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EFFECT OF COLLAGEN AND CHLORIDE ADDITIONS ON ELECTROLYTIC COPPER DEPOSITS

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Summary

The effects of collagen concentration and molecular weight on the morphology and crystal orientation of electrolytic copper deposits have been determined and compared. The effect of chlorides in the presence of collagen on the above properties has also been investigated.

Three different molecular weight collagens were studied and the consumption rate of each was determined by chemical analysis of the electrolyte before and after electrodeposition. Two-hour deposits were made in an electrolyte containing the subject collagens in concentrations ranging from 1.2 to 38.4 mg l^{-1}.

Scanning electron and light microscopes and X-ray diffraction were used to evaluate the electrodeposits.

1. Introduction

The effect of various operating conditions on the structure and properties of copper deposits from acid sulfate electrolyte is very important to commercial operations [1, 2]. Most attention has been paid to the effect of bath composition on the structure of deposits, since to a large extent it governs critical properties such as purity, surface smoothness and hardness. Recognition of the factors that influence the structure is therefore important, since this often permits the prediction of those conditions or changes which will yield a product having certain desirable properties.

There are many parameters of the electrodeposition process that affect the nature of the deposit, such as temperature, metal ion and acid concentrations and current density. However, it is also well documented [3 - 7] that relatively small variations in certain addition agents produce more significant changes, in terms of relative concentrations, in deposit characteristics than does any other variable.

Collagen glue is commonly used as an addition agent and has been found to have a most pronounced effect in counteracting dendritic growths, thus

improving current efficiency, deposit purity and appearance. Temperance must be practiced, however, when using collagen as an addition agent since excessive amounts may adversely affect operating costs and power consumption.

Successful use of collagen requires that an optimum low concentration of this addition agent must be established and controlled. Owing to the difficulty in analyzing low concentrations of collagen in the electrolyte, most plants rely on reagent additions based on the weight of the deposit produced. This method of control is undesirable since residual levels of collagen in the electrolyte are not known and therefore are difficult to correlate with changes in process conditions [8]. In addition, collagen itself may vary in chemical and physical properties from different sources, thus introducing more variables into the process.

In view of the fact that little work has been reported on the effect of different types and concentrations of collagen glues in copper deposition, a study of molecular weight and bath concentration variations on deposit texture, structure and properties was made. Attention was also given to the effect of chlorides [9] on deposit properties and their deactivating effect on collagen itself as an addition agent.

Collagen selection was based on available molecular weight variations and those collagens in common use in industry.

2. Experimental conditions

2.1. Structure evaluation cell

The experimental cell was constructed by shortening the length of a 1.0 l Plexiglas Haring cell to contain a volume of 600 ml. An additional 40 ml of electrolyte were held in the recirculation system during operation to make an effective cell volume of 640 ml.

In order to minimize stratification, electrolyte was circulated from one end of the cell to the other at a rate of 40 ml min^{-1} through electrolyte diffusion panels by means of a Technicon auto analyzer peristaltic pump. The electrolyte diffusion panels were made of 1/4 in thick Plexiglas sheet and were perforated uniformly with 1/16 in diameter holes in a 1/2 in grid spacing. The working cell contained two anodes and one cathode each with a working area of 0.033 ft^2 (30.7 cm^2) per face and were spaced (anode to anode) at a distance of 4.50 in (11.43 cm) apart. The anodes were fabricated from pure electrolytic copper sheet produced at the Cerro Copper Products refinery. The cathode substrate was fabricated from cold-rolled alloy 110 copper sheet (0.021 in thick).

2.2. Materials

The electrolyte was prepared from reagent grade sulfuric acid and cupric sulfate pentahydrate at a concentration of 144 g l^{-1} acid and 42 g l^{-1} copper Deionized water used as the solvent was passed through an activated carbon

filter in order to remove trace amounts of organic substances that might be present in the water. The electrolyte was prepared in 20.5 l batches and was assayed to ensure uniformity of composition.

