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SUMMARY OF RESULTS

The standard lead reduction method for the determination of tin in alloys has been investigated with respect to its suitability for the analysis of Zircaloy. Results show that it cannot be used for this purpose; since nickel and chromium, two elements which are present in Zircaloy, interfere seriously. Nickel gives a negative error and chromium gives a positive error.

The investigation was extended to include the use of iron powder, aluminum foil and nickel foil as reducing agents. All three of these proved to be satisfactory; but, in the case of the iron powder, it is essential that a small quantity of antimony trichloride be present; otherwise low tin values will be obtained.

The occurrence of considerable segregation in Zircaloy has been demonstrated and it is shown that remelting of the alloy is a means of reducing the segregation.

It is shown that contamination with iron is negligible, when Zircaloy is sampled with a steel shanked, Carboloy tipped drill.

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CONTENTS

INTRODUCTION

This investigation was initiated because of the erratic values obtained for the tin content of four samples of Zircaloy II, which were submitted to the Chemical Laboratory by Mr. H.V. Kinsey, Head of the Refractory Metals Section, Physical Metallurgy Division.

The tin, iron and chromium in these samples were intended to be in the normal range for this alloy; but the nickel was varied through an approximate range of 0.003, 0.05, 0.10 and 0.5%.

Analyses yielded the following results:-

TABLE 1

Apparent Variation in the Tin Content of
Four Samples of Zircaloy II

Sample No.	Per cent			
	Sn	Fe	Cr	Ni
1	1.42	0.14	0.094	0.003
2	1.34	0.27	0.109	0.056
3	1.34	0.15	0.102	0.094
4	0.52	0.12	0.105	0.515

Since no appreciable differences were expected in the tin contents of the samples, it was decided to run check analyses on samples No. 1 and 4. The results were:-

No. 1 - 1.42% Sn

No. 4 - 0.53% Sn

It appeared from this, that the higher nickel content of sample No. 4 may be the cause for the low tin result obtained.

The method of analysis used for the tin determination was the well known standard lead reduction method. Briefly stated, a 2 g sample was dissolved in a flask containing 60 ml of water, 5 ml of H_2SO_4 and about 20 drops of HF. To this was added 1 g H_3BO_3, 150 ml H_2O, 80 ml HCl and 5 g of granulated lead. The solution was then boiled for 45 minutes, cooled in a CO_2 atmosphere and titrated with N/10 iodine. This procedure is essentially the same as one of two methods given in a 1957 U.S. Atomic Energy Commission publication (4).

Also, Hillebrand and Lundell (1) stated that nickel and chromium do not interfere in the lead reduction method for the determination of tin. However, in the 2nd edition of the same book (2), while it is still stated that nickel does not interfere, the statement with reference to chromium has changed and it is claimed that chromium gives a positive error in both the lead and nickel reduction method for tin.

A check of the literature was made back to 1950, to

ascertain whether nickel had been reported as interfering in the lead reduction method for the determination of tin; but no information was found on this subject. A search for earlier references was not made, because it was assumed that recent textbooks on analytical chemistry would include such references.

It was, therefore, decided to carry out experiments to determine whether, in fact, nickel does interfere in a manner to cause low results for tin and, also, to check the extent of the interference by chromium.

EXPERIMENTAL WORK

1. The Interference of Nickel in the Determination of Tin by the Lead Reduction Method

A series of solutions was made up containing the following quantities of elements, plus the reagents used to dissolve a sample of Zircaloy:

	mg
Sn	30
Fe	2
Cr	2

To these were added varying amounts of nickel. The solutions were then carried through the lead reduction procedure and titrated with iodine. The results were as follows:-

TABLE 2

Determination of Tin in Synthetic Solutions Containing Varying Quantities of Nickel

Nickel Added mg	Iodine Titration ml	Tin Recovered mg
nil	5.0	29.7
2	4.2	24.9
10	1.8	10.7

These results indicated a very serious negative error with only 2 mg of nickel being present. The data were confirmed in the following more extensive tests, in which increasing quantities of nickel were added to solutions, each containing 40 mg of tin. These were reduced with lead and titrated with N/10 iodine.

The results are given in Table 3.

TABLE 3

Tin Recovered from Solutions to which Increasing Quantities of Nickel were Added

Tin Present mg	Nickel Added mg	N/10 Iodine ml	Tin Recovered mg
blank	nil	0.10	--
40.00	"	6.55	40.00
"	1.0	6.10	37.15
"	5.0	4.62	28.00
"	10.0	3.12	18.70
"	15.0	1.85	10.83
"	20.0	0.57	2.91
"	25.0	0.10	0.00
"	30.0	0.10	0.00

It is evident from the above results, that the lead reduction method for the determination of tin cannot be used when nickel is present in the solution.

