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Double Step Chronocoulometric Studies on Industrial Copper Alloy in Acidic Copper Sulfate Electrolytic solutions - Part II

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Double potential step chronocoulometic studies on industrial copper anodes are carried out in various acidic copper sulphate electrolytic solutions (60, 100 and 180 gl^{-1}copper sulphate). The aim of this investigation is to understand and decide the optimum conditions to recover pure copper from copper alloy scrap by electrolytic refining. The copper electrode is actually made from the industrial scrap. The composition of the industrial copper anode is: Cu, 96.66 wt. %, Ag, 2.54 wt. % and Zr, 0.8wt. %. Parameters like internal resistance, net coulometric charge and surface excess are determined using this technique. From the surface excess values, 100 gl^{-1} copper sulphate concentration in the electrolyte is decided to be the optimum for the copper recovery process.

Keywords: Double step chronocoulometry; Industrial copper electrode; Surface excess; Copper recovery; Acidic copper sulphate electrolytes

1. INTRODUCTION

Chronocoulometry is a controlled potential technique, where the electrochemical response is to integrate the current, so that the charge passed as a function of time Q(t) is obtained. In double potential step chronocoulometry, the potential is shifted from an initial potential E_1 where no redox reaction occurs to a final potential E_2 where the reaction of interest occurs. Chronocoulometry is well suited for studies of electroactive substances adsorbed on electrode surfaces [1-3]. The charge resulting from a potentiostatic perturbation is related to the amount of material adsorbed on the electrode surface, the flux of reactant at the surface, and to the charging of the electrode/electrolyte interface. Chronocoulometry has been used for kinetic studies [4], for rapid capacitance measurements at solid electrodes [5l, and for determination of surface excesses of adsorbed materials [6]. Double potential step chronocoulometry also allows the determination of adsorbates through an in-situ estimate of the double layer charge from the reverse pulse response in cases where the electrode process is irreversible and the product of reduction adsorbs [7]. It has been shown that this analytical technique can be successfully used to determine electrochemical capacitances of materials like nano SnS and complexes like Prussian blue/crown ether as well to prove their ideally polarizable nature that exhibits no self-discharge or current leakage so that they remain charged indefinitely [8, 9].

In our lab, refining of copper alloy anodes is done with two aims in mind: (1) to recover copper in pure form so that it can be reused amicably; (2) to recover silver that was present in about 2-3% by weight in the copper alloy. In our trail experiments with copper alloy anodes and pure copper cathodes, we noticed that after an electrolysis period of 24 h, the cell voltage increased and did so in increments until the anode dissolved completely. To understand and solve these problems in copper refining electrolysis, we planned some basic experiments to study the dissolution of the copper anode in acidic copper sulfate solutions. To our knowledge, research papers pertaining to this subject is very limited and most of the published papers deal with the nature of additives to be added to reduce the passivation of anode. In our earlier work, we reported the chronopotentiometric behavior of copper alloy in various electrolytes and current densities and concluded that 100/140 gl^{-1} copper sulfate in the electrolyte would be ideal for electrolysis [10]. As part II of this research work, herein we report the chronocoulometric responses of copper alloy (CA) in electrolyte solutions with varying copper sulfate concentrations.

The present work focuses on the double potential step chronocoulogramic (DPCC) measurements of copper alloy (CA) in acidic electrolyte solutions with varying copper sulfate concentrations. These measurements allow to determine the surface excess of cupric ions, resistance at the double layer and cumulative charges due to the redox species which throw light on the processes occurring at the metal/solution interface during the electrolysis.

2. EXPERIMENTAL PART

All electrochemical experiments were conducted with a PGSTAT 302 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES software. GPES software was used for all electrochemical data analysis. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a pure copper sheet. The working electrode was the copper electrode used as anode (CA) in the electrolysis. A three electrode cell assembly was used. 1 cm^2 area of the working electrode was exposed to the electrolyte solutions. For this purpose, the cell usually employed for corrosion testing measurements was used. The cell design(Flat cell: Wear and Friction Tech, Chennai, India) is such that only 1 sq. cm of the working specimen will be exposed to the solution irrespective of the dimension of the electrode.