The collagen used was Swift's technical colloid protein supplied in three molecular weights (MW), namely, TCP-EZ3 enzyme degraded collagen (MW = 10 000), TCP-69 gel-depressed collagen (MW = 30 000) and TCP-5V granular collagen (MW = 80 000). Stock solutions of 1.0 g l^{-1} collagen were prepared and stabilized in a solution of 1.0 g l^{-1} cupric sulfate to retard enzymatic degradation.

2.3. Operation

All deposits were made galvanostatically at 25 A ft^{-2} (269 A m^{-2}) for a period of 2 h. The cells were submerged in a water bath to maintain a uniform electrolyte temperature of 50 °C. Voltage was monitored and values recorded throughout the tests.

To reduce epitaxial growth tendencies and to produce a reproducible substrate the electrodes were prepared by water sanding the surface of the plate in the direction of rolling with 600 grit metallography paper. All cathodes were water washed, followed by ultrasonic cleaning in acetone prior to installation in the cell.

2.4. Structure evaluation cell

After immersion of the cell in the water bath, 640 ml of electrolyte containing a given concentration of the subject collagen were introduced into the cell and the electrolyte circulation system was started.

A prepared cathode plate was inserted into the center position of the slotted Plexiglas cell top. Clean anodes were then placed into the slots on both sides of the cathode and the cell was polarized to yield a current equal to 25 A ft^{-2} (269 A m^{-2}) of cathode area. Periodically, it was necessary to add deionized water to correct for volume losses due to evaporation.

After 2 h of plating time, the power supply was turned off and the cathode was immediately removed, flushed with copious amounts of tap water and rinsed with deionized water and then acetone to prevent staining.

Deposits were made from electrolytes containing a concentration range of each collagen investigated. In addition, long-term deposits were made, starting with a nominal initial collagen concentration of 9.6 mg l^{-1}, to determine the consumption rate of each collagen during the electrolysis of copper. The collagen-depleted solution was analyzed for collagen concentration by a colorimetric method [10]. The analyses were used to determine whether the morphology of deposits made in depleted solutions is similar to that of deposits made from the same concentration of freshly prepared collagen electrolyte solutions.

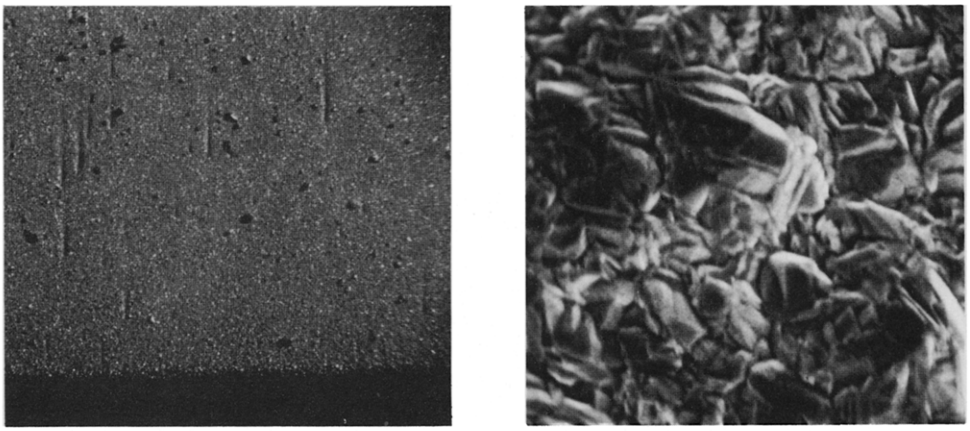
Deposits were examined and compared by scanning electron microscopy, X-ray diffraction and optical microscopy.

3. Results and discussion

Since several different properties and effects of collagens and chlorides were investigated, the results and discussions are divided into sections for clarity.

3.1. Structure as a function of molecular weight and concentration of collagen

Deposits made in the absence of collagen produced very fine-grained and smooth surfaces. These deposits had randomly distributed small metal whiskers which would probably result in dendritic growths on long term deposits. The orientation was essentially (220), as shown in Table 1. Optical and scanning electron microscope (SEM) photomicrographs of the deposits are included in Fig. 1. Note that the SEM photomicrographs show a structure with multiple facets and undefined geometry.