In order to try to establish the mechanism of the interference by the nickel, that is, whether it is due to incomplete reduction of the tin to the stannous condition, or to the complete reduction of the tin to the metallic state and its removal from the solution by precipitation, the following experiment was done in duplicate.

A solution containing 40 mg of tin and 15 mg of nickel was reduced with an excess of lead in the usual way. It was then filtered and the residue of lead and deposited material washed with 1:3 hydrochloric acid. Any precipitated tin and nickel were dissolved from the lead with a mixture of hydrochloric acid and hydrogen peroxide. This solution and the filtrate were then reduced with iron powder; 2 - 3 drops of a 1% solution of antimony trichloride having previously been added, as catalyst. The solutions were then cooled in an atmosphere of carbon dioxide and titrated with iodine.

The results obtained in the two experiments are given in Table 4.

TABLE 4

The Distribution of Tin After a Solution Containing Tin
and Nickel has been Reduced with Excess Lead

No.	Tin in Filtrate mg	Tin Deposited on Lead mg	Total Tin mg
1	10.2	30.0	40.2
2	10.8	29.1	39.9

As shown in the above table, the total tin found in the filtrate and in the deposit on the lead was very close to the 40 mg of tin that were present in the solution originally. The results also prove that the tin is actually precipitated on the lead in the presence of

nickel and, further, since the solutions each carried 15 mg of nickel, it appears that 1 part by weight of nickel will precipitate 2 parts by weight of tin. (1:1 atomic ratio)[*].

2. Composition of the Deposit Which Forms on the Lead when a Tin Solution Containing Nickel is Reduced with Lead

In order to try to establish the nature and physical structure of the deposit that forms on the lead, two samples were prepared from two solutions. One solution contained 25 mg of nickel and 50 mg of tin; the other solution contained 50 mg of nickel and 100 mg of tin. Both were adjusted to the usual acidity with hydrochloric acid and then, in each case, boiled with 2.5 g of lead foil. Boiling was continued until just short of complete solution of the lead. The solutions were then cooled, decanted and the precipitates washed by decantation.

After drying, the precipitates were examined by X-ray and the diffraction patterns obtained were identical and corresponded to a nickel-tin alloy containing approximately 58% Ni - 42% Sn (atomic %)[*], having a hexagonal structure.

These results lead to the conclusion that the interference, caused by the presence of nickel in a tin solution which is being analyzed by the lead reduction procedure, is the result of complete reduction of the nickel and tin to the metallic state and precipitation of the two as an alloy.

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* No explanation has been found for the discrepancy indicated for the composition of the residue. The chemical data indicated an atomic ratio of Ni:Sn = 1:1, the X-ray data, 58:42.

3. <u>The Magnitude of the Interference Caused by Chromium in the Determination of Tin by the Lead Reduction Method</u>

Three synthetic solutions were made up and used in this investigation. They were similar in composition, with respect to reagents, to a Zircaloy sample solution being analyzed for tin, except that no tin was present. One solution contained no chromium (blank) and the other two solutions contained 2 mg and 10 mg of chromium respectively.

These were boiled, reduced with lead in the regular way and titrated in duplicate with N/10 iodine.

The results are shown in Table 5.

TABLE 5

<u>Iodine Consumed by Chromium</u>

Solution No.	Chromium Present mg	Titration, N/10 Iodine ml
blank	nil	0.1
"	"	0.1
No. 1	2	0.2
"	2	0.2
No. 2	10	0.9
"	10	1.1

From the above, a calculation shows that a positive error of 0.03% tin would be introduced by the chromium present in a 2 g sample of Zircaloy II containing 0.10% chromium.

Obviously then, the lead reduction method is not satisfactory for determining tin in alloys containing appreciable quantities of chromium.

It was necessary, therefore, to expand this investigation in an effort to find a suitable substitute reducing agent for lead; one that would be free from interference by nickel and chromium, when used for determining tin in Zircaloy.

4. Other Reducing Agents Investigated

a) Iron Powder

The acid and other reagents used are essentially the same as for the lead reduction and are those given by W.A. Dupraw (3). Dupraw's procedure has become the A.S.T.M. method (5) for the analysis of tin in titanium alloys.

In applying the method to zirconium alloys, a few changes were made; such as, using a larger sample, e.g., 2 g and substituting N/10 iodine for 0.02 N potassium iodate, because the latter gave a very high blank.