Double potential step chronocoulometric (DPCC) measurements were carried out in two ways; firstly, by steeping the potential from 1.0 to 0.0 V in the forward step and 0.0 to 1.0 V in the reverse step. In this set of experiments (say A), the potential step in the forward direction involves reduction process and the reverse step that of oxidation process. Secondly, the potential was stepped from 0.0 to 1.0 V in the forward step and from 1.0 to 0.0 V in the reverse step. In this set of experiments (say, B) the potential step in the forward direction involves oxidation process and the reverse step that of reduction process. Overlapping both the curves gives an idea about the redox processes that occur on the CA surface. A plot of Q vs. $t^{1/2}$ (called Anson plot) was also employed to calculate the surface concentrations of reactive species (surface excess in mol/cm^2).

The following three electrolyte solutions were used for DPCC measurements: (1) $CuSO_4$ $5H_2O$, 180 gl^{-1} ; Conc. H_2SO_4, 100 mll^{-1}; (2) $CuSO_4$ $5H_2O$, 100 gl^{-1} ; Conc. H_2SO_4, 100 mll^{-1}; (3) $CuSO_4$ $5H_2O$, 60 gl^{-1} ; Conc. H_2SO_4, 100 mll^{-1}. Acid concentration of the electrolyte was kept constant in all the electrolyte solutions.

3. RESULTS AND DISCUSSION

3.1. Internal resistance

A typical double potential step chronocoulogram (DPCC) for the 5 consequent steps recorded for CA in solution 1 is shown in Fig. 1. One could see in the time window of 50 seconds, the forward curve reached a plateau proving that sufficient time was given for the reaction of interest to occur. In this case, the forward step (initial 50 seconds) involves the reduction of cupric ions to copper as the potential is stepped from 1.0 to 0.0 V. As the initial points in the chronocoulogram, those before the plateaus are reached are influenced by the rate of double layer charging and reaction of adsorbates, sufficient time should be provided for the system so that errors in the calculation of intercepts do not occur [7]. However, the DPCC curve in step 1 did not reach zero as in the starting point but keep on rising with subsequent cycling. Measuring the height from zero line (a line parallel to X-axis) to the

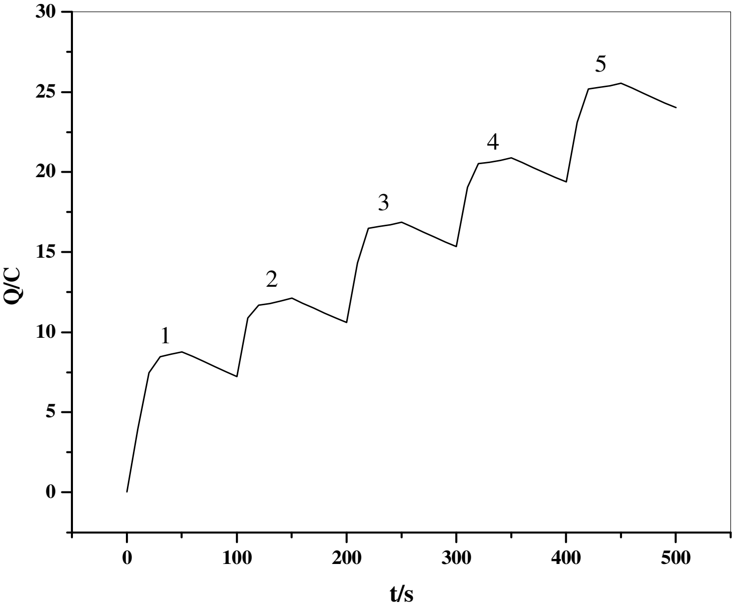

Figure 1. Double step chronocoulograms for copper alloy in solution 1 (180 gl^{-1}) copper sulfate concentration; five successive steps recorded (each step = 100 s).

