CAUSE OF FORMATION OF NODULAR COPPER PARTICLES ON ELECTROREFINED COPPER SUBSTRATE①

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ABSTRACT

The microanalysis by EDAX and XPS is used to identify elements and their valences of the initial growth sites of nodular copper particles on electrodeposited copper. Crystal orientation and the copper sheet cut out along the growth axes of nodular copper particles are also studied by EDAX and XPS. It shows that the adhesion of some suspended slime, such as copper and silver corpuscles, oxides of arsenic, antimony, bismuth and copper, sulfides of copper, makes crystal face(220) be preferred orientation and causes the growth of nodular copper particles. Nonconductor corpuscles such as silicates, calcium and magnesium sulphates would not produce nodulation and are occluded in electrodeposited copper.
Key words: copper electrorefining nodular copper particle XPS EDAX

1 INTRODUCTION

Copper electrorefining, especially of long-time and high current density, usually leads to particle growth on electrodeposited copper[1]. These particles not only tend to cause short circuits, increase impurity content, but also have detrimental effect on quality and appearance of electrorefined copper. It is generally agreed that pyramid particles and oblate ones tightly combined with copper substrate originate from inappropriate composition of additives, uneven current density and other unsuitable operating conditions[2-4]. The cause of nodular copper particle growth was empirically regarded as the adhesion of some suspended slime in the electrolyte. It was reported that some solid corpuscles such as graphite, copper, silver, antimony and copper sulfide were responsible for nodular copper particles[2,5,6], while aluminium oxide was occluded in electrodeposited copper[7]. Few papers have reported the cause of formation of nodular copper particles by using X-ray photoelectron spectroscopy (XPS) and EDAX. In this paper, we have made some microanalysis by XPS and EDAX on the initial growth sites of nodular copper particles. In order to determine the existing elements and their valences, we also examined the copper sheet cut out along the growth axes of nodular copper particles. Last, some discussion about the cause of formation of nodular copper particles on electrodeposited copper was given.

2 EXPERIMENTAL

We sampled electrorefined copper from a smeltery. Since nodular copper particles are slightly combined with copper substrate, we gently pull them out from copper substrate. Correspondingly, on copper substrate there left pits which are the initial growth sites of nodular copper particles; the contacting area between copper substrate and nodular copper particle is below 0.5 mm^2. Before experi-

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ment, the sample with nodular copper particles and pits is prepared by rinsing with distilled water, soaking in acetone, removing oxides in dilute H_2SO_4 solution, rinsing by redistilled water, immediately drying by blowing high pure nitrogen gas and keeping in vaccum vessel for test.

For contrast, we also investigated the sample with pyramid particles and oblate ones from the same smeltery, which is pretreated as described above. The specimens to be analyzed are made as follows: spark slicer is employed to cut a nodular copper particle along the growth axis. The thin copper sheets cut out are numbered 1 to 8 from the initial growth site, the thickness of each sheet is 1 mm. Before experiment, these sheets are prepared by soaking in acetone and dilute H_2SO_4 solution successively, rinsing by distilled water, then polishing with 3#, 4# metallography grade paper and polisher to mirror face, rinsing with redistilled water, finally drying by blowing high pure nitrogen gas and keeping in vaccum vessel for test.

EDAX analysis was performed using model S-570 scanning electron microscopy equipped with EDAX-PV 9100 X-ray energy dispersion analyzer. Elements to be analyzed are Al, Mg, Si, Cl, Ag, K, Sb, Ca, Te, Ba, Fe, Cu, As, Bi, Se.

XPS analysis was performed using a ESCALAB MK-Ⅱ X-ray photoelectron spectrometer at an operating pressure of 10^{-8} Pa, with MgK_{α}($h\nu$ = 1 253.6 eV) radiation. The adventitious carbon C1*s* peak(284.5 eV) was used for charge referencing and binding energy calibration. XPS analysis was made on C1*s*, As3*d* (Sb4*d*), Cu2*p*, O1*s* (Sb3*d*), Se3*d*, Au4*f*, S2*p* (Bi4*f*), Cl2*p*, Ag3*d*, Te3*d*, Pb4*f*, respectively. The spectrum of each peak is to be recorded over 10 times and smoothing processed by special computer software. The elements existed in the specimen and their valences were identified against the standard XPS table[8, 9].

