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Mechanically Stable Insoluble Titanium-Lead Anodes for Sulfate Electrolytes

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Abstract: *Different formulations of a new material to be used as an insoluble anode for copper electrowinning, a Ti-Pb composite, were investigated for both mechanical and electrochemical properties. Mechanical and metallographic characteristic tests, as well as short-term deposition tests were used to study the effect of the Ti/Pb ratio on anode performance. Yield strength and elastic modulus, obtained through tensile testing, significantly exceed that of lead. Metallographic procedures were used to assess the uniformity of lead distribution in the material, as well as porosity, which would be decreased below 1 % for most of the compositions under study. Short-term deposition tests were used to determine power consumption, deposit quality, current efficiency and weight loss characteristics of the new anode material. The material with only 30 vol.% lead shows approximately the same electrochemical performance as a pure lead anode, but has much higher mechanical properties which prevent warping and extend the lifetime of the anode.*
Keywords: *Titanium; Lead; Electrodes; Electrowinning; Mechanical Properties.*

Резюме: *Исследованы механические и электрохимические свойства различных составов нового материала композита Ti-Pb, который будет использован в качестве нерастворимого анода для получения меди методом электролиза. Механические и металлографические исследования, а также и кратковременное испытание осаждения использованы для изучения влияния отношения Ti-Pb на характеристики анода. Предел текучести и модуль упругости, полученные при испытании напряжения, значительно превышают значения для свинца. Металлографическим исследованием оценена однородность распределения свинца в материале, а также пористость, которая для большинства исследованных соединений оказалась меньше 1 %. При помощи кратковременного испытания осаждения исследован расход электричества, качество осадка, эффективность тока и потеря веса нового анодного материала. Материал, содержащий только 30 об.% свинца, проявляавет почти одинаковые электрохимические характеристики как и анод из чистого свинца, но механические свойства намного лучшие, они предупреждают коробление и увеличивают время жизни анода.*
Ключевые слова: *Титан; свинец; электроды; электролиз; механические свойства.*

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Садржај: *Проучена су механичка и електрохемијска својства различитих састава новог материјала, композита Ti-Pb, који ће се користити као нерастворљива анода за добијање бакра електролизом. Механичка и металографска испитивања, као и краткотрајни тестови депозиције коришћени су ради проучавања ефекта односа Ti-Pb на карактеристике аноде. Гранични напон и еластични модул, добијени тестирањем напрезања, знатно превазилазе вредности за олово. Металографским испитивањем процењена је униформност дистрибуције олова у материјалу, као и порозност, која је мања од 1 % за већину проучаваних композиција. Краткорочним тестовима депозиције одређивана је потрошња енергије, квалитет депозита, ефикасност струје и губитак тежине новог анодног материјала. Материјал са само 30 зап.% олова показује скоро исте електрохемијске перформансе као анода од чистог олова, али има много боља механичка својства која спречавају кривљење и продужавају век трајања аноде.*

Кључне речи: *Титан; олово; електроде; електролиза; механичка својства.*

1. Introduction

The use of electrowinning technologies in the extraction of copper from concentrate has been gaining a great deal of interest in industry over the past few years for obtaining copper deposits of high purity [1-3]. Electrowinning still remains the process that uses the highest amount of energy, about 8-10 times more than smelting and electrorefining, in the production of pure copper [4]. In an effort to reduce this energy burden, new anode materials have been under development [5-10]. For the most part, lead alloys have replaced pure lead as the insoluble anodes of choice in the electrowinning industry [5, 8]. The most common insoluble anodes are Pb-Sb for copper electrowinning and Pb-Ag for zinc electrowinning [8, 11-13]. Though Sb helps to lower the oxygen overvoltage on Pb, it can lead to increased corrosion and a shortened anode lifespan [7]. Concentrations of the alloying elements, Ag and Sb, are relatively low, usually less than 5-10 %, but still significantly increase the cost of anodes.