The procedure calls for dissolving 2 g of alloy in a 500 ml flask containing 60 ml of water, 10 ml of 1:1 sulphuric acid and 10 ml of fluoboric acid. The solution is then diluted with 100 ml of water and 80 ml of hydrochloric acid and 2 drops of

1% antimony trichloride solution added. Five grams of iron powder are then added and the flask stoppered with a bent tube dipping into a saturated solution of sodium bicarbonate in a beaker. The flask is heated gently until all the iron is dissolved and the solution is boiled 2 minutes, cooled to about 15°C while the bent tube is still submerged in the sodium bicarbonate solution. Titration with the N/10 iodine is done in the usual manner.

In order to determine if nickel interferes in this procedure and, also, if the presence of a small quantity of antimony trichloride is essential for accurate tin results, a series of solutions was made up in which the quantity of tin present was constant at 30 mg and the quantities of nickel and antimony trichloride were varied. These solutions were then reduced with iron and titrated.

The results are given in Table 6.

TABLE 6

The Effects of Antimony Trichloride and Nickel on the Results
Obtained when a Tin Solution is Reduced with Iron Powder

Solution No.	Composition mg		$SbCl_3$ Added	N/10 Iodine ml	Sn Found mg
1	Sn Ni	30 2	nil	1.0	5.9
2	Sn Ni	30 2	2 drops	5.0	29.7
3	Sn Ni	30 10	nil	3.0	17.8
4	Sn Ni	30 10	2 drops	5.0	29.7

These results were confirmed in other tests and show that iron is a satisfactory reducing agent, if antimony trichloride is present in a small quantity and, also, that nickel does not interfere under these conditions.

It was not felt necessary to check possible interference due to chromium, as Dupraw (3) had investigated this and found no interference from as much as 40 mg of chromium.

The procedure was then applied to the analysis of the four Zircaloy samples listed in Table 1, and which were also analyzed by a method involving sulphide separation of the tin, followed by solution of the sulphides and reduction of the tin with test lead.

The results are shown in Table 7.

TABLE 7

Comparison Between Iron Reduction and H_2S Separation
Followed by Lead Reduction

Sample No.	Iron Reduction Method % Sn	H_2S Separation and Lead Reduction Method % Sn
1	1.47 1.47	1.45
2	1.47 1.47	1.48
3	1.53 1.53	1.52
4	1.47 1.50	1.48

The agreement between the results obtained by the two methods is quite satisfactory.

Also, the National Bureau of Standards' standard sample No. 360, Zircaloy II, with a certificate value of 1.43% Sn was analyzed in quadruplicate by the iron reduction method and the following percentages obtained:-

% Sn = 1.42, 1.42, 1.45, 1.42 Average = 1.42 (6)

b) Aluminum Foil (6)

Satisfactory results were obtained, also, when aluminum foil was used as the reducing agent. Three grams of the foil were adequate for the reduction of a 2 g sample of Zircaloy II. As with iron, the solution is boiled until all the aluminum metal is used up and then the boiling is continued for another two minutes.

c) Nickel Foil (2)

Ten square inches of foil, 0.005 in. thick were used per 2 g sample of Zircaloy II and proved satisfactory for the tin reduction. The acidity of the solution and other conditions were similar to those that prevailed when the other metals were used and, as with lead, it is not necessary to remove the excess nickel before titrating. The solution, however, must be cooled before the titration can be done.

The main disadvantage to the use of nickel as the reducer, is the green colour it imparts to the solution, thereby making it

difficult to see the blue end point of the starch.

Duplicate determinations of the tin in N.B.S. standard sample No. 360, Zircaloy II, using nickel foil as the reducer, gave the following results:-

$$\% \text{ Sn} = 1.41, \ 1.42$$

The certificate value for this sample is:-

$$\% \text{ Sn} = 1.43$$

However, it should be recognized that, in the case of alloys containing higher percentages of chromium, reduction with nickel may result in positive errors for the tin.

INVESTIGATION OF SEGREGATION IN ZIRCALOY

Difficulty has been experienced in obtaining samples of Zircaloy that were uniform in composition. This probably stems from the fact that the alloying of zirconium with the tin, chromium, nickel and iron is accomplished by the consumable electrode melting process.

In April 1961, seven samples were obtained from an ingot of Zircaloy II which had been melted once and in which the target analysis was as follows:-

Sn - 1.50%

Cr - 0.10

Ni - 0.05

Fe - 0.12

These were analyzed with the following results, on individual samples, given in Table 8.

