction.

Hence
$$m' = \frac{2\sqrt{2}\; I_{rms}\; t.\; Aw}{\pi\, nF}$$

If m is the actual weight of the metal dissolved during electrolysis, the current efficiency is calculated as:

Current efficiency, % = $m/m' \times 100$

RESULTS

Influence of HCl Concentration

To study the effect of acid concentration, 0.5 -2.0 N HCl solutions were used. The experiments were performed at various frequencies and current densities. The results are presented in Fig. 1. It may be seen that, in general the effficiency for Ni dissolution increases with HCl concentration, in the range studied.

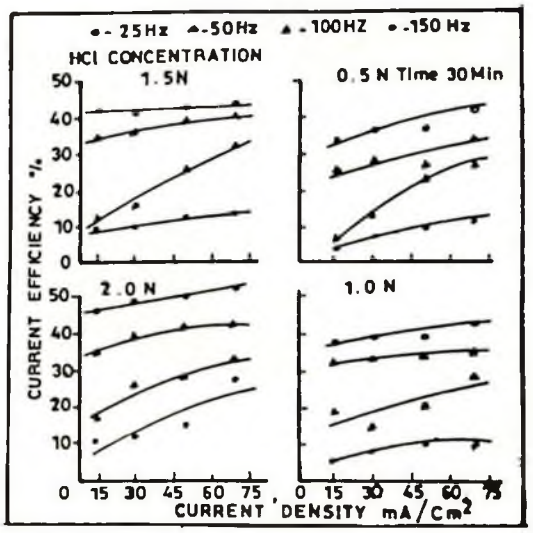


Fig. 1 Influence of current density on Ni dissolution

Influence of Current Density

The influence of current density on Ni dissolution is given in Fig.2. In the range studied (15-70 ma/ cm^2), the dissolution of Ni increases with current density slightly.

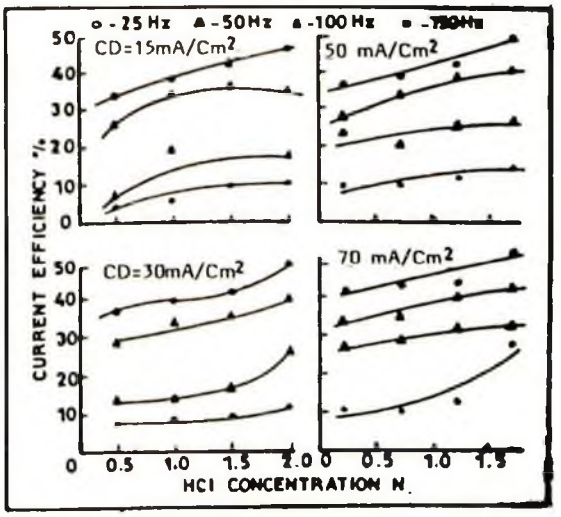


Fig. 2 Influence of HCl concentration on Ni dissolution

One experiment was also carried out to study the influence of much higher current densities. Fig. 3 Shows that upto 200 ma/cm^2 , the dissolution efficiency increase, but beyond that it drops drastically.