The mechanical properties of the electrodes in electrowinning are becoming increasingly important. Deformations of the soft lead anode that can occur during operations are enough to cause non-uniformity in deposits on the cathode, irregular current density and, in extreme cases, short circuits [8, 14]. Therefore, materials that have mechanical properties that limit the amount of warping and still retain the electrochemical properties need to be designed.

This paper reports on the mechanical and electrochemical properties of a new kind of electrowinning anode, a titanium-lead composite [9-10]. This novel material was tested against pure lead to assess its benefits over conventional electrowinning materials.

2. Materials and Experimental Procedure

The material we worked on was a Ti-Pb composite. It was supplied by Electrodes International. Titanium powder was consolidated into a porous titanium compact. The porous titanium compact was then infiltrated with lead by placing the appropriate amount of solid lead below the porous titanium compact and heating to 650-700°C in a neutral atmosphere.

Titanium compacts of different porosities were used, creating samples with different lead contents, as can be seen in Fig. 1. Lead content ranged from 20 to 51 vol.%, with a 20 vol.% porous Ti sample (titanium sponge) and a fully dense Pb sample serving as references (Tab. I).

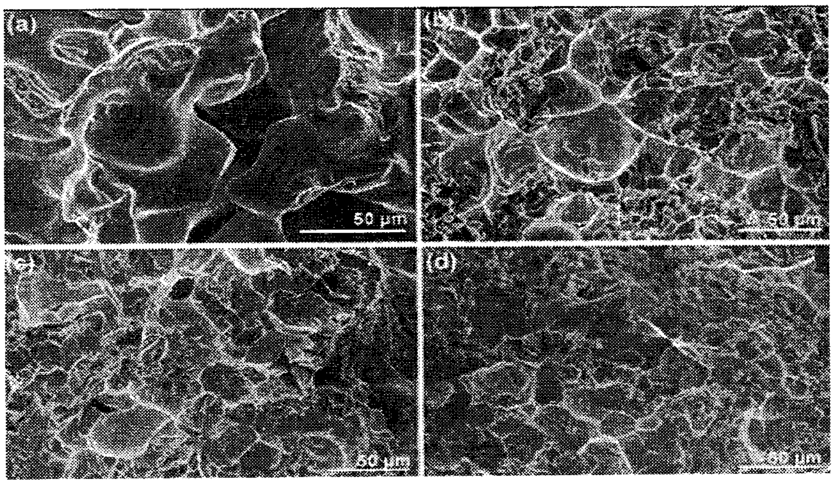

Fig. 1 SEM images of Ti-Pb composite material fracture surface: (a) is 20 % porous Ti; (b) 24 % Pb, 75 % Ti, 1 % pores; (c) 51 % Pb, 49 % Ti, 0 % pores; (d) 37 % Pb, 61 % Ti, 2 % pores.

Tab. I Composition of tested materials

Ti (vol.%)	Pb (vol.%)	Porosity (vol.%)
49	51	0
61	37	2
66	33	1
70	30	0
70	25	4
75	24	1
79	20	1
80	0	20

The samples were further machined, using standard machining techniques to produce samples of the correct dimensions for mechanical and electrochemical tests. The tensile samples were in accordance with ASTM standard E8 (Fig. 2a). 3cm square plates were used in the electrochemical analysis (Fig. 2b), with a 3 cm square stainless steel plate serving as the cathode.

An MTS tensile testing machine was used to mechanically test the samples are atmospheric conditions. A universal locating coupling was used on the machine to ensure proper alignment of the samples prior and during loading. Samples were then pulled until failure, measuring the force, displacement and time. From these values, subsequent values for stress, strain and elastic modulus were calculated using the following equations:

$$\sigma = F/A, \tag{1}$$

$$\varepsilon = \Delta l / l_o, \tag{2}$$

$$E = \sigma / \varepsilon, \tag{3}$$

where F is the instantaneous force applied, A is the cross sectional area of the reduced section, Δl is the instantaneous change in length of the reduced section, and l_o is the original gauge length. The elastic modulus was calculated by determining the slope of the stress strain diagram in the elastic regime. The calculated modulus value was found using the rule of mixtures

$$E = V_{Ti}E_{Ti} + V_{Pb}E_{Pb}, \tag{4}$$

where V is the respective volume fraction and E is the elastic modulus.