TABLE 8

Analyses of Seven Samples Taken from an Ingot of Zircaloy II

Lab. No.	Sample No.	Per cent			
		Sn	Cr	Ni	Fe
1798	1	2.25	0.05	0.040	0.125
		2.34	0.07	0.041	0.120
		2.25	0.08		0.125
					0.130
1799	2	1.41	0.06	0.046	0.150
		1.39	0.08	0.045	0.125
		1.45	0.07		0.140
					0.140
1800	3	1.33	0.07	0.039	0.130
		1.33	0.05	0.041	0.112
		1.36	0.08	0.040	0.130
1801	4	1.57	0.08	0.040	0.315
		1.63	0.13	0.047	0.375
		1.57	0.13		0.305
					0.38
1802	5	2.19	0.08	0.041	0.195
		2.16	0.09	0.037	0.195
		2.13	0.11		0.21
					0.21
1803	6	0.98	0.08	0.053	0.170
		0.95	0.10	0.053	0.157
		1.07	0.12		0.130
1804	7	0.77	0.09	0.059	0.158
		0.77	0.12	0.062	0.145
		0.74	0.13		0.170

It is clearly seen that there are very large variations in the tin contents of the above samples. Variations in the other elements are, in some cases, large also.

It was thought that remelting and rolling the ingot should eliminate some of the variations in composition due to segregation. This was therefore done and samples were taken from five locations on the rolled plate by drilling right through the plate. Also, a solid Carboloy drill was used in order to eliminate any possible chance of contamination with iron.

The analyses of these samples are recorded in Table 9.

TABLE 9

Analyses of Five Samples Taken from a Remelted and
Rolled Ingot of Zircaloy II

Lab. No.	Sample No.	Per cent			
		Sn	Cr	Ni	Fe
3214	1	1.70	0.11	0.053	0.178
		1.70			
		1.68			
		1.50			
3215	2	1.65	0.11	0.054	0.165
		1.66			
		1.71			
		1.74			
3216	3	1.62	0.10	0.050	0.170
		1.70			
		1.59			
		1.68			
3217	4	1.70	0.10	0.056	0.169
		1.46			
		1.53			
		1.40			
3218	5	1.57	0.10	0.053	0.180
		1.50			
		1.40			
		1.40			

The above figures show there was a distinct improvement in the uniformity of composition of the alloy. The individual results for chromium, nickel and iron are close enough that they may be considered to be within the limits of experimental error. However, there are still considerable variations in the percentages of tin; but these are not of the same magnitude as prevailed after a single melting of the alloy. These discrepancies were considered to be still due to segregation; since standard samples run at the same time and by the same procedure gave correct results.

In order to check further on the segregation theory, three drilled samples were obtained from each of three locations on the rolled plate. The Carboloy drill was used again in order to insure against iron contamination. At each location, the first sample was from the top 1/8 in. of the plate, the second was from the centre 1/4 in. and the third was from the bottom 1/8 in. In every case the whole sample was dissolved and a suitable aliquot taken from the solution.

The analyses are given in Table 10 below.

TABLE 10

Tin Content of Samples Taken from the Top, Centre and Bottom Sections of a Zircaloy Plate

Lab. No.	Sample No. and Description	% Sn
4164	1 T - Top 1/8 in. of plate	1.36
4162	1 C - Centre 1/4 in. of plate	1.69
4160	1 B - Bottom 1/8 in. of plate	1.67
4165	5 T - Top 1/8 in. of plate	1.39
4163	5 C - Centre 1/4 in. of plate	1.66
4161	5 B - Bottom 1/8 in. of plate	1.62
3903	6 T - Top 1/8 in. of plate	1.46
3902	6 C - Centre 1/4 in. of plate	1.70
3901	6 B - Bottom 1/8 in. of plate	1.70

It is readily seen from the above figures, that all samples taken from the top section of the plate contain appreciably less tin than the samples from the centre and bottom sections. This is definitely a case of segregation and it follows that if a sample is obtained by drilling right through the plate, then individual fragments comprising the sample used for the analytical determination could differ widely in tin content, depending on the location in the plate from where they originated.

In some earlier work, samples had been taken with a steel shanked, Carboloy tipped drill and with some of these samples, difficulty had been experienced in obtaining check results of the iron. This was thought to be due to smearing of the drillings with iron from the steel shank. To prove if this was the case, the drillings were treated with 1:3 hydrochloric acid, then washed with water and dried before taking the sample for the iron determination. Results were still erratic, indicating that the trouble was due to segregation in the alloy and not to contamination from the drill.

In the case of a series of samples, which had been leached with acid in this way, a quantitative determination was made of the iron that had been removed and it was found that the contamination was not serious; since it ranged from 0.002 to 0.006% Fe.

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