The Photometric Determination of Copper in Aluminium Alloys with Tetraethylene Pentamine

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SYNOPSIS—For the control analysis of aluminium alloys a rapid and reasonably accurate method for determining copper is essential. A photometric method based on the complex formed with sodium diethyldithiocarbamate has been used, but this reagent is somewhat too sensitive for the purpose because the maximum concentration of copper that can be measured in a standard 4-cm. cell is but $2\cdot 5 \ \mu$ g. per ml. As a consequence, the conversion factor from extinction to percentage is large and, under routine conditions, the standard error for alloying quantities becomes excessive. Furthermore, in the important group of aluminium - copper - nickel alloys the nickel interferes. The ammonia reaction, on the other hand, is not sufficiently sensitive.

Tetraethylene pentamine is about three times as sensitive as ammonia and about one-fortieth as sensitive as sodium diethyldithiocarbamate.

The method described is rapid. It is free from interference and has a standard error of 0.04 per cent. for the range 1 to 4.5 per cent. of copper.

THE photometric diethyldithiocarbamate method for the determination of copper in aluminium alloys¹ is not very specific, several metals form complexes with the reagent and interfere with the determination. In particular, nickel forms a greenish-brown product, iron a goldenbrown ferric citrate, and lead, tin, antimony, cadmium and chromium, if present in quantity, form white turbidities. A separation from the interfering metals is then necessary. Furthermore, the method has not proved particularly reliable in routine use, especially for the larger quantities of copper.

During an investigation of a number of amines as possible reagents for copper, tetraethylene pentamine was found to be the most sensitive of those available, its sensitivity being more than three times that of ammonia. This amine was suggested as a reagent for copper by Crumpler² who stated that it was subject to the same interferences as those associated with ammonia. This statement, for which no experimental evidence was offered, was not confirmed. Crumpler's tests were made by adjusting the pH of an acid copper solution to $3 \cdot 5$ to $4 \cdot 0$ with dilute sodium hydroxide solution, followed by the addition of 10 ml. of a 2 per cent. solution of the amine. Experiments using an ammoniacal citrate or tartrate solution carried out in these laboratories showed no appreciable intereference from the metals usually found in aluminium alloys.

It was therefore appreciated that a method based on the use of tetraethylene pentamine for the determination of copper in aluminium alloys might represent a considerable improvement on the existing diethyldithiocarbamate method. A full investigation was therefore undertaken.

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EXPERIMENTAL

CHOICE OF AMINE-

A standard copper solution was prepared from electrolytic copper, and aliquots representing 0.01 g. of copper were treated with ammonia until formation of the cuprammonium complex began. Five ml. of a 5 per cent. solution of the amine were added, the solutions diluted to 200 ml. and their extinctions measured on the Spekker absorptiometer in 4-cm. cells. The results are shown in Table I for the full range of available amines.

TABLE I

Ilford filter No.

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Amine	605	606	607	608	609
Ethanolamine	0.150	0.158	0.152	0.160	0.083
Diethanolamine	0.172	0.208	0.225	0.268	0.152
Triethanolamine	0.116	0.120	0.197	0.262	0.223
Ethylene diamine	0.218	0.220	0.190	0.205	0.112
Diethylene triamine	0.232	0.308	0.350	0.398	0.310
Triethylene tetramine	0.390	0.410	0.402	0.402	0.255
Tetraethylene pentamine	0.245	0.372	0.485	0.580	0.505
Hydroxyethyl ethylene diamine	0.230	0.265	0.262	0.308	0.193
Mixed isopropanolamine	0.116	0.157	0.196	0.270	0.220
Tri-isopropanolamine	0.110	0.123	0.200	0.285	0.222
Diethylamino ethanol	0.245	0.232	0.202	0.225	0.124
Phenyl diethanolamine	0.179	0.223	0.248	0.293	0.182
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These results show that tetraethylene pentamine is the most sensitive amine and that the Ilford No. 608 filter gives the highest sensitivity. A calibration graph using this amine and filter gave a straight line plot of extinction against concentration.