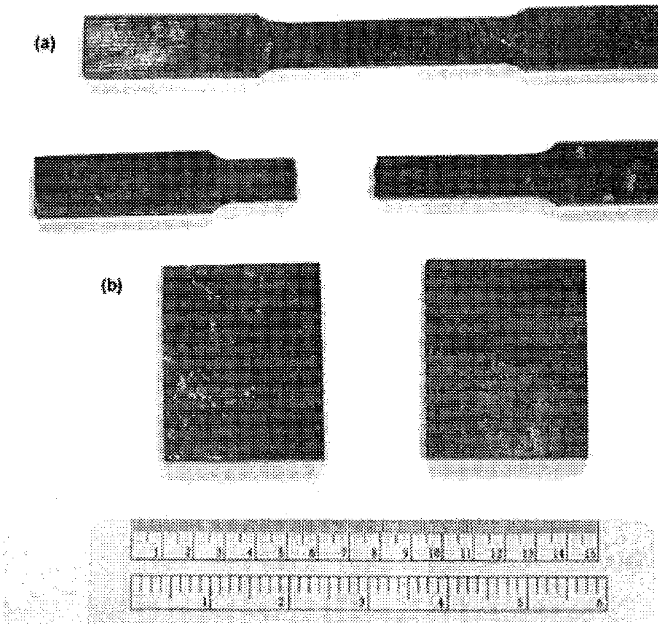

Fig. 2 Photograph of tensile samples (a) and electrochemical samples (b) before and after testing.

For metallographic preparation, a small section (approximately 5 mm) was cut off of the reduced section of each tensile bar. These sections were then mounted in a hot mounting press that operated at 180°C. The samples were then polished, four at a time, using the following sequence: S#240 SiC paper until plane; S#500 SiC, 5 N, 10 min; 4 μm diamond 5 N 10 min; 1 μm alumina hand polish until smooth. The samples were cleaned between polishing stages to remove excess polishing material, which ensured a better surface finish. After mounting and polishing, they were examined under an optical microscope to determine lead content, porosity, and grain size distribution throughout the sample.

For electrochemical testing, short-term deposition tests in a 250 ml beaker were utilized to compare the Ti-Pb composite material with lead. The beaker was filled with 150 ml of electrolyte and heated to 49°C. The electrolyte was composed of 40 g/l Cu^{2+}, 190 g/l H_2SO_4, and 1.5 g/l Fe^{2+} in distilled water. A single cathode (stainless steel) and anode (Ti-Pb material) setup was then placed face to face in the electrolyte solution 2 cm apart. A constant current density of 325 A/m^2 was passed through the setup for two hours. The cell voltage and electrolyte temperature were measured in half hour intervals. After two hours, the current was interrupted, the anode and cathode were rinsed in distilled water, dried and weighed and the electrolyte was replenished. These two-hour cycles were repeated up until 14 hours.

X-Ray diffraction tests were performed for a materials characterization study, specifically to determine the phase composition of the anodes. The samples tested were of compositions 51 vol.% Pb, and porous Ti with 0 vol.% Pb. The results indicate that the samples did not contain any intermetallic compounds, as can be seen by the absence of peaks other than Ti, Pb, and PbO in Fig. 3. Scanning electron microscopy (SEM) analysis was also conducted using an Amray SEM.