starting point of each DPCC curve will give the incremental increase in Q from the Y-axis. Dividing Q with t (in seconds) gives the ‘i’ value in amperes. From Ohm’s law (E = IR), resistance at the double layer at each step can be calculated considering the E value to be 1.0 V. Table 1 presents the resistance values determined using this exercise. This resistance values were due to the resistance offered to the movement of copper species at the double layer but not in the bulk solution. DPCC technique is highly commendable for this particular application. In the higher $CuSO_4$ concentration (solution 1), the resistance was less in the beginning of the potential step but increased with increase in subsequent steps/time. With decrease in $CuSO_4$ concentration (solution 2), the resistance values started at a higher value in the beginning of the potential step but increased with time as in the previous case but the incremental increase in resistance decreased. In both solutions, increase in resistance with time indicates a restriction to the free movement of copper species at the double layer, which would make the system’s voltage to shift to a higher side to the smooth continuous workability of the electrolysis. In the third case where the solution is more dilute in terms of $CuSO_4$ concentration, the resistance decreases with time, suggesting this concentration of $CuSO_4$ in the electrolyte solution is favorable for electrolysis. The plausible reason for the decrease in resistance could be the proportionate increase in acidic concentration as against the copper ion concentration in the electrolyte, as the concentration of acid was kept constant for all the electrolytes.

Table 1. Internal resistance values of copper alloy determined from DPCC experiments (set A) for the successive five steps; step duration = 500 s (cf. Fig. 1)

Steps	Time in seconds	Internal resistance (in ohms)		
		Solution 1 ($180\ gl^{-1}$)	Solution 2 ($100\ gl^{-1}$)	Solution 3 ($60\ gl^{-1}$)
1	100	13.3	20.0	20.0
2	200	18.2	20.6	20.0
3	300	19.2	20.8	18.7
4	400	20.0	21.3	18.7
5	500	21.3	21.3	18.5

The diffusion of copper plays a critical role in the transfer of ions from the anode to the cathode during copper electrorefining, copper plating and copper foil manufacturing. Understanding these fundamental measurements helps to delineate the problems faced during these industrial processes. The rate at which copper can transfer across the Nernst boundary layer influences anode dissolution and cathode deposition characteristics. The three main transport processes that occur during electrorefining are diffusion, convection, and ion migration. While natural convection plays a very important role within the bulk of the electrolyte, hydrodynamics predicts a stagnant layer at the electrode surface. This double layer is usually called as Nernst boundary layer. Transport across the boundary layer typically occurs by diffusion or migration. Cupric ions have a small transport number i.e 0.02 only [11, 12]. Hence the migration of cupric ions during the electrorefining process is rather limited. Henceforth, diffusion of these ions across the double layer decides the success of the processes. In this context, the data in Table 1 helps to understand the effect of cupric ion concentration on the diffusion as reflected by the resistance values determined from the DPCC measurements.

3.2. Coulometric charge

Table 2 presents the total charge under each DPCC curve integrated between the assorted time windows. For example, the Q values presented against the time window of 100 seconds is determined by integrating the curve between 0 and 100 s time scale assigned for the first step of DPCC curve. The net Q values are calculated for the two set of DPCC measurements (cf. Figs. 2-4); in set A, the stepping potential starts at 1.0 V and ends at 0.0 V vs. Ag/AgCl. This means that reduction of Cu^{2+} ions to copper occurs in the forward step and oxidation of copper to cupric ions occurs in the reverse step. Assuming the contribution from other side reactions is negligible, the Q value reflects the efficiency with which this process occurs. In the second set of experiments, say B the stepping potential starts at 0.0 V and ends at 1.0 V. In this case, oxidation of copper to cupric ions occurs in the forward step the reverse reaction in the backward step. In copper electrorefining, we apply a reverse current to the anode for a time span to get a uniform and non-dendritic deposit on the cathode. To understand the electrochemical changes that occur during the current reversal, this exercise is carried out.

Table 2. Coulometric charges of copper alloy determined from the DPCC curves for set A (forward reduction step) and set B (forward oxidation step) experiments for the three electrolytic solutions

Time in seconds	Q (in C x 10^2) for DPCC- A set of experiments			Q (in C x 10^2) for DPCC- B set of experiments		
	Solution 1	Solution 2	Solution 3	Solution 1	Solution 2	Solution 3
100	7.3	5.4	5.2	2.2	2.1	2.8
200	11.2	10.2	10.6	8.3	7.2	9.7
300	15.8	14.8	16.1	12.6	11.6	15.3
400	19.9	19.4	21.6	17.3	16.1	20.8
500	24.5	23.9	26.9	21.8	20.7	26.3

