ANL-7331

ANL-7331

RECEIVED BY DTIC OCT 9 1967

Argonne National Laboratory

SPECTROGRAPHIC ANALYSIS OF
BISMUTH-TIN EUTECTIC ALLOYS
BY SPARK-IGNITED, LOW-VOLTAGE
AC-ARC EXCITATION

by

E. A. Huff and S. J. Kulpa

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	The University of Iowa	Northwestern University
Carnegie Institute of Technology	Kansas State University	University of Notre Dame
Case Institute of Technology	The University of Kansas	The Ohio State University
The University of Chicago	Loyola University	Purdue University
University of Cincinnati	Marquette University	Saint Louis University
Illinois Institute of Technology	Michigan State University	Washington University
University of Illinois	The University of Michigan	Wayne State University
Indiana University	University of Minnesota	The University of Wisconsin
Iowa State University	University of Missouri	

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America
Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CESTI PRICES

H.C. \$ 3.00, MN. 65

SPECTROGRAPHIC ANALYSIS OF
BISMUTH-TIN EUTECTIC ALLOYS
BY SPARK-IGNITED, LOW-VOLTAGE
AC-ARC EXCITATION

by

E. A. Huff and S. J. Kulpa

Chemistry Division

May 1967

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
I. INTRODUCTION.	4
II. EXPERIMENTAL PROCEDURE	5
A. Reagents and Materials	5
B. Standard Preparation	5
C. Sample Preparation	6
D. Spectrographic Analysis	7
III. RESULTS AND DISCUSSION	8
IV. SUMMARY	11
ACKNOWLEDGEMENTS	11
REFERENCES	12

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Analytical Curve for Iron.	8
2.	Analytical Curves for Chromium, Manganese, and Nickel . . .	8

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Chemical Analysis of a Type 304 Stainless Steel	6
II.	Composition of Bi-42 w/o Sn Solution Standards.	6
III.	Spectrographic Conditions	7
IV.	Analytical Line Pairs	8
V.	Comparison of Chemical and Spectrographic Results	9
VI.	Accuracy Data at Low Element Concentrations	9
VII.	Precision Data.	10
VIII.	Precision As a Function of Sample Size	11

SPECTROGRAPHIC ANALYSIS OF
BISMUTH-TIN EUTECTIC ALLOYS
BY SPARK-IGNITED, LOW-VOLTAGE
AC-ARC EXCITATION

by

E. A. Huff and S. J. Kulpa

ABSTRACT

The spark-ignited, low-voltage ac-arc discharge was used as an excitation source for the spectrographic determination of chromium, iron, manganese, and nickel in bismuth-tin eutectic alloys. These impurities could be determined over a concentration range of a few parts per million to 1%. Samples were dissolved, and cobalt was added to serve as an internal standard. Both copper and silver rods were used as supporting electrodes. Excellent sensitivity with good accuracy and precision could be realized. The applicability of this procedure to the quantitative analysis of other matrices is also discussed.

I. INTRODUCTION

Research studies in the Metallurgy Division of the Argonne National Laboratory on the solubility of Type 304 stainless steel in a molten bismuth-42 w/o tin eutectic required the development of an analytical method for the determination of individual stainless steel components in the melt. Variables in the metallurgical experiments produced samples which had a wide concentration range (0.005 to 1%) of these elements. An accuracy of better than $\pm 10\%$ was required. The large number of samples submitted for analysis and the low element concentrations encountered in some alloys made standard wet chemical techniques impractical. Analysis by emission spectroscopy appeared to be advantageous from the standpoint of detection sensitivity and speed. Direct dc-arc excitation of the solid material was not satisfactory because the lack of adequate standards did not provide the required accuracy. Furthermore, a preliminary examination of pins cast showed that segregation of impurities occurred during sample solidification. Therefore, the usual small sample weight used in dc-arc analysis was not representative of the entire alloy melt.

These considerations led to the development of a spectrographic method utilizing the high sensitivity and precision of the spark-ignited, low-voltage ac-arc excitation of samples rendered homogeneous by dissolution.

II. EXPERIMENTAL PROCEDURE

A. Reagents and Materials

High-purity hydrochloric acid was prepared by passing hydrogen chloride gas into chilled, distilled, deionized water. Pure nitric acid was obtained by distillation of the reagent-grade product from a quartz still. These reagents were stored in polyethylene bottles.