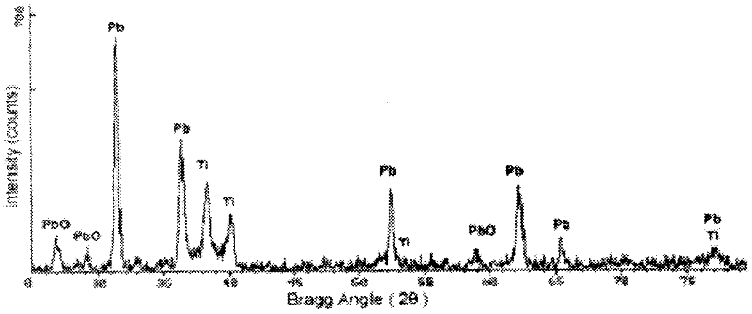

Fig. 3 X-ray diffraction spectrum for 51 vol.% Pb composite material.

3. Results and Discussion

3.1. Mechanical Testing

The goal of this portion of testing was to determine the mechanical properties of the material under stress. Given the tensile test results, an estimate of the new material's behavior under normal electrowinning tankhouse conditions, as compared with traditional materials, can be established.

From tensile test data analysis, all of the samples broke in the elastic regime before any plastic deformation could take place (Fig. 4). The stress at fracture, as well as the elastic modulus both increased with increasing Ti content, as can be seen in Figs. 5-6. From the data it is apparent that the elastic modulus (Fig. 6), the tensile strength (Fig. 5), and the strain at fracture (Fig. 7) all increase fairly linearly with decreasing Pb content.

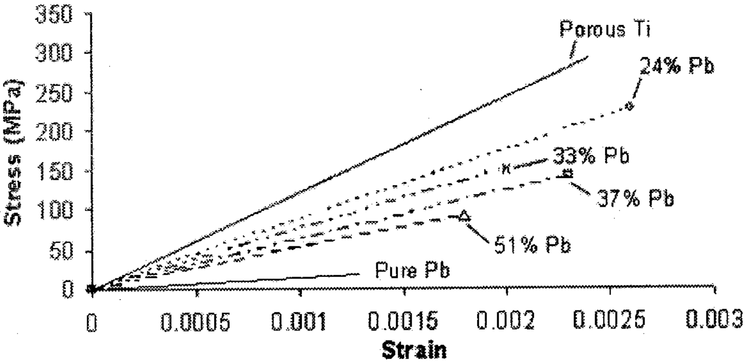

Fig. 4 Elastic behavior of the Ti/Pb composite, as compared to a porous Ti sponge and a fully dense Pb sample.

Using SEM analysis (Fig. 1) of the new fracture surface, it can be shown that the mode of fracture is brittle and intergranular in all cases. There is virtually no plastic deformation in either the Ti or the Pb grains. The fracture occurred primarily at the interface between grains. Another thing to note is the amount of porosity present between the Ti and Pb grains. These pores most likely serve as the crack initiation points, with the cracks propagating along the boundaries between grains. Even in the samples that were nominally dense (based on density measurements), some pores were found of the fracture surfaces (Fig 1c). Impure Ti, as well as Ti sponge, are brittle and show low deformability.

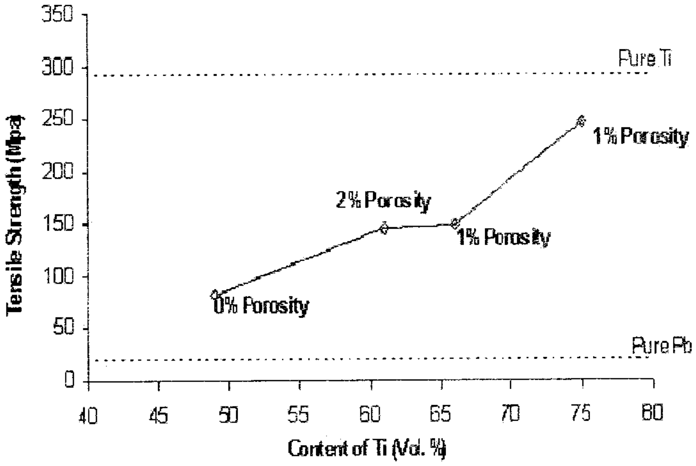

Fig. 5 Measured tensile of the Ti-Pb composite with varying Pb and porosity a room temperature.