3 RESULTS AND DISCUSSION

3.1 EDAX *Microanalysis*

In this section, nodular copper particle is represented by symbol A; symbol B and C stand for pyramid particle and oblate one, respectively. The results of EDAX microanalysis are summarized in Table 1.

Table 1 The results of EDAX analysis

Code	Elements	Code	Elements
A01	Mg, Al, Si, S, K, Sb, Fe, Cu	A12	S, Ba, Cu
A02	Si, Cu	A13	Al, Si, S, K, Sb, Ba, Fe, Cu
A03	Mg, Al, Si, S, Sb, Fe, Cu	A14	Al, Si, K, Sb, Cu
A04	Sb, Fe, Cu	B01	Al, Si, Cl, K, Ca
A05	Mg, Si, S, K, Sb, Cu, Ba, As	B02	Al, Si, Cu
A06	Mg, Si, Sb, Cu	B03	Cu
A07	Al, Si, Ag, Sb Ba, Fe, Cu	C01	Al, Si, K, Ca, Cu
A08	S, Cu	C02	Si, S, Cu
A09	S, Sb, Cu, As	C03	Si, S, Ca Ba, Cu
A10	Si, S, Ba, Cu		
A11	Si, S, Cl, K Sb, Cu	C04	S, Ba, Cu

The impurities of sample B and C are mainly K, Ca, Al, Si, S, Ba. It is likely that they are suspended slime such as calcium sulphates, barium sulphates and potassium aluminium silicates. These substances belong to non-conductors. In copper electrorefining, they are occluded in electrodeposited copper[7]. It may be concluded that the growth of pyramid particles and oblate ones originate from unsuitable operating conditions such as $C_{Cu^{2+}}/C_{H_2SO_4}$, current density, temperature, additives and their combination[3, 10]. EDAX microanalysis shows that, besides Fe, Mg, Al, Si, K, Ca, Ba, S, specimen A also contains Sb, As and sometimes silver. It is likely that some substances containing Sb, As and Ag adhere to copper substrate as the detrimental substances and tend to formulate crystal nuclei of nodular copper particles. As and Sb probably exist in the form of Sb_2O_3, Sb_2O_5, As_2O_3 and As_2O_5(or $SbAsO_4$) in the slime and they are semiconductors. Silver and copper corpuscles, Cu_2O, CuO, CuS, Cu_2S also tend to formulate crystal nuclei. These results will be further confirmed by XPS microanalysis on the pits and

EDAX microanalysis on the sheet which cut out along the growth axis of nodular copper particle.

3. 2 *Study of Preferred Crystal Orientation by* XRD

The copper deposit's crystal orientation was identified by X-ray diffraction (XRD) analysis. Riguku-Rotaflex max/rB X-ray diffractometer using monochrome CuK_α radiation at 40 kV and 50 mA was employed to obtain smooth chart at 4°/min. The results of XRD analysis are summarized in Table 2. The data of standard copper are given for contrast.

Table 2 The results of XRD analysis

Specimen	Crystal distance and relative intensity of diffraction					
	(111)	(200)	(220)	(311)	(222)	(400)
standard Cu	2.088	1.808	1.278	1.090	1.044	0.904
	(100)	(46)	(20)	(17)	(5)	(3)
A	2.087	1.806	1.278	1.089	1.043	0.903
	(4)	(1)	(100)	(24)	(1)	(0)
B	2.088	1.810	1.279	1.090	1.044	0.905
	(76)	(30)	(100)	(13)	(4)	(1)
C	2.088	1.810	1.278	1.091	1.044	0.906
	(100)	(55)	(5)	(5)	(3)	(2)

XRD results show that the growth of (111) and (200) crystal face of specimen A is retarded; meanwhile (220) is the preferred orientation of nodular copper particle. The crystal face growth of specimen B and C is basically normal; to say more exactly, (220) crystal face of specimen B grows predominately, but that of specimen C is slightly retarded.