(a) (b)

Fig. 1. Photomicrographs of deposits made from electrolyte without addition agents: (a) 12 ×; (b) 800 ×.

In contrast to the uniformity of the deposits made with no collagen additions, deposits made from 1.2 mg l^{-1} of each collagen had macroscopic vertical variations in deposit thickness and appeared as parallel ridges on the plating. The greatest predominance of the ridges appeared on the bottom of the cathode, suggesting that a higher current density at the edges or a greater electrolyte density may be contributing to this effect. Deposits made from each collagen at this concentration were essentially the same, although the deposit from TCP-69 showed a more irregular macroscopic surface appearance. As in the case of deposits made with no collagen, the orientation was (220) although small amounts of (111), (200), (311), (331) and (420) started to appear. Figure 2 shows optical and SEM photomicrographs for comparison. Only TCP-5V deposits are shown since the EZ3s were so similar to them.

TABLE 1

X-ray diffraction orientation data

Entry	Addition ($mg\ l^{-1}$)	(111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)
1	Blank	0	0	100	0	0	0	0	0
2	TCP-EZ3, 1.2	0	0	100	10	0	0	0	0
3	TCP-EZ3, 2.4	1	1	100	9	0	0	2	0
4	TCP-EZ3, 4.8	45	25	100	54	3	1	16	34
5	TCP-EZ3, 9.6	100	100	64	50	7	3	19	29
6	TCP-EZ3,19.2	47	100	2	6	2	5	4	2
7	TCP-EZ3,38.4	73	100	19	14	6	4	5	5
8	TCP-EZ3, 2.5 (depleted)	0	0	100	0	0	0	5	0
9	TCP-69, 1.2	0	0	100	0	0	0	4	0
10	TCP-69, 2.4	4	6	100	4	0	0	8	2
11	TCP-69, 4.8	3	3	100	4	0	3	9	5
12	TCP-69, 9.6	5	0	100	16	0	0	7	0
13	TCP-69, 19.2	2	2	100	14	0	0	5	1
14	TCP-69, 38.4	100	2	4	5	0	0	5	0
15	TCP-69, 76.8	100	0	0	0	3	0	0	0
16	TCP-69, 3.5 (depleted)	0	0	100	0	0	0	13	1
17	TCP-5V, 1.2	6	2	100	2	0	0	29	12
18	TCP-5V, 2.4	1	0	100	8	0	0	3	0
19	TCP-5V, 4.8	30	40	100	60	4	3	26	71
20	TCP-5V, 9.6	51	100	60	48	11	11	41	75
21	TCP-5V, 19.2	82	100	20	19	3	3	9	13
22	TCP-5V, 38.4	100	59	62	27	10	4	11	18
23	TCP-5V, 2.5 (depleted)	6	4	100	20	0	0	13	3
24	TCP-5, 9.6/$CaCl_2$,1.4	5	4	100	8	0	0	5	1
25	TCP-5V, 9.6/Cl^-,0.9	9	5	100	6	0	2	6	3
26	TCP-5V, 9.6/Cl^-,30	0	0	100	1	0	0	0	2
27	$CaCl_2$, 1.4	0	0	100	0	0	0	6	0
28	Photo-Flo, 0.5	30	30	100	40	0	0	0	0
29	TCP-EZ3, 1.2/P-Flo,0.1	0	0	100	5	0	0	6	0
30	Amino acid, five each	2	0	100	0	0	0	8	1
31	Random orientation	100	46	20	17	5	3	9	8