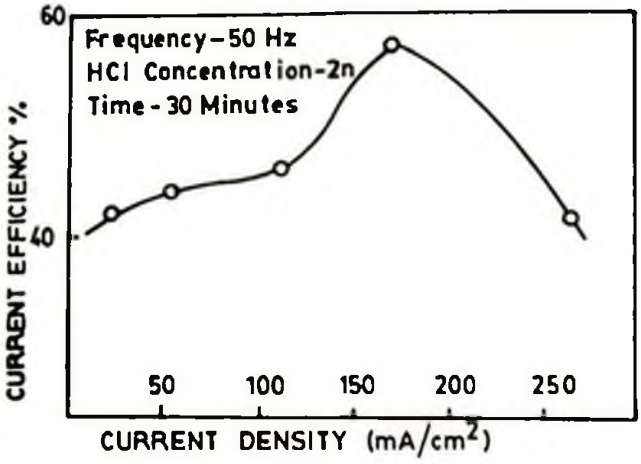


Fig. 3 Influence of current density on nickel dissolution

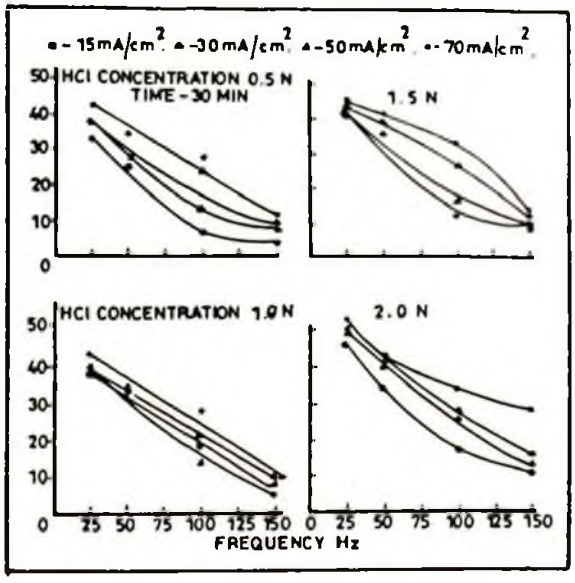


Fig. 4 Influence of frequency on Ni dissolution

Of all the parameters studied, it can be said that frequency has the most significant effect on Ni dissolution. Fig. 4 Shows that as the frequency increases from 25 Hz to 150 Hz, the dissolution drastically drops.

Influence of Time

To study the influence of time of electrolysis, one experiment was carried out for 3 hours. Fig. 5 Shows that the dissolution decreases with the progress of electrolysis.

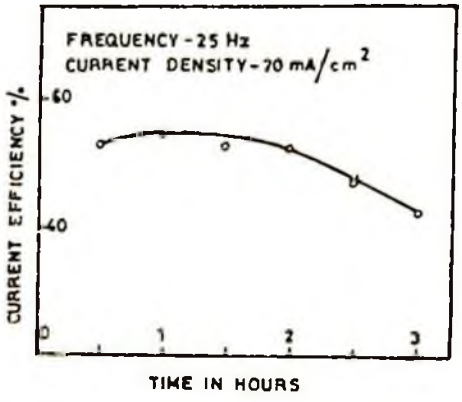


Fig. 5 Time dependence of nickel dissolution

DISCUSSION

When A.C is passed through a cell containing the superalloy electrodes, in HCl, the following reactions can occur at the electrode 1 in the positive half cycle.

$$M \longrightarrow M^{2+} + 2e \quad .. (1)$$

$$2OH^- \longrightarrow H_2O + 1/2\ O_2 + 2e \quad .. (2)$$

$$2Cl^- \longrightarrow Cl_2 + 2e \quad .. (3)$$

During this inverval, the other electrode acts as a cathode and the following reactions can occur at that electrode.

$$M^{2+} + 2e \longrightarrow M \quad .. (4)$$

$$H^+ + e \longrightarrow 1/2\ H_2 \quad .. (5)$$

In the next half cycle, the situation at the electrodes will be exactly the reverse, electrode 1 now acting as the cathode and electrode 2 as the anode.

For ideal metal dissolution only reaction 1 should occur in the positive half cycle and only reaction 5 in the cathodic half cycle.

The rates of these electrode reactions may be expressed, in general, in terms of current density, i, by the use of the Tafel relationship as follows:

$$i^M = i_o^M \exp.(-\alpha^M \eta^M .F/RT) \quad ..(6)$$

$$I^G = i_o^G \exp.(-\alpha^G \eta^G .F/RT) \quad ..(7)$$

Where M is the metal and G is the gas, i is the actual current density, i_o is the exchange current density determined by the composition of the electrolyte, α is the transfer coefficient, T is the temperature, F and R are the usual constants and

η is the overvoltage required for anodic or cathodic reaction. The total current density.

$$I_{avg} = i^M + i^G$$

In an anodic cycle, i^M is the current utilized for metal dissolution. In the present investigation, an alloy electrode has been used and hence i^M should represent the current utilized for the dissolution of all the metals. However, the experimental results indicate that only Ni dissolves. i^G represents the current for gas evolution.