All polypropylene beakers, volumetric flasks, and pipettes used in the experiments were boiled in hydrochloric acid and thoroughly rinsed with distilled, deionized water. This cleaning procedure effectively eliminated any random blank contamination.

One gram of Apiezon-N grease was dissolved in 1 liter of low-boiling petroleum ether. A drop of this solution was used to coat freshly machined electrode surfaces.

Electrodes were cut from commercially available 1/4-in.-diam silver and copper rods. These were analyzed spectrographically prior to use, to ascertain the absence of interfering trace impurities.

B. Standard Preparation

Since no bismuth-42 w/o tin eutectic alloys of certified stainless steel content were available, synthetic standards had to be used in the construction of spectrographic working curves. The Metallurgy Division prepared several alloy melts from high-purity bismuth and tin matrices, and these were analyzed spectrographically by the dc-arc method. The material that was free of stainless steel constituents was used as the matrix in the preparation of solution standards, and as a blank in the dilution of samples of high-impurity content.

To approximate the composition of samples and standards as closely as possible, a portion of a Type 304 stainless steel disc that was to be used in the dissolution studies was analyzed chemically; the results are shown in Table I. These values were used as the basis in the preparation of alloy standards of known element concentrations by successive dilutions.

TABLE I. Chemical Analysis of a
Type 304 Stainless Steel

Element	Concentration, %
Chromium	18.13
Iron	70.10
Manganese	1.29
Nickel	9.72

Solution standards were prepared by dissolving 100-mg portions of the pure alloy matrix in a hydrochloric-nitric acid mixture. Polypropylene beakers were used in this procedure. Nitric acid was eliminated by two evaporations with hydrochloric acid. This prevented attack on the electrodes in the subsequent spectrographic analysis. The resultant residue was redissolved in hydrochloric acid and transferred quantitatively to a thoroughly cleaned 10-ml volumetric flask. Appropriate volumes of a standard stainless steel solution and a cobalt internal standard were added to produce a series of alloy matrices having the composition shown in Table II.

TABLE II: Composition of Bi-42 w/o Sn Solution Standards*

Standard No.	Element Concentration, %				
	Co	Fe	Cr	Ni	Mn
1	0.01	0.1682	0.0435	0.0233	0.0031
2	0.01	0.0841	0.0218	0.0117	0.0015
3	0.01	0.0421	0.0109	0.0058	0.0008
4	0.01	0.0210	0.0054	0.0029	0.0004
5	0.01	0.0084	0.0022	0.0012	
6	0.01	0.0042	0.0011	0.0006	
7	0.01	0.0016	0.0004		

*Sample Concentration: 10 mg/ml.

C. Sample Preparation

Analytical samples were received as 1/4-in.-diam pins. A series of drillings was taken along the length of the pin, and these were combined to minimize segregation effects. A 100-mg sample portion was accurately weighed and dissolved in a hydrochloric-nitric acid mixture. Nitric acid was eliminated by evaporation, and the redissolved residue was transferred quantitatively to a 10-ml volumetric flask. Then 0.1 ml of a 100- μ g/ml cobalt internal standard solution was added, and the sample was brought to volume with 6N hydrochloric acid.

Visual observations on the color intensity of the dissolved sample gave a good indication of the approximate stainless steel content. For alloys of high stainless steel content, only a portion of the original sample solution was taken, and a sufficient amount of alloy blank was added to give a final 10-mg/ml sample concentration in a 10-ml volume.

D. Spectrographic Analysis

The inherent high concentrational sensitivity of the spark-ignited, low-voltage ac-arc discharge put a severe limitation on the choice of acceptable electrode materials. Preliminary investigations showed that even trace amounts of common metal impurities could be detected in available high-purity aluminum and copper rods. Copper electrodes were, however, found to be free from manganese and were thus suitable for the determination of this element. Available silver electrodes, on the other hand, did contain some manganese, but showed the complete absence of chromium and nickel. Only a slight trace of iron could be detected. This electrode material was therefore found to be acceptable for the analysis of chromium, iron, and nickel.