PROPERTIES OF THE CUPRAMINE COMPLEX-

Experiments showed that the complex was not influenced by temperature variations and was stable for a long period of time, at least 7 days. The effect of cellulose was studied and two filtrations through a medium texture filter paper had no effect; although repeated filtrations or the addition of accelerators and subsequent filtration resulted in slightly high extinctions.

AMOUNT OF AMINE REQUIRED---

It was found that 0.01 g. of copper required approximately 5 ml. of a freshly prepared 2 per cent. solution of the amine for complete colour development; excess of the amine solution had no effect on the result. As there was some evidence that the amine solution deteriorated and became less reactive after several weeks' standing, 10 ml. was decided upon as being sufficient, even if old reagents were used.

THE EFFECT OF SOME ANIONS-

Since the amines are related to ammonia, the radicals showing interference with the cuprammonium complex might be expected to show the same effect with the cupramine

Anio	n			Anion added, p.p.m.	Cu found, p.p.m.	
Tartaric acid	••	••	••	20,000 50,000	50·2 50·9	
Citric acid	•••	••		10,000 20,000 50,000	50·2 50·2 50·6	
Sulphuric acid	••	••	••	25,000 50,000 100,000	50·0 50·2 50·4	
Nitric acid		••		20,000 50,000 100,000	49·6 49·8 49·6	
Hydrochloric a	cid	••	••	50,000 100,000	49-8 50-2	

TABLE II

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complex. Table II shows the effect of some of the anions that may be present as their ammonium salts with aluminium in ammoniacal solution. In each experiment 50 p.p.m. of copper was present in solution and the radical was added as free acid and then neutralised with ammonia.

Since the variations in these results are all within ± 2 per cent. of the theoretical result the experiment showed that it was permissible to have tartrate, citrate, sulphate, nitrate or chloride present in at least the amounts shown. These amounts are far in excess of the quantities likely to be required in practice. The quantity of tartaric acid finally decided upon corresponds to 25,000 p.p.m. so that the variation is reduced to ± 1 per cent.

As was to be expected, the presence of cyanide in the solution inhibits the formation of the cupramine complex.

THE EFFECT OF SOME METALS-

Similar experiments were carried out to study the effect of the commoner metals likely to be found in aluminium alloys, the results of these are shown in Table III. In each experiment the test solution contained 50 p.p.m. of copper, 10 ml. of 20 per cent. tartaric acid solution and sufficient ammonia to form the cuprammonium complex before the addition of the amine.

	Metal			Metal added, p.p.m.		Cu found, p.p.m.
Aluminium	••	••	••	2000 5000		49·8 50·2
Antimony	••	••	••	10 20		50·0 49·6
Cadmium		••	••	60		49.6
Chromium	••	••		10		50-2
Iron	••	••	••	$\frac{10}{20}$		49·4 49·6
Lead	••	••	••	$\frac{2}{10}$		50·0 49·8
Magnesium	••	••	•••	20 100		49·8 49·6
Manganese	••	••	••	10 20		$50.0 \\ 51.3$
Nickel	••	••		20 40 60		50·2 49·8 50·0
Silicon	••	••	•••	$\begin{array}{c} 20 \\ 100 \end{array}$	}	precipitation occurred
Tin	••	••	••	2 10		$50.2 \\ 50.2$
Titanium	•••	••	••	5 10		49·8 49·4
Zinc	••	••	••	$50 \\ 240$		$50.2 \\ 50.6$

TABLE III

These experiments showed that none of the elements commonly present in aluminium alloys (with the exception of silicon and possibly manganese) interfered in ammoniacal tartrate solution, even when present in the maximum amounts likely to be encountered.

In an attempt to prevent precipitation of silicic acid, experiments were made in sodium hydroxide - tartrate solution. Satisfactory results were obtained, but in the presence of manganese the extinctions were high owing to the formation of yellow colloidal hydroxide.

A number of attempts were made to prevent the formation of this hydroxide by keeping the pH of the final solution below 9 (at which pH manganous hydroxide is formed) but over the range pH 4 to 9 the results were sensitive to changes of acidity, the colour of the solution changing from violet to blue. After a number of other tests had been made, which showed no prospect of overcoming the problem of manganese interference, it was decided not to proceed further with the use of a caustic medium.

