The Polarographic Determination of Small Amounts of Tin in Zinc Die Casting Alloys

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Zinc alloys for die-castings should, on account of the danger of intergranular corrosion, contain only minute amounts of Cd, Pb, Tl, Bi and Sn.

The alloys designated Zamak 2, 3 and 5, for example, may contain a maximum of 0.005 % Cd, Pd and Sn. For some other zinc alloys (Commercial rolled zinc) and Zilloy 15 and 10 the maximum content of Sn is 0.001 %. These small percentages may be determined polarographically, as it is very difficult to apply ordinary methods of chemical analysis.

When the sample contains traces of Cu, a reliable analysis of Pb, Cd and Sn is easily obtained; the polarogram gives the copper content as well. With a larger copper content, such a high voltage has to be applied that a direct determination of Sn cannot be carried out. In such cases Sn has to be separated from Cu. Methods have been described according to which Cu may be electro-deposited from solutions containing hydrochloric¹ or sulphuric acid². As the ratio of the copper and tin percentages is often 10 000 : 1, there is great risk, however, that Sn is codeposited with Cu. Direct determination of Sn in amounts less than 0.0015 % is not to be recommended¹. The tin content, therefore, has to be enriched and this may be brought about by precipitation as sulphide together with Cu³, as sulphide together with Mo (in steel)⁴, as metastannic acid together with manganese dioxide, as metastannic acid together with aluminium hydroxide and finally with kupferron². In these methods the Sn content is determined volumetrically with potassium iodate^{3,5,6} or with colorimetric⁶ or polarographic methods^{2,4,7}. For routine analysis all these procedures are far too time-consuming. Moreover, they are not very suitable for the determination of traces of Sn in Zn alloys with high Cu content.

The present investigation was undertaken with a view to obtaining a direct and sufficiently accurate method for routine analysis.

The procedure developed is the following: The Zn alloy is dissolved in hydrochloric acid. After this operation Cu and Sn are obtained as a metallic residue, which is dissolved in nitric acid. Sn is precipitated as metastannic acid, which is fused with sodium hydroxide and the Sn is determined polarographically as Sn^{4+} .

PRECIPITATION OF TIN AS METASTANNIC ACID

Precipitation of small amounts of tin as metastannic acid has been studied by, among others, Hagen, Hoffman-Bang and Gjertsen⁵. These authors point out that metastannic acid is thereby precipitated in a very finely divided, partly colloidal form. Quantitative filtration through filter paper is therefore impossible. Furthermore, a considerable loss of tin is caused by the fact that metastannic acid adheres very firmly to the beaker. In an experiment, carried out by these authors, 6.61 mg of Sn was precipitated as metastannic acid after boiling with nitric acid. 57 % of the tin content stuck to the beaker and could not be removed. Heating was done with a small flame.

It is also known that the presence of iron and chromium ions fosters the formation of metastannic acid in colloidal form. The precipitation of metastannic acid is also disturbed by the presence of phosphoric acid, hydrochloric acid and sulphuric acid. As to the adsorption of the metastannic acid on the bottom of the beaker in the investigation referred to above, this was undoubtedly due to too high a temperature, caused by the flame. This difficulty was to a large extent avoided in the present investigation by heating the beaker on a heating plate with a temperature of 280–300° C.

The precipitates have been filtered through close-texture filter paper with filterpulp (filter paper macerated with nitric acid to make it more retentive). By this means it has also been possible to avoid the use of any collecting substance (as manganese dioxide), which adsorbs copper, which in its turn interferes with the polarographic determination of tin.