Similarly, in the cathodic cycle, i^M is the current for metal deposition and i^G for H evolution.

It has been found that with dilute acid, the dissolution is not much and it increases with the concentration of acid. The lower dissolution of Ni in dilute acids is apparently the consequence of the formation of insoluble oxide films on the electrode surface during the anodic half cycle. With increase in the acid concentration, the passivating effect of such films decreases owing to the ability of more concentrated acid to dissolve the oxide film. In an earlier work, it has been shown that HCl is more effective than H_2SO_4 with respect to Ni dissolution. Hence in this study only HCl was used as the electrolyte. The corrosive nature of chloride ions and its ability to break up the passive film and expose fresh metal surface is considered the reason for the better performance of HCl compared to $H_2\ SO_4$.

With regard to the influence of current density, it has been shown that initially there is an increase and then a decrease in efficiency. The initial increase may be due to the fact that higher oxides of Ni may be reduced to the lower oxides which will dissolve in the acid. It is also possible that the following reaction contributes to the increase in Ni dissolution.

$$NiO_2\ 2H_2\ O + 4H^+ + 2e \longrightarrow Ni^{2+} + 4H_2O$$

At much higher current densities, more gas evolution takes place during the anodic half cycle rather than the dissolution of the metal. This contributes to the lower dissolution rate at very high current densities.

With increasing A.C frequency, the interval between successive anodic and cathodic half cycles becomes progressively shorter. Hence in each half cycle less metal will dissolve comparatively. Also, as the time interval is short, the metal ions formed at the electrode in the anodic half cycles would be available for immediate redeposition in the cathodic half cycles. In addition to this, at higher frequencies the H atoms formed in the cathodic half cycle do not have the time to form H_2 molecules. Thus, for the next anodic cycle, there exists a layer of H atoms on the electrode surface, which prevents the metal dissolution reaction to some extent and H ionization takes place instead. With increasing frequency, this effect intensifies and hence the current efficiency for Ni dissolution falls. At very high frequencies, no effects of A.C would be observed, since all current would pass via the double layer.

With the progress of electrolysis it has been found that the metal dissolution is decreased. This is due to the passivity of the electrodes which increases with the time of electrolysis. Also, the possibility of redeposition is high as more metal ions are available. It should also be noted that as the metal ion concentration in the bath increases, there is less tendency for the metal to dissolve during the anodic half cycles.

From the foregoing discussion, it is clear that A.C causes the dissolution of Ni from the superalloy. It would be of interest to study the influence of D.C on the Ni dissolution. Under similar conditions, it was found that the current efficiency was only 45% with D.C., whereas it was 60% with A.C. This can be explained by the fact that using A.C prevents the passivation while D.C cannot do so. An experiment to study whether any chemical dissolution occurs, showed that there is no chemical dissolution without the passage of a current. This is to be expected because of the highly corrosion resistant nature of the superalloys.

Lastly we may make a comparison between the efficiencies obtained for a sample of pure Ni and that of the Ni base superalloy. The current efficiencies were greater for the pure Ni sample than that for the superalloy under all conditions. This is due to the fact that Ni was present in the superalloy to the extent of only 75% and the additional corrosion resistance is due to the presence of other alloying elements.

CONCLUSIONS

Based on the results of this investigation, this following conclusions can be drawn:

1. Increasing HCl concentration upto 2N increase dissolution efficiency.
2. Ni dissolution increases initially with current density but subsequently falls.
3. Increasing the frequency of A.C decreases the dissolution of Ni.

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