The 1/4-in. electrodes were cleaned by a hydrochloric acid wash, and one end was machined on a lathe to a smooth surface. This operation did not introduce any measurable contamination. A drop of a 1-g/liter Apiezon-N in petroleum ether solution was applied to each electrode before sample loading. A 0.1-ml sample aliquot, equivalent to 1 mg of alloy, was divided equally between two electrodes, and these were dried under infrared heat lamps.

Samples and standards were exposed in triplicate, using the excitation source conditions and the spectrograph parameters shown in Table III. Spectra were recorded on Eastman Kodak 103-0 plates, which were developed under standard conditions.¹ Spectral line transmissions were measured with a Jarrell-Ash nonrecording microphotometer. The analytical

TABLE III. Spectrographic Conditions

a. Jaco Varisource		b. Jaco Spectrograph	
Analytical Gap:	3 mm	3.4 m, Ebert Mount, Plane Grating, 15,000 Lines/in.	
Auxiliary Gap:	4.5 mm	Electrode Image Focused on Collimating Aperture	
Capacitance:	0.0025 μ F	Dispersion:	2.5 $\text{\AA}$ /mm (second order)
Inductance:	40 μ H	Wavelength:	3450 to 4050 $\text{\AA}$ (second order)
Resistance:	Residual	Slit Width:	30 μ
Rf Current:	2.5 Amps	Photographic Plate:	Eastman Kodak 103-0
AC-arc Current:	4.4 Amps	Developing Conditions:	Standard ¹
Exposure Time:	30 sec		

lines used are indicated in Table IV. Line transmission readings were converted to line intensity ratios by means of a Respectra calculator. The experimental analytical working curves for the evaluation of element concentrations are shown in Figs. 1 and 2.

TABLE IV. Analytical Line Pairs

Element	Analytical Line, Å	Internal Standard Line, Å	Concentration Range, %	Concentration Index
Chromium	CrI 3593.49	CoI 3474.02	0.0004 to 0.0435	0.00239
Iron	FeI 3719.94	CoI 3474.02	0.0042 to 0.1680	0.0130
Manganese	MnI 4033.07	CoI 3569.38	0.0004 to 0.0031	0.0091 ^a
Nickel	NiI 3492.96	CoI 3474.02	0.0012 to 0.0233	0.0100
	NiI 3524.54	CoI 3474.02	0.0006 to 0.0233	0.00435

^aExtrapolated.

Fig. 1. Analytical Curve for Iron.

Fig. 2. Analytical Curves for Chromium, Manganese, and Nickel.

III. RESULTS AND DISCUSSION

Kassner² has presented an extensive compilation of data obtained on experimental alloys by this method. His tabulations give a good indication as to the capability of this procedure in covering a wide range of element concentrations. Kassner's report, though, does not discuss in detail the technique by which these results were obtained.

Table V lists data pertaining to the accuracy of the reported method. The spectrographic and chemical results obtained for two representative alloys show an agreement of better than $\pm 10\%$ for all elements. No wet-chemical data could be readily obtained for alloys of low stainless steel

content. As an alternative, successive dilutions of a chemically certified sample were analyzed spectrographically; the results are listed in Table VI. The good agreement of the data show that the discussed procedure is capable of adequate accuracy even at low element concentrations.

TABLE V. Comparison of Chemical and Spectrographic Results

Element	Sample No.	Concentration, %		Difference, %
		Chemical	Spectrographic	
Iron	S-12	0.587	0.608	3.6
	S-13	0.560	0.593	5.9
Chromium	S-12	0.414	0.387	5.9
	S-13	0.407	0.408	0.2
Nickel	S-12	0.825	0.845	2.4
	S-13	0.837	0.832	0.6
Manganese	S-12	0.128	0.129	1.3
	S-13	0.128	0.121	5.1

TABLE VI. Accuracy Data at Low Element Concentrations^a

Element	Concentration, %		Difference, %
	Known ^a	Found	
Iron	0.0825	0.0830	+0.6
	0.0215	0.0232	+7.9
	0.0083	0.0086	+3.6
	0.0041	0.0041	0.0
Chromium	0.0143	0.0138	-3.5
	0.0057	0.0059	+3.5
	0.0029	0.0028	-3.4
Nickel	0.0290	0.0270	-6.9
	0.0116	0.0117	+0.9
	0.0058	0.0058	0.0

^aKnown concentrations are based on dilutions of a chemically analyzed sample.