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THE EFFECT OF MANGANESE IN AMMONIACAL SOLUTION-

When a sample weight of 0.2 g. was used, pure aluminium and aluminium - manganese alloys with additions of a copper solution were attacked with five pellets of sodium hydroxide and a little water, acidified with 5 ml. of nitric acid and made just ammoniacal in the presence of 10 ml. of 20 per cent. tartaric acid solution. Ten ml. of 2 per cent. tetraethylene pentamine solution were added, the assays diluted to 100 ml. and their extinctions measured. The results are shown in Table IV.

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Sample	Cu added,	Cu recovered,	
Pure aluminium	 76 1.00 2.50 5.00	% 1·01 2·48 5·00	
Al - Mn alloy (1.00% Mn)	 $1.01 \\ 2.51 \\ 5.01$	1-00 2-49 5-01	
Al - Mn alloy (1.75% Mn)	 1·17 1·67 5·17	1·15 1·62 5·27	

These results indicate that there is no systematic error due to the presence of manganese in ammoniacal tartrate solution.

THE EFFECT OF SILICON IN AMMONIACAL SOLUTION-

Tests on a number of alloys by the method outlined in the preceding section showed that with silicon contents greater than 2 per cent., silicic acid was precipitated on the addition of the amine and with silicon contents of 1 to 2 per cent., precipitation occurred slowly and caused uncertain results. When such samples were diluted to volume and were filtered after standing to complete the precipitation of silicic acid, the results obtained were low, the error increasing with increasing silicon content. This suggested that the error was due to adsorption of the cupramine complex on the gelatinous silicic acid. When the precipitate was filtered off and washed well before diluting to volume no improvement was evident. It therefore became necessary to remove silicon by some other technique and a number of possibilities was investigated.

The usual method of hydrochloric - nitric acid attack followed by filtration through a very fine texture filter-paper is extremely slow and was not favoured as the filtrates are not always perfectly free from turbidity. The latter consideration is not so important in the diethyldithiocarbamate method in which a small aliquot of the filtrate is used for the final test, but in the present method in which no aliquot is taken a slight turbidity will cause markedly high results. Filtration through a pad on a Buchner funnel is not suitable for a large number of samples. The addition of gelatin solution to the acid mixture was found helpful, and filtration could then generally be accomplished on a filter-paper of medium texture but a general rule could not be applied; occasional samples gave turbid filtrates.

The addition of a few drops of hydrofluoric acid to a hydrochloric - nitric acid solution, dissolved all the silicon, but precipitation frequently occurred on adding the amine.

Fuming with sulphuric or perchloric acids gave some good results, but here again there were several objections to the use of either acid. Fuming with sulphuric acid resulted in a great deal of "spattering" and losses frequently occurred. To overcome this by the use of more acid was not practicable as the extra acid had then to be neutralised with ammonia, which generated enough heat to boil the solution with the accompanying danger of loss. Perchloric acid is readily fumed and neutralised, but filtration after fuming is slow and the dangers of using fuming perchloric acid in a routine process are well known.

Precipitation of silica with gelatin in several acid media was attempted without much success. Here again a strong acid concentration was required.

By using a hydrochloric - nitric acid attack, making ammoniacal after the addition of tartaric acid and then adding the amine solution, it was found that the silicon was coagulated and readily removed by filtration, generally on a Whatman No. 541 paper, invariably on a Whatman No. 40 paper. The time of filtration was shortened considerably by this method, and no loss of copper occurred. As a result, this procedure was adopted as standard for all types of alloys. It is worth recording that the same experiment carried out substituting

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citric for tartaric acid resulted in only slight coagulation of the silicon, filtration not being reliable on a medium texture paper.

THE EFFECT OF NICKEL AND IRON-

In view of the serious interference from nickel and to a lesser extent from iron in the colorimetric method for determining copper as the blue cuprammonium complex and of the statement by Crumpler, a more comprehensive investigation of the effects of these metals in the cupramine process was thought desirable. Standard samples with varying iron and nickel contents and other samples with additions of standard iron and nickel solutions were analysed. Some of the results obtained are shown in Table V.