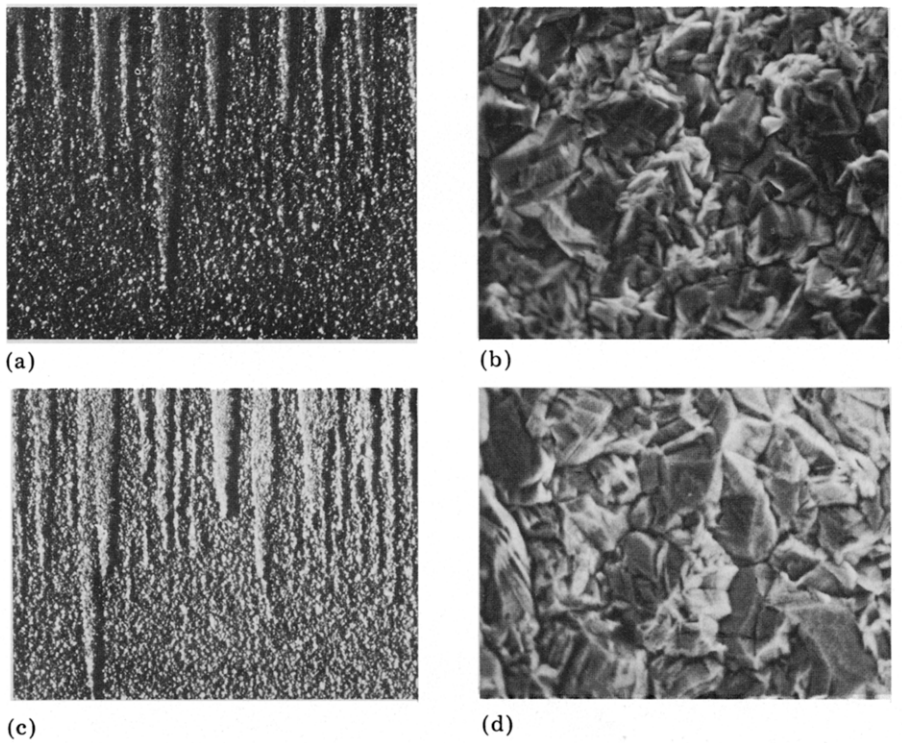


Fig. 2. Photomicrographs of deposits made in electrolyte containing 1.2 mg l^{-1} collagen: (a) TCP-69 (12 ×); (b) TCP-69 (800 ×); (c) TCP-5V (12 ×); (d) TCP-5V (800 ×).

At a concentration of 2.4 mg l^{-1} collagen, there was a marked difference in macroscopic appearance of the deposits. Both TCP-5V and EZ3 now showed very smooth and fine-grained deposits. TCP-69 had a finer overall grain structure but the striations were more well defined. The randomly distributed dendrites as observed in deposits with no collagen were completely eliminated, as seen in Fig. 3. The orientation of these deposits was still essentially (220).

Although the lower concentrations of collagen produced differences in macroscopic structure varying with type and concentration used, the microscopic morphology and orientation was essentially the same for all collagens and concentrations. However, at 4.8 mg l^{-1} of TCP-5V and EZ3, there was a noticeable shift in orientation. Although the (220) orientation was still predominant, other orientations were now starting to be significant in magnitude. A change in the morphology could also be observed in that large pyramid-shaped crystallites were recognizable in a field of fine multiple faceted crystallites with undefined geometry. This shift in morphological configuration and orientation was not seen in deposits from the TCP-69 collagen. Macroscopically, the striae tend to form more nodular and tear-drop-like protuberances than are observed with the lower concentrations of collagen.