In all the measurements, a uniform observation is that Q increased in all the three solutions in both set of experiments on increasing the time scale from 100 to 500 seconds; this means, irrespective of the initial mode of polarization, the charge accumulation at the double layer would happen at prolonged times. At shorter times, however there is a difference. For instance at 100 s, the Q values are higher for DPPC-A than for DPPC-B set of experiments. This indicates that the rate of reduction of cupric ions (from solution) to form copper is lower than the rate of oxidation of CA to produce cupric ions. Excess cupric ions contribute to the charge accumulation at the double layer. Both the processes approach an equilibrium at prolonged times. This implies that the shorter time span we provide for the current reversal during anodic dissolution of CA is not sufficient to prevent the passivation originated from the $CuSO_4$ formed from the cupric ions. In our experiments, we observed dendritic growth on cathodic copper when the electrolyte was not stirred. At longer times, the concentration of copper sulphate in the electrolyte do not make any noticeable change in the net charge at the double layer, suggesting that the resistance originated from the passivation of CA surface by non-conductive $CuSO_4$ layer.

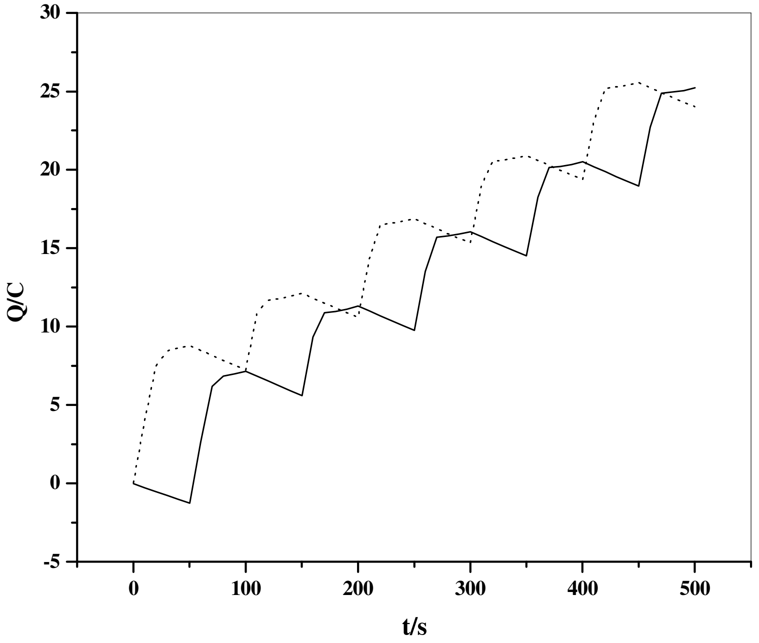

Figure 2. Double step chronocoulograms for copper alloy in solution 1 (180 gl^{-1}) copper sulfate concentration; - - - set A (forward reduction step), —— set B (forward oxidation step).

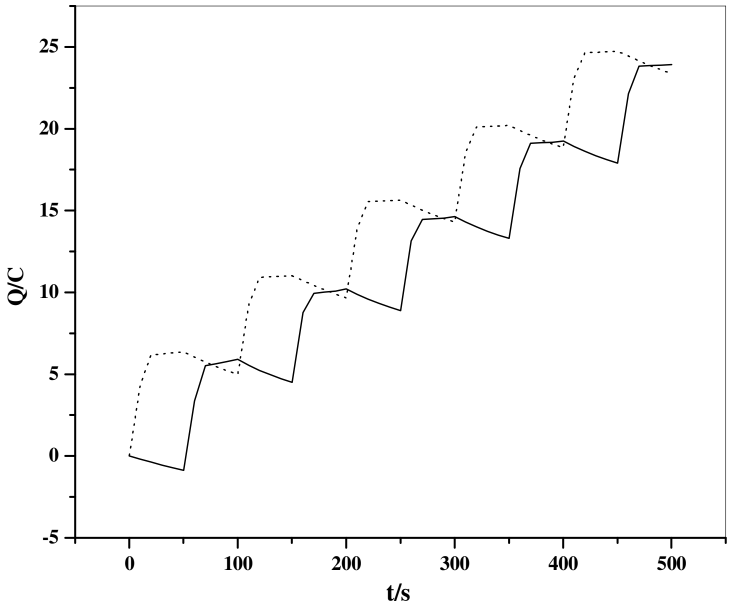

Figure 3. Double step chronocoulograms for copper alloy in solution 2 (100 gl^{-1}) copper sulfate concentration; - - - set A (forward reduction step), —— set B (forward oxidation step).