In order to investigate how completely metastannic acid can be precipitated from a nitric acid solution containing a large excess of copper ions, the following series of experiments was carried out: 2.50 g of cupric oxide (Baker's C.P.) was added to a known quantity of hydrochloric acid tin standard solution (1 ml = 1 mg of Sn), dissolved in 15 ml of conc. nitric acid and evaporated to 3 ml. In order to volatilize completely the hydrochloric acid two further portions of 5 ml of nitric acid were added and after each addition the solution was evaporated to 3 ml. Finally 5 ml of conc. nitric acid was added, and then the solution was diluted with hot water to 50 ml and was kept in a warm place over-night. The precipitated metastannic acid was filtered

off on a close-texture filter paper, which was coated with filter pulp. The beaker was thoroughly wiped with filter paper. The precipitate was washed with a warm solution containing 5 % ammonium nitrate and 2 % nitric acid until Cu had been washed out. The filter paper was placed in a platinum crucible, dried and ignited in an electric furnace at 500—600° C. The residue was transferred to a silver crucible and fused with 0.2—0.3 g of sodium hydroxide over a gas flame. Before heating, the silver crucible was placed in a porcelain crucible. After the fusion, which proceeds very rapidly and is completed in 2—3 min. after the sodium hydroxide has melted, the contents of the crucible were dissolved in 3—4 ml of water, which was added in 3 portions and heated

Table 1. Precipitation of tin as metastannic acid.

The tin was determined polarographically as Sn^{4+} .

Experiment No.	Addition of Sn mg	Diffusion current in relative units (mm)		Tin mg	Corrected tin content mg	Error %
		Sample	Reference solution ***			
1	0.00	5	0.0	0.05 *	—	—
2	0.30	31.5	27.6	0.34	0.29	— 3.3
3	0.30	30.8		0.33	0.28	— 6.7
4	0.30	29.7		0.32	0.27	— 10.0
5	0.50	37.4	35.1	0.53	0.48	— 4.0
6	0.50	36.2		0.52	0.47	— 6.0
7	0.50	35.0		0.50	0.45	— 10.0
8	1.00	44.3	48.2	0.92	0.87	— 13.0
9	1.00	45.4		0.94	0.89	— 11.0
10	2.00	54.7	57.7	1.90	1.85	— 7.5
11	2.00	53.0		1.83	1.78	— 11.0
12	3.00	59.8	64.8	2.75	2.70	— 10.0
13	3.00	59.5		2.75	2.70	— 10.0
14	3.00	33 **	35.1 **	2.85	2.80	— 6.7
15	3.00	32.6		2.79	2.74	— 8.7
16	3.00	34.9		2.98	2.93	— 2.3
17	3.00	35.5		2.86	2.81	— 6.3

* Corresponds to the tin content of the cupric oxide.

** The sample was diluted to 25 ml.

*** Contained exactly as much Sn as was added to the test example.

to boiling each time. Finally the crucible was washed with 3 ml of conc. hydrochloric acid, which was mixed with the alkaline solution previously obtained. 1 ml of perchloric acid was added and the solution heated to boiling. After cooling the sample was diluted to 10 ml with polarographic supporting electrolyte (330 ml of conc. hydrochloric acid, 100 ml of a 2 % gelatin solution and 570 ml of water) and was run into the polarographic cell. At the same time reference solutions containing a known amount of tin standard solution and sodium hydroxide, hydrochloric acid and perchloric acid in amounts mentioned above and tempered under the same conditions as the samples were run into the cell.

In the polarographic tin determination the tin was determined as Sn^{4+} , this being the simpler procedure compared to the determination of Sn^{2+} which involves reduction of Sn^{4+} and the use of an inert atmosphere. The advantages gained by the determination of Sn^{4+} have been pointed out by Stackelberg⁸. The conditions in this determination have been more closely investigated by Lingane⁹. For the investigation the present author has used the Radiometer-København Type PO 3a polarograph.

The results of the experiments with the isolation of tin as metastannic acid are shown in Table 1.

SEPARATION OF TIN FROM ZINC ALLOYS BY INTERNAL ELECTROLYSIS

After the favourable results reported above a series of experiments was made on the separation of tin (together with copper) from zinc alloys. The alloy designated Zamak 5 and containing 2.84 % of copper and a very low percentage of tin was used for this purpose. It was dissolved in hydrochloric acid and to this solution was added a known volume of tin standard solution. The same result was obtained, if the tin standard solution was directly added to the sample.