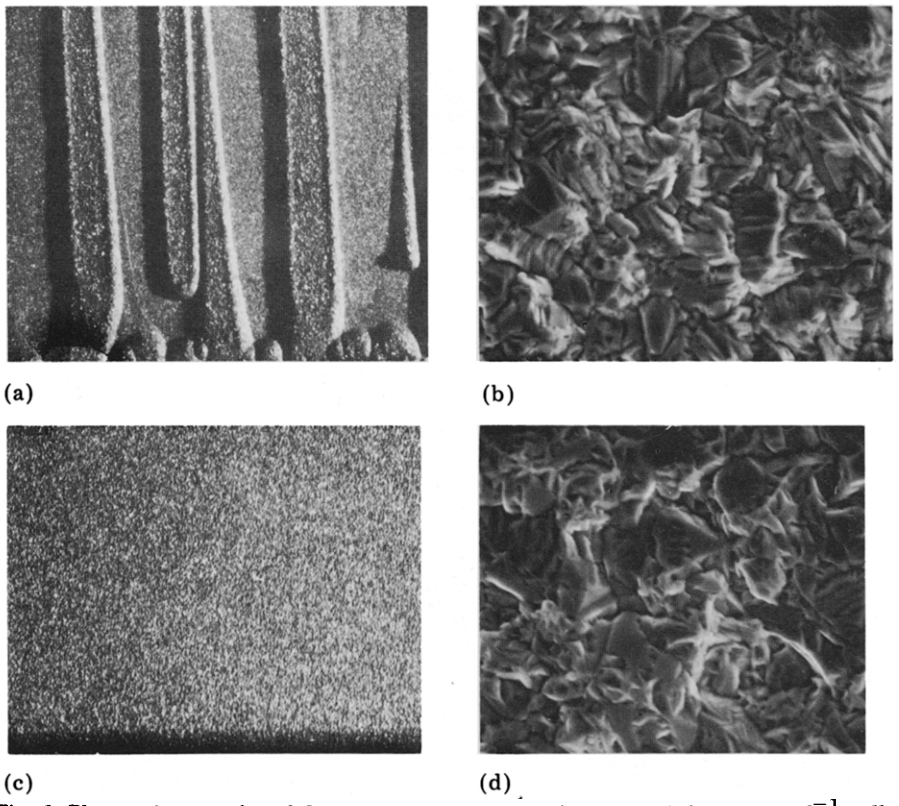


Fig. 3. Photomicrographs of deposits made in electrolyte containing 2.4 mg l^{-1} collagen: (a) TCP-69 (12 ×); (b) TCP-69 (800 ×); (c) TCP-5V (12 ×); (d) TCP-5V (800 ×).

The trend in shifting morphology and orientation described above is more pronounced with collagen concentrations at 9.6 mg l^{-1}, as shown in Fig. 4. At this concentration, the orientation is predominantly a mixture of (111), (200), and (220) for TCP-5V and EZ3 but the orientation of TCP-69 essentially is still (220). The microscopic morphology is still fine grained and geometrically undefined with TCP-69.

At a concentration of 19.2 mg l^{-1}, TCP-5V and EZ3 show larger grain size both macroscopically and microscopically. Visual examination of the deposits suggests that collagen concentrations at this level may produce large amounts of dendritic structures in long-term deposits. The grain size of TCP-69 is still very fine and, instead of the striated and tear-drop-like protuberances, knots and nodules form in a fine-grained field.

The morphology produced from electrolyte containing 38.4 mg l^{-1} of TCP-EZ3 and 5V was similar, although there was indication that the deposits made with TCP-5V were more prone to dendrite formation than those produced with TCP-EZ3. Strangely enough, the tendency of TCP-69 to produce protuberances was reduced, with nodules only occurring on the bottom edge of the plate, when its concentration was increased to 38.4 mg l^{-1}. At this