3. 3 XPS *Microanalysis*

We use XPS to examine the pits after pulling out A type nodular copper particles. The results are given in Table 3. Considering the approximately equal value of binding energy of $Cu2p$ peaks between Cu and Cu^+, we examined Auger $CuKL_{23}L_{23}$ peak to identify Cu^+, and $Sb3p_{3/2}$ satellite peak to ensure existence of Sb. XPS microanalysis shows that the elements' valences of the initial growth sites of nodular copper particles are Cu^+, Cu^{2+}, Ag, Ag^-, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Bi^{3+} and S^{2-}, SO_4^{2-}, Se^{2-}, etc. Possibly existing compounds are Cu_2S, CuS, Cu_2O, $CuSO_4$, Cu_2Se, $CuSiO_3$, Ag, Ag_2SO_4, Ag_2Se, As_2O_3, As_2O_5, Sb_2O_3, Sb_2O_5, Bi_2O_3, BiOCl; among these more often existing are Ag, Cu_2O, $CuSO_4$, As_2O_3, As_2O_5, Sb_2O_3, Sb_2O_5, Bi_2O_3. It must be taken notice that these substances mostly belong to semiconductors or metal conductors.

Table 3 The data of XPS microanalysis

Code	1	2	3	4	5	6
$As3d$, $Sb4d$	44.7	—	—	45.5	44.5	44.6
					35.7	35.4
					($Sb4d$)	($Sb4d$)
$Cu2p_{3/2}$	932.4	932.4	932.3	932.4	932.4	932.4
	933.8		934.6	933.6		
$O1s$, $Sb3d_{5/2}$	530.2	531.8	531.8	532.0	531.2	530.2
		533.8		534.1	533.5	532.2
	531.8	530.4*		530.4*	530.4*	530.4*
		540.3				
$Se3d_{5/2}$	52.9		53.5	—	—	54.2
	54.2	—59.4				
	55.2					
$C1s$	285.0	284.9	285.0	285.0	285.0	284.8
$S2p$, $Bi4f_{7/2}$	168.8	170.8	168.8	168.8	169.2	169.1
		168.8	160.0*	160.4*	159.8*	159.8*
$Cl2p$	—	—	198.9	—	—	—
$Ag3d_{5/2}$	368.1	—	—	—	—	368.2
$Te3d_{5/2}$	576.7	—	—	—	—	—

* satellite peak.

3. 4 EDAX *Microanalysis of Copper Sheet Cut Out from Nodular Copper Particle*

SEM analysis shows that many defects appear in the cross sections of the copper sheets cut out from nodular copper particle along its growth axis; elements existed is only copper except some occlusions. The EDAX microanalysis results of the occlusions of nodular copper particles are summarized in Table 4.

Table 4 shows that the occlusions mainly contain K, Al, Mg, Ca, Si, Fe, S; some also contain Mn, Ba, Ti. Nevertheless, we have not found elements As, Sb, Bi and Ag. So we think that in copper electrorefining, the occlusions in copper originate from suspended solid corpuscles in the electrolyte solution such as silicates, calcium and magnesium sulphates. These solid corpuscles belong to nonconductors not possibly leading to nodular copper particle growth.

Table 4 The EDAX microanalysis results of the occlusions of nodular copper particles

Code	Elements	Code	Elements
101	Al,Si,K,Ca,Cu	402	Mg,S,Si,Ca,Cu
102	Al,K,Cu	501	Si,Cu
103	Al,Si,S,K Ca,Fe,Cu	502	Si,Cu
104	Al,S,K,Ca,Cu	601	S,Cl,Ca,Cu
201	S,Fe,Cu	602	Mg,Si,S,Ca,Cu
202	S,Ca,Cu		
301	S,Si,Cu	701	Mg,Al,Si,S,Cl K,Ca,Mn,Fe,Cu
302	S,Si,Cu	702	S,Ca,Mn Fe,Cu
401	S,Cu	801	S,Ca,Fe,Cu
		802	Al,Si,Ca,Ti,Cu

4 CONCLUSION

In long-time and high current density copper electrorefining, the adhesion of some suspended non-conductor corpuscles in the electrolyte solution such as calcium, magnesium and barium sulphates tends to produce occlusions in the bulk of copper. As a result, the impurities of electrodeposited copper are increased. Silver, copper corpuscles from disproportionation reaction of cuppric ions and some semiconductors such as As_2O_3, As_2O_5, Sb_2O_3 (or $SbAsO_4$), Sb_2O_5, Bi_2O_3, Cu_2O, CuO, Cu_2S, CuS are detrimental to electrodeposited copper. These substances adhere to copper substrate and become crystal nuclei of the initial growth sites of nodular copper particles, which make (220) orientation become predominant and nodular copper particles grow. While the formation of pyramid particles and oblate ones is due to unsuitable copper electrorefining operation, additives and their combination.

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