It is interesting that alone, very pure titanium and lead have an elongation of approximately 50 and 40 % respectively, but the composite material had an elastic elongation of about 3-5 %. The major factors influencing these values are porosity, impurities in Ti, and Ti-Pb interfacial energy. Impure Ti, as well as titanium sponge also show low deformability and brittle fracture.

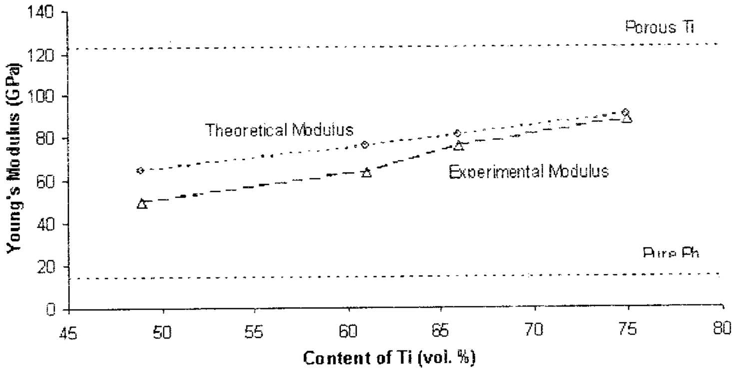

Fig. 6 Measured variation of the Young's modulus of the Ti-Pb compound with varying Pb concentration.

The calculated elastic modulus for the porous Ti sample from the rule of mixtures (Eq. 4) was slightly higher than the actual modulus of titanium (116 GPa), but this may be due to the slight inconsistency in the porosity values that were stated by the material provider, or hardening of the Ti sponge due to impurities that took place during compacting, resulting in a higher stiffness compared with pure Ti. The higher strength, modulus and low deformability of the Ti/Pb composites should completely eliminate undesirable deformation and warping of the anodes.

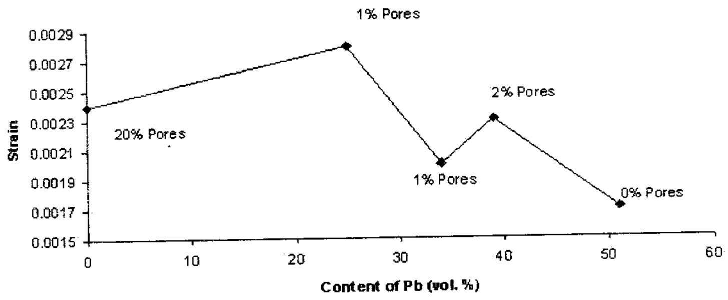

Fig. 7 Measured variance of the elongation to failure of the material with changing Pb and porosity values.

3.2. Electrochemical Testing

All of the deposits were smooth, compact and uniform. The mass of Cu deposited, along with the current efficiency was fairly constant with all of the anodes. The current efficiency of both the lead anodes and the Ti-Pb composite anodes varied between about 89 and 95 %, as shown by Fig. 8. The voltage also decreased approximately the same amount in all cases. In pure lead, however, the voltage dropped approximately 3 % more than with the new anode material (Fig. 9).

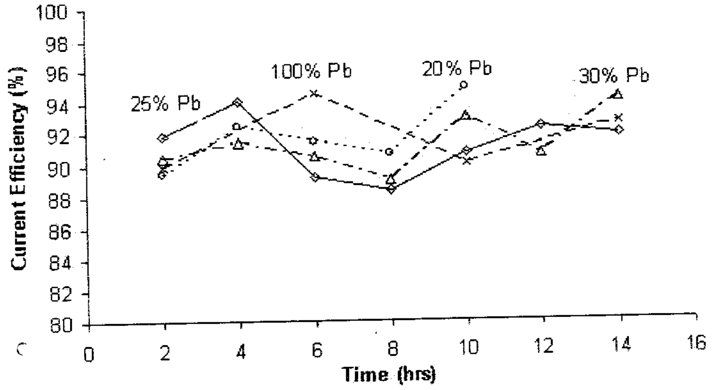

Fig. 8 Measurement of the non-variant current efficiency with respect to time.