Separation of tin is assumed to proceed in the following way. In the dissolution of the alloy, copper which has been dissolved primarily is reduced to the metallic state by the zinc. An element $\text{Zn}/\text{HCl}/\text{Cu}$ is then formed. Here, Zn is the anode and goes into solution and tin is deposited on the cathode. This may be regarded as an example of internal electrolysis, in which both electrodes are supplied by the specimen that is to be dissolved.

Lead, cadmium and bismuth can be deposited on the copper in the same way as tin but lead does not interfere with the determination of tin, since it goes into solution in the subsequent treatment of the sample with nitric acid. It has been verified experimentally, however, that no appreciable amounts of lead or cadmium accompany the copper, and the filtrate is well suited for

the polarographic determination of lead and cadmium. This has also been verified by L. C. Copeland and F. S. Griffith¹⁰. The copper is so sparingly soluble in the filtrate that it does not interfere with the polarographic determination of lead and cadmium.

Elementary silicon ("black" silicon), that is often present in Zamak alloys, is carried along with the tin but in this case it plays a useful role since it aids the separation and ignition of the metastannic acid.

PROCEDURE

100 g of zinc alloy turnings was dissolved in 330 ml of conc. hydrochloric acid in a 3 l beaker, cooled in running water during the dissolution. When only one or two turnings were left, the precipitated copper and tin was filtered off on a large glass filter (Jena GL) and washed 5 times with water (altogether 500 ml).

The precipitate was transferred to a 100 ml beaker and after most of the water had been decanted the precipitate was dissolved in 15 ml of conc. nitric acid. After the dis-

Table 2. Separation of tin from a zinc alloy (containing 2.84% of copper) by internal electrolysis. The tin was determined polarographically as Sn^{+4} .

Exp. No	Addition of tin mg	Diffusion Current in relative units (mm)		Tin content mg	Corrected tin content mg	Error %
		Sample	Reference solution ***			
18	0.00	3	—	0.03 *	—	—
19	0.30	31.0	28.8	0.32	0.29	— 3.3
20	0.30	31.6		0.33	0.30	0.0
21	0.30	30.5		0.32	0.29	— 3.3
22	0.50	37.6	35.5	0.53	0.50	0.0
23	0.50	37.7		0.53	0.50	0.0
24	0.50	37.5		0.53	0.50	0.0
25	0.50	29.0		0.48	0.45	— 10.0
26	1.00	44.7	47.9	0.93	0.90	— 10.0
27	1.00	46.3		0.97	0.94	— 6.0
28	2.00	55.0	59.0	1.87	1.84	— 8.0
29	2.00	36.4 **	38.3 **	1.90	1.87	— 6.5
30	3.00	31.3 **	33.3 **	2.82	2.79	— 7.0

* Determined with reference solution 0.3 mg Sn.

** Solution diluted to 25 ml.

*** Contained exactly as much Sn as was added to the test example.

solution was completed the solution was evaporated to 3 ml. In order to expel the hydrochloric acid completely two further portions of 5 ml of conc. nitric acid were added and after each addition the solution was evaporated to 3 ml. Finally 5 ml of conc. nitric acid was added, and then the solution was diluted with hot water to about 50 ml and was allowed to stand hot over-night. The metastannic acid was treated further as described above.

The results are shown in Table 2.

As seen the error range is between 0 % and - 10 %. If the result is increased by 5 % (or multiplied with 1.05) a value is obtained having an error of ± 5 %.

SUMMARY

A procedure has been developed for the determination of tin in amounts from 0.0003 % to 0.003 % Sn in zinc die-casting alloys with high copper contents. The sample is treated with hydrochloric acid, and copper and tin are obtained as a residue, which is dissolved in nitric acid. Tin is precipitated as metastannic acid, then fused with sodium hydroxide and finally tin is determined polarographically as Sn^{4+} as the diffusion current between -0.4 and -0.6 V. By this method, tin can be determined with an accuracy ± 5 % when present in amounts from 0.0003 % to 0.003 %. The procedure is useful for the routine determination of trace amounts of tin in zinc die-casting alloys with a high copper content.

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