The precision of the method was evaluated by repeated analyses of a single sample. Separate 100-mg portions of alloy were weighed and analyzed. The results for chromium, iron, and nickel are tabulated in Table VII. The data indicate that the attainable precision is comparable to the accuracy of the proposed technique.

TABLE VII. Precision Data

Aliquot No.	Iron Concentration, %	Chromium Concentration, %	Nickel Concentration, %
1	0.083	0.0170	0.0109
2	0.081	0.0150	0.0107
3	0.080	0.0172	0.0098
4	0.079	0.0167	0.0105
5	0.081	0.0167	0.0109
6	0.082	0.0178	0.0098
7	0.085	0.0163	0.0103
8	0.081	0.0170	0.0098
9	0.085	0.0148	0.0104
10	0.080	0.0183	0.0103
11	0.081	0.0153	0.0100
12	0.082	0.0147	0.0100
13	0.083	0.0145	0.0115
14	0.079	0.0157	0.0110
15	0.084	0.0177	0.0103
16	0.081	0.0165	0.0113
17	0.079	0.0150	0.0108
18	0.084	0.0193	0.0113
19	0.079		
20	0.080		
21	0.077		
22	0.080		
23	0.079		
24	0.082		
Average	0.081	0.0164	0.0105
Standard Deviation	0.002	0.0014	0.0005
Coefficient of Variation	2.5%	8.5%	4.8%

In any analytical procedure, the choice of sample size is of considerable importance for a meaningful characterization of a material. The precision of experimental data as a function of sample weight is generally a good indicator of homogeneity and thus of the required sampling technique. Table VIII compares experimental precision results obtained on 10- and 100-mg alloy weights. The data clearly show that the submitted samples were not homogeneous and thus required a weight of at least 100 mg for reliable average results. This conclusion was further substantiated by separate dc-arc analyses of sample drillings taken along the length of the pin.³

TABLE VIII. Precision As a Function of Sample Size

Element	Coefficient of Variation, %	
	10-mg Sample	100-mg Sample
Chromium	17.6	8.5
Iron	22.8	2.5
Nickel	8.8	4.8

The amount of sample consumed per analysis is one of the factors that determines the attainable sensitivity of a particular technique. In the copper spark method,⁴ line-suppression effects by the matrix limit the sample weight to 50 to 100 μg per electrode pair. In comparison, arc procedures are less restrictive

in this respect. Line intensity ratios as a function of electrode loading were investigated using the spark-ignited, low-voltage ac-arc excitation. An optimum sample weight of 1 mg per electrode pair was found for the bismuth-42 w/o tin alloys.

This procedure has also been successfully applied to the analysis of other types of samples. As an example of the versatility of the method, a 60 w/o MgCl_2 -22 w/o NaCl -18 w/o KCl salt mixture, which was circulated through a Type 304 stainless steel loop by a nickel pump, was submitted for corrosion-product analysis. Since this material was of lower density, a smaller sample weight (0.5 mg per electrode pair) was used in an exposure. Despite the smaller sample size, adequate sensitivity was attained, and the results agreed quite well with independent dc-arc data.³

IV. SUMMARY

The reported experimental data show that the spark-ignited, low-voltage ac arc can be readily applied as an excitation source in emission spectroscopy. The high sensitivity that can be realized with this mode of discharge compares favorably with conventional dc-arc methods. Good accuracy is attained and the gain in precision can present distinct advantages over dc-arc techniques.

ACKNOWLEDGEMENTS

Thanks are extended to D. R. Huff for the numerous dc-arc results and to K. J. Jensen for the required wet-chemical determinations.

REFERENCES

1. ASTM Committee-E2, *Methods for Emission Spectrochemical Analysis*, 4th ed., American Society for Testing and Materials, Philadelphia, Pennsylvania (1964).
2. T. F. Kassner, *A Convective-diffusion Study of the Dissolution Kinetics of 304 Stainless Steel in the Bismuth-Tin Eutectic Alloy*, ANL-6985 (Nov 1965).
3. D. R. Huff, ANL, private communication (1965).
4. M. Fred, N. H. Nachtrieb, and F. S. Tomkins, *J. Opt. Soc. Am.* 37, 279 (1947).