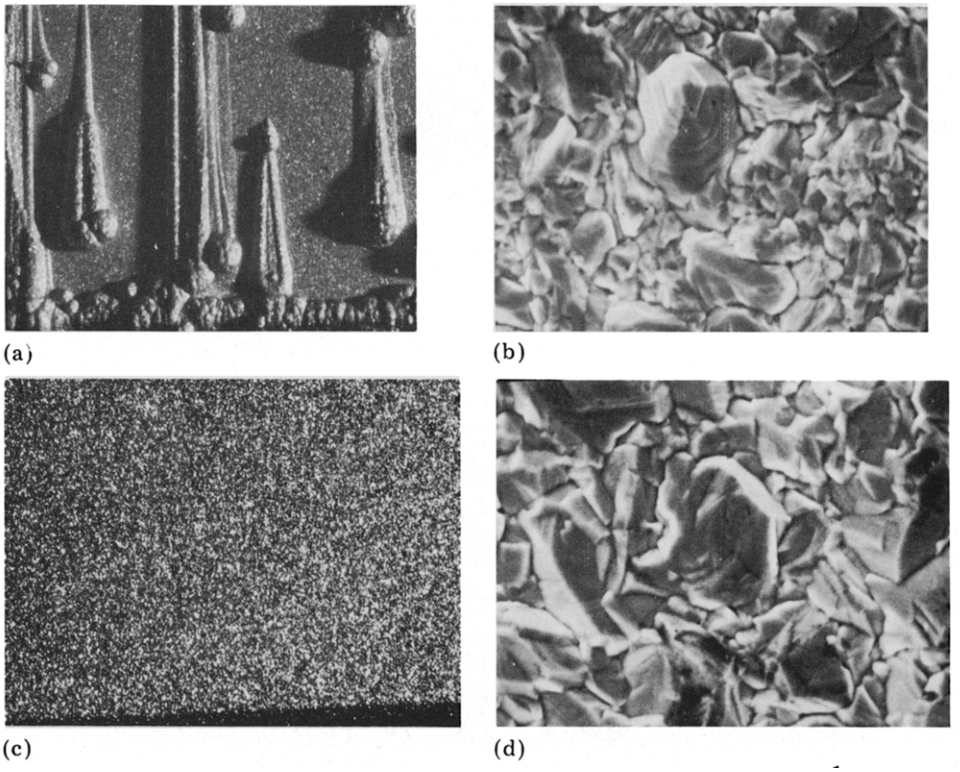


Fig. 4. Photomicrographs of deposits made in electrolyte containing 9.6 mg l^{-1} collagen: (a) TCP-69 (12 x); (b) TCP-69 (800 x); (c) TCP-5V (12 x); (d) TCP-5V (800 x).

concentration, the orientation made a drastic shift from the previously dominant orientation of (220) to essentially all (111). The microscopic morphology also showed a corresponding shift from a fine-grained structure to smooth-faceted geometrically regular and defined deposits.

In general, increasing concentrations of collagen produce a change in morphology and orientation of the crystal structure. Blanks and low concentrations of collagen (1.2 - 4.8 mg l^{-1}) produce deposits with crystal orientation in the (220) direction. Higher concentrations tend to produce predominant (111) and (200) orientations. In addition, morphology can be related to orientation. A (220) orientation corresponds to stepped parallel facets on an undefined geometric crystal. (200) and (111) orientation corresponds to smooth-faced triangular pyramidal forms.

From a macroscopic texture standpoint, low concentrations of collagens (~ 1 mg l^{-1}) produce striations, and high concentrations (~ 20 mg l^{-1} and above) produce dendritic growths. From a deposit smoothness and grain refinement standpoint, the optimum concentration of collagen is about 5 - 10 mg l^{-1} when used by itself.

Although there were significant structural differences produced from the different collagens and concentrations used, molecular weight in itself

had a minor effect on the morphology and orientation changes of the crystal structure. This fact can be illustrated by the close correspondence in structure between TCP-EZ3 (MW 10 000) and TCP-5V (MW 80 000) at each concentration studied. At high concentrations, however, there was a slight tendency for the TCP-5V to produce deposits with more dendrites than observed on deposits made with the same concentration of TCP-EZ3. X-ray orientation data also show a similar trend for both TCP-EZ3 and TCP-5V, but at high concentrations there is a distinguishable difference in orientation between these collagens.

3.2. Structure as a function of chloride concentration

As discussed previously, deposits made in electrolytes containing TCP-69 were structurally different and lagged behind in structural modification patterns that were produced when using the same concentration of TCP-5V and EZ3. It was also noted that at a concentration of 38.4 mg l^{-1}, when TCP-5V and EZ3 were producing progressively poorer deposits, TCP-69 produced the smoothest deposit, with the exception of the nodulation on the bottom edge of the plate.

Deposits made at a concentration of 76.8 mg l^{-1} of TCP-69 produced the smoothest surface of all deposits made with this collagen, and caused a complete shift in orientation to (111), being visually identical to deposits made with the other collagens at concentrations ten to twenty times lower. TCP-69 did not start to form dendrites until a concentration of 307.2 mg l^{-1} was reached.

In another set of tests, the addition of a proportionate amount of calcium chloride (the gel depressant used in TCP-69) to TCP-5V produced a macroscopic structure nearly identical to that of deposits made in TCP-69, indicating that the different behavior of TCP-69 from TCP-5V and EZ3 is due primarily to the presence of chlorides. In addition, the orientation data and SEM photomicrographs were very similar for these deposits. Figure 5 and Table 1 show the comparable structures and orientations.