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Sample			Fe content, %	Ni content, %	Cu by volumetric method, ³ %	Cu by amine method, %		
DTI).133C				1.53	1.33	1.96	1.95, 2.00, 1.99
DTI	0.424				0.78	0.09	2.48	2.45
DTI	0.424		••		0.69	0.23	2.97	2.97, 2.97, 2.94
2L.2	4				0.62	$2 \cdot 14$	4.37	4.36
2L.2	4	••	••	••	0.78	2.51	4.48	4.53, 4.45, 4.46
DTI).364A		• •		0.16	0.02	3.44	3.40
DTI).364A				0.88	0.02	2.96	2.90
2L.4	0		••		0.49	0.03	3.23	3.22, 3.21, 3.23
,,	+ 0.00	02 g. Ni	••		0.49	1.03	3.23	3.21
"	+ 0.00)4 g. Ni			0.49	2.03	3.23	3.19
,,	+ 0.00)6 g. Ni	••		0.49	3.03	3.23	3.19
"	+ 0.00	02 g. Fe			1.49	0.03	3.23	3 ·21
"	+ 0.00)3 g. Fe	••	••	1.99	0.03	3.23	3.21

The results showed that satisfactory figures are obtained in the presence of iron and nickel.

Method

Reagents-

Hydrochloric - nitric acid mixture-1 vol. of hydrochloric acid, sp.gr. 1.16, and 1 vol. of nitric acid, sp.gr. 1.42.

Tartaric acid-A 20 per cent. w/w solution.

Tetraethylene pentamine—A 2 per cent. solution. Dissolve 10 ml. of the amine in 500 ml. of water, heat to between 60° and 70° C. with activated charcoal, cool and filter through a Whatman No. 40 paper.

PROCEDURE-

Attack 0.2 g. of the sample with 5 ml. of hydrochloric - nitric acid mixture in a 100-ml. squat beaker. When the attack is complete, wash down the sides of the beaker with a little water and boil for 3 to 4 minutes. Remove from the hot-plate, dilute to between 10 and 15 ml. and allow to cool somewhat. Add 10 ml. of tartaric acid solution, 10 ml. of concentrated ammonia, sp.gr. 0.880, and 10 ml. of tetraethylene pentamine solution. Mix the liquid thoroughly after each addition. Filter through a 9-cm. Whatman No. 40 filter-paper into a 100-ml. graduated flask and wash the residue six times with cold water and dilute to the mark. Mix well and measure the absorption on the Spekker absorptiometer in 4-cm. cells, with Chance No. ON13 and Ilford No. 608 filters, and the tungsten filament lamp. Deduct a blank determination on the reagents.

Notes-

(1) For copper contents of 5 to 10 per cent. reduce the sample weight to 0.1 g.

(2) The instrument is calibrated by carrying aliquots of a standard copper solution through the above procedure.

RESULTS

The method has been in use on a routine scale for several months. The standard error has been calculated from some 200 determinations made on a series of standard samples of DTD.424, 2L.24, LAC.112A, DTD.364A and DTD.687; all the results being obtained under routine conditions. The copper contents of these standards range from 1.2 to 4.5 per cent. and the standard error is ± 0.04 per cent.

SUMMARY

1. The method is applicable to the determination of copper in all types of aluminium alloys in which it is an alloying constituent.

2. The procedure is direct; no interference is caused by any of the normal constituents.

3. The method has several advantages over the alternative photometric methods. It is much more sensitive and at the same time less subject to interference and variation from extraneous causes than that based on the cuprammonium reaction. It is less sensitive than the diethyldithiocarbamate method, which is more suited to the determination of trace quantities. This enables a larger and more representative sample to be taken and also obviates the necessity to take an aliquot of the solution. It is less subject to interference than the diethyldithiocarbamate method and the separation of silicon has been simplified.

4. The colour is stable and the precision is satisfactory for a photometric method.

5. Tetraethylene pentamine is about three times as sensitive as ammonia and about 1/40 as sensitive as sodium diethyldithiocarbamate. The method is rapid. It is free from interference and has a standard error of ± 0.04 per cent. for the range 1 to 4.5 per cent. of copper.

By reducing the sample weight of 0.1 g. the upper limit of the method can be extended to 10 per cent.

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