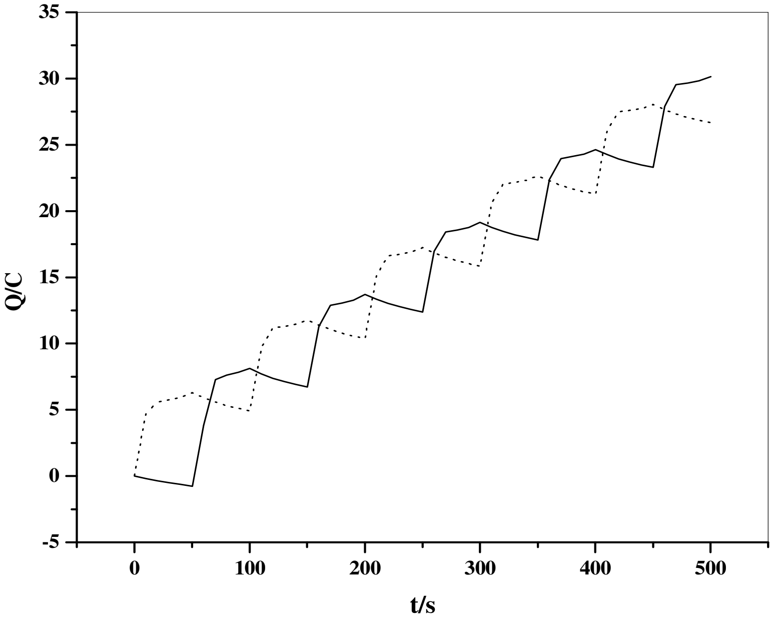

Figure 4. Double step chronocoulograms for copper alloy in solution 3 (60 gl^{-1}) copper sulfate concentration; - - - set A (forward reduction step), —— set B (forward oxidation step).

3.3. Surface excess

Another parameter that helps to decide the surface concentration of reacting species in the double layer is the surface excess in mol cm^{-2}. At times greater than 10 s, natural convection tends to make δ (diffusion layer thickness) a constant, i.e independent of time. For a simple redox reaction where the intermediate radicals are not formed, longer time scales allow diffusion-free surface concentration changes when a large potential step is applied. Anode dissolution of copper and deposition of cupric ion on the cathode do not involve any intermediate radicals and DPCC can be safely employed to calculate the surface excess of copper species at the double layer. The forward chronocoulometric response of diffusing reactants is described by the integrated Cottrell equation [6].

$$Q_d = 2nFACD^{1/2}t^{1/2}/\pi^{1/2}$$

where

n = equivalents $mole^{-1}$
F = Faraday constant, Coulomb $equivalent^{-1}$
A = area of the electrode, cm^2
D = diffusion co-efficient, $cm^2\, sec^{-1}$
C = bulk concentration, mol cm^{-3}
t = time, seconds

A plot of total charge Q vs. $t^{1/2}$ generally does not pass through the origin because of additional components arising from double layer charging and from the electroreduction of any molecule that might be adsorbed at E_1. These components are not time dependent and the total forward chronocoulometric response can be described by,

$$Q_d = 2nFACD^{1/2}t^{1/2}/\pi^{1/2} + Q_{dl} + nFA\Gamma_O$$

where

Q_{dl} = capacitative charge, C
Γ = surface excess of reactant, mol cm^{-2}

The linearisation of the chronocoulometric response can be done and the slope of the Q vs. $t^{1/2}$ plot gives $2nFACD^{1/2}/\pi^{1/2}$ while the intercept is $Q_{dl} + nFA\Gamma$. The diffusional component and interfacial components of the response are easily separted by this method. It is often useful to step the potential back to the E_1 and record the charge due to reaction of the species produced on the forward step. The response of the reverse step is,

$$Q_r = Q_{dl} + 2nFACD^{1/2}/\pi^{1/2}\,\theta + nFA\Gamma_R$$

where

$Q_r = Q_{max} - Q_t$
$\theta = (\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2})$
τ = forward step width in seconds
t = total integration time in seconds

By subtracting the intercept of the forward and reverse steps, the capacitative charge is eliminated to yield nFA ($\Gamma_O - \Gamma_R$). If only one of the species adsorbs, this then gives that species surface excess directly. This method is used successfully in our earlier work to determine the surface excesses of carbonate ions during the passivation of iron in alkaline carbonate solutions [13, 14].