In general, the presence of chlorides in combination with collagen produced a synergistic effect on the deposit which is different from chlorides alone or collagen alone. Additions of relatively low concentrations of chlorides suppress the behavior of collagen to change the deposit orientation, as observed with deposits made in chloride-free electrolyte containing collagen.

3.3. Collagen consumption rate as a function of its molecular weight

There are at least two sources of collagen depletion in the acid copper sulfate bath: (1) hydrolysis and (2) occlusion in the electrodeposit. Hydrolysis will occur in the electrolyte with or without electrolysis, but adsorption followed by occlusion in the deposit occurs only during the electrolytic process.

Under experimental conditions, the average collagen consumption rate of all collagens investigated, which includes the depletion due to hydrolysis and occlusion by electrolysis, was determined as 0.035 lb per short ton

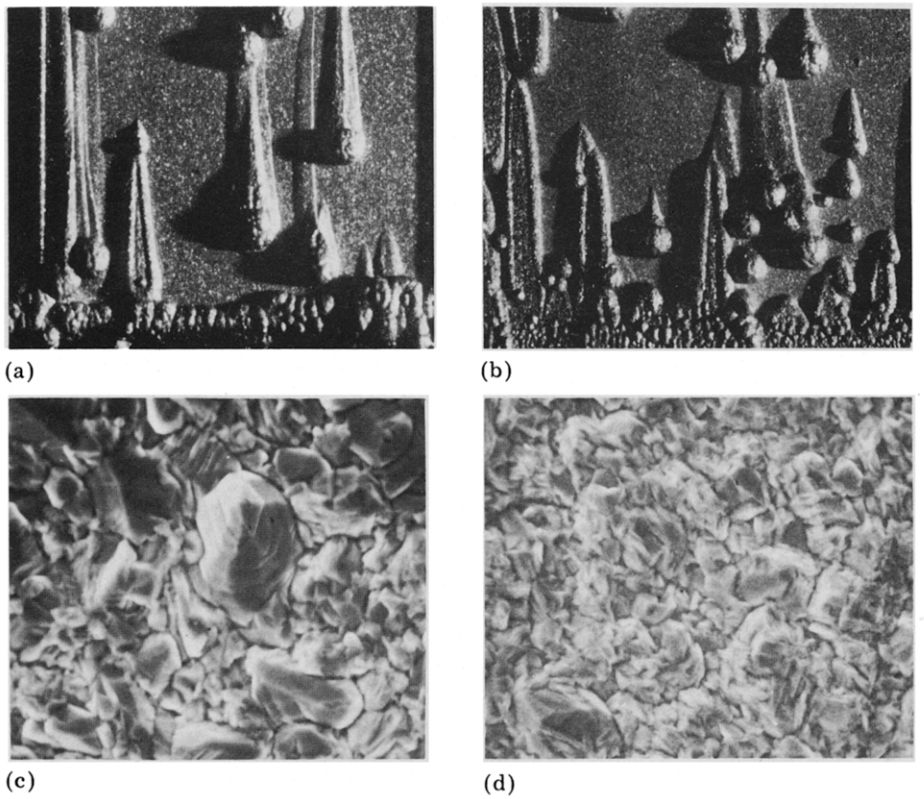


Fig. 5. Comparison of deposits made with TCP-69 *vs.* TCP-5V with an equivalent amount of calcium chloride: (a) TCP-69, 9.6 mg l^{-1} (12 ×); (b) TCP-5V, 9.6 mg l^{-1} + 1.44 mg l^{-1} $CaCl_2$ (12 ×); (c) TCP-69, 9.6 mg l^{-1} (800 ×); (d) TCP-5V, 9.6 mg l^{-1} + 1.44 mg l^{-1} $CaCl_2$ (800 ×).

(0.018 kg per metric ton) of cathode produced. The data in Table 2 indicate that the lower molecular weight collagens appear to be consumed at slightly higher rates than the higher molecular weight variety.

To determine to what extent collagen was being consumed by degradation from the electrolyte itself, hydrolysis experiments were also conducted for each of the different molecular weight collagens.