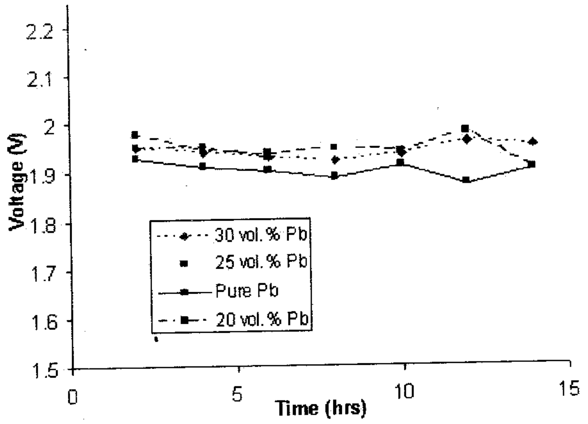

Fig. 9 Measurement of the voltage drop of the Ti-Pb composite with varying values for Pb composition with respect to time.

Anode weight loss characteristics show that the new material is comparable to lead, in this respect. All of the tests were within the range of data scatter of the lead reference. There was slightly more loss of material in the anode with 25 vol.% Pb, whereas the material with 30 % Pb is very similar in behavior to pure lead (Fig. 10).

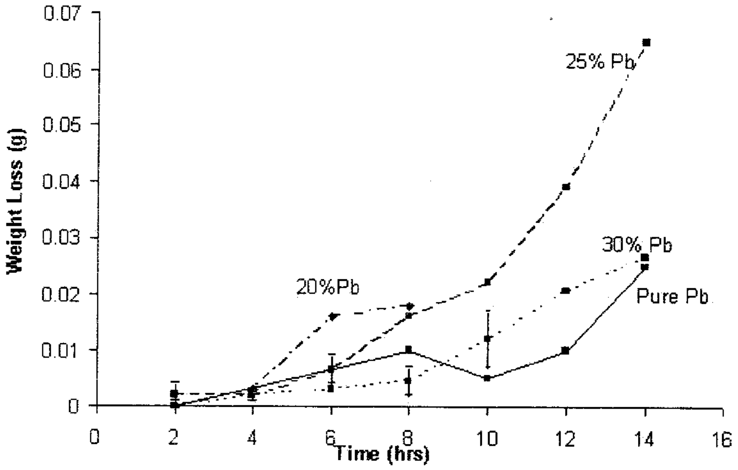

Fig. 10 Measurement of the weight loss of the anode with respect to time.

The 25 % lead anode had a porosity of about 5 % after metallographic analysis, whereas the other anodes have porosities from 0-2 %. That may explain why it has a behavior that is slightly different than the rest. Considering all of the tests fall within in same range of scatter, it is safe to say that the anode weight loss behaviors are comparable to what is currently in use. Porosity seems to have a dramatic effect on the loss properties, though; so minimizing porosity in the material should be a design criterion. Also, during the short-term deposition testing, the titanium helped to stabilize the lead, preventing it from spalling, eliminating the need for the addition of Co to the solution. This would help to decrease costs considerably. Future polarization tests would help to confirm the feasibility of this.

4. Conclusions

The Ti-Pb composite far outperformed traditional electrowinning alloys in terms of mechanical properties. This should translate into anodes that have a longer lifespan under industrial operating conditions. Deformations in the anodes under normal electrowinning conditions will be eliminated completely by using the Ti/Pb composite. Irregular current density, uneven deposits and short circuits due to anode warping that occur when lead anodes are used would be greatly lessened by the implementation of the composite. The composite with 30 vol.% lead showed electrochemical behavior similar to pure lead. Thus, Ti/Pb composite with 30 % lead has the optimal combination of mechanical and electrochemical properties.

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