Table 3 shows the surface excess values calculated from the set A measurements for the three solutions. Assuming the only reactive species in both forward and backward steps is the cupric ions, the values of surface excess presented in Table 3 denotes its concentration in the double layer with prolonged times. The values increase with time for all the three solutions. One could see it has no relevance with the bulk concentration where the cupric ions decrease from solution 1 to solution 3. As the solution was not stirred, the concentration at the double layer provides a clue to the extent of anodic dissolution and diffusion of cupric ions towards the cathode for deposition as metallic copper. At the time scale of 400 s, the lowest value of surface excess (16.8 mol cm^{-2}) was observed for solution 2 while for the other two solutions with higher and lower $CuSO_4$ concentration in bulk, the values were on the high side. This observation suggests that cupric ions were consumed at a higher rate in solution 2 where the acid and copper sulphate concentration remains to be in optimum levels. This inference can be further confirmed by looking at the surface excess values showed in Table 4 for the set B experiments. Here also, the trend remained the same confirming that solution 2 could be considered as the best combination of acid and copper sulfate concentration to yield the best results.

Table 3. Surface excess values of copper alloy determined from the double step chronocoulometic experiments (set A) for the three electrolytic solutions

Steps	Time in seconds	Surface excess in mol cm^{-2}		
		Solution 1 (180 gl^{-1})	Solution 2 (100 gl^{-1})	Solution 3 (60 gl^{-1})
1	100	3.59	2.59	2.87
2	200	8.61	8.14	9.00
3	300	13.34	12.53	14.14
4	400	17.27	16.84	19.23

Table 4. Surface excess values of copper alloy determined from the double step chronocoulometic experiments (set B) for the three electrolytic solutions

Steps	Time in seconds	Surface excess in mol cm^{-2} for set B measurements		
		Solution 1 (180 gl^{-1})	Solution 2 (100 gl^{-1})	Solution 3 (60 gl^{-1})
1	100	3.47	4.02	5.89
2	200	8.54	8.01	10.99
3	300	12.96	12.06	16.02
4	400	17.15	16.30	21.14

In both set of experiments, the observed increase in surface excess values with prolonged times shows a tendency for cupric ion accumulation if the solution is not stirred. This result confirms the need for stirring which prevent the formation of a stagnant double layer at the electrode surface. Such stagnancy would lead to the formation of metallic copper due to the chemical disproportionation reaction which affects the efficiency of the process. Secondly, the formation of non-conductive copper sulphate would be enhanced which in turn passivates the anode and reduces the dissolution rate. In our pilot scale refining, we noticed a decrease in voltage from 60 to 43 V for an electrolysis period of 5 days. The applied current was kept constant. The decrease in voltage indicates a corresponding decrease in internal resistance; this is expected as the electrolyte was continuously stirred and the temperature was kept at 45 ° C. Also the cathode surface will have a higher active surface area with the freshly deposited copper compared to the copper sheet used initially. However, dendritic growth of copper still occurred if the cathode sheets were not replaced periodically.

4. CONCLUSIONS

Double step chronocoulometric studies carried out on the industrial copper alloy in 180, 100, 60 gl^{-1} copper sulfate electrolytic solutions were highly useful in providing information regarding the internal resistance at the surface of the copper electrode (double layer), surface excess of cupric ions and the net coulometic charges accumulated at the interface. All these values increase with time irrespective of the concentration of copper sulfate as the solutions were not stirred. This study identifies the use of this technique to study these parameters in electrolysis so that the process is understood better which helps to solve the problems. From the surface excess values, 100 gl^{-1} copper sulfate concentration in the acidic electrolyte was found to be more suitable for the copper recovery process. This result is consistent with our earlier result (ref. No. 10) based on chronopotentiometric studies on the same copper alloy.

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