The test cell hydrolysis experiments were conducted by heating electrolyte of a known collagen concentration to 60 °C for 50 h. This temperature was 10 °C higher than that used in all other experimental work. The concentration was analyzed before and after heating the electrolyte and the loss in collagen was expressed in mg l^{-1} h^{-1} (see Table 2). The hydrolysis rate under these conditions accounted for losses of about 0.063 mg l^{-1} h^{-1}. This represents about 43% of the collagen lost in the consumption rate test performed at 50 °C.

The exact extent of hydrolysis expressed as a percentage of total consumption during electrolysis cannot be calculated since the hydrolysis exper-

TABLE 2

Collagen depletion data

Collagen	Concentration ($mg\ l^{-1}$)			Depletion rate	
	Initial	Final	Difference	lb per short ton	kg per metric ton
Depletion during electrolysis at 25 A ft^{-2} (269 A m^{-2}) at 50 °C					
TCP-EZ3	10.6	2.5	8.1	0.040	0.020
TCP-69	10.5	3.5	7.0	0.033	0.017
TCP-5V	9.0	2.5	6.5	0.031	0.016
Average				0.035	0.018
Collagen	Concentration ($mg\ l^{-1}$)			Hydrolysis rate ($mg\ l^{-1}\ h^{-1}$)	
	Initial	Final	Difference		
Depletion due to hydrolysis at 60 °C					
TCP-EZ3	10.6	6.7	3.9	0.080	
TCP-69	10.5	8.0	2.5	0.050	
TCP-5V	9.0	6.0	3.0	0.058	
Average				0.063	

iments were conducted at temperatures different from those of the collagen depletion experiments. It is not, however, the major contributor to collagen depletion during electrolysis and is estimated to account for about 15 to 20% of the amount consumed during electrolysis.

4. Conclusions

The properties and structure of copper electrodeposits were significantly altered by the presence of collagens and chlorides.

In general, increasing concentration of collagen produced a change in morphology and orientation of the crystal structure. Blanks and low concentrations of collagen (less than 5 $mg\ l^{-1}$) produced deposits with crystal orientation in the (220) direction. Higher concentrations produced predominant (111) and (200) orientation. In addition, morphology was found to be related to orientation. A (220) orientation corresponded to stepped parallel facets on a fine and undefined geometric crystal. (200) and (111) orientation corresponded to smooth pyramid-shaped crystals.

From a macroscopic texture standpoint, a low concentration (1 $mg\ l^{-1}$) of collagen by itself produced striations, while very high concentrations (greater than 20 $mg\ l^{-1}$) produced dendritic growths.

Although there were significant structural differences produced from various collagen concentrations, molecular weight in itself had relatively minor effects on the morphology or orientation of the crystal structure.

Lower molecular weight collagens, however, appeared to be more efficient in grain refinement and in eliminating dendrites.

The presence of chlorides in combination with collagen produced synergistic effects on the deposit which were different from collagen alone or chlorides alone. Additions of relatively low concentrations of chlorides suppress the ability of collagen to change the deposit orientation from the (220) direction as observed in deposits made in collagen-free electrolyte. For the ratios studied, low concentrations of chlorides in the presence of collagens tend to favor the formation of striae and nodular growths, whereas higher concentrations produce smooth and level deposits with a grain size smaller than is obtained with the same concentration of collagen without chlorides. The analyzed concentration of collagen in the electrolyte is not the active concentration in the presence of chlorides. Other ions or addition agents may also alter the activity of collagen, limiting the value of the collagen analysis to predict the structural characteristics of deposits.

Collagen in acid electrolyte is unstable with respect to time and is hydrolyzed to its constituent amino-acids.

Under experimental conditions, the average consumption rate of the collagens studied, including the effect of hydrolysis and electrolysis, was determined as 0.035 lb per short ton (0.018 kg per metric ton). The lower molecular weight collagens appear to be consumed at a slightly higher rate than the higher molecular weight variety.

The results of this study also indicate the extreme sensitivity of the electrocrystallization process to minor changes in the chemistry of the solution. It becomes obvious that it is essential to characterize the quantity of additive that is electrochemically active, rather than to rely on the physical weight or amount of glue or other organic added to an electrolyte.

Acknowledgments

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