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ELECTRON MICROPROBE ANALYSIS OF PLUTONIUM-
GALLIUM ALLOYS

by

M. R. Harvey and D. H. Riefenberg

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ABSTRACT

Electron Microprobe Analysis of Plutonium- Gallium Alloys

By

M. R. Harvey & D. Riefenberg

A calibration curve of relative intensity versus gallium concentration was obtained on a series of plutonium-gallium alloys. The concentration range studied was 0.56 to 2.12 w/o. The relative intensity was found to vary linearly with concentration in this range. Based on the standard deviations observed in this work, 19 determinations were required for an accuracy of ± 0.05 w/o absolute at a confidence level of 99%.

REVIEWED FOR CLASSIFICATION

By R. B. McDonald

Date 4/21/66

ELECTRON MICROPROBE ANALYSIS OF PLUTONIUM-GALLIUM ALLOYS

By

M. R. Harvey and D. Riefenberg

The electron microanalyzer has the unique capability of elemental analysis of areas approximating one micron in diameter. As a result it can be extremely useful in identifying unknown inclusions and precipitates, in studying diffusion down grain boundaries and in determining microsegregation. Before quantitative results can be obtained however, the relationship between the relative intensities of the X-rays generated in a sample and the concentration of the element being analyzed must be obtained. One method is to determine this relationship from a series of known homogeneous alloys, i.e., obtain a calibration curve. In many systems however, homogeneous alloys cannot be made. Corrections due to fluorescence, atomic number, and absorption must be applied to the X-ray intensities. An excellent discussion of these is given by Ziebold¹.

Of the two methods, the calibration curve is the most accurate. A variation of this method has been proposed in another paper by Ziebold², in which only one known alloy is needed to convert intensity data into concentrations. He proposes the following relationship of Castaing's³

$$\frac{1-K}{K} = \alpha \frac{1-C}{C} \quad (1)$$

with the following important differences.

Ziebold defines K as the ratio^{of} X-ray intensities, seen by the spectrometer, of an alloy to that of an elemental standard. Castaing's definition was based on the intensity generated in the sample. Originally α was defined in terms of a single correction factor, but Ziebold includes all three corrections, i.e., fluorescence, etc. in it. The term C remains unchanged being defined as the weight fraction of the alloy being analyzed.

Ziebold's procedure consisted assuming α to be constant and determining it from a known alloy. It was then applied to the entire concentration range in determining unknown compositions.

Hakkila, et al⁴, applied Ziebold's equation to a Pu-1 w/o Ga alloy and from this standard determined α to be 0.33. Next he assumed a linear relationship between the relative intensity K , and the concentration C

$$K = \beta C \quad (2)$$

for concentrations of less than 1.5 w/o gallium. The slope β was determined from the Pu-1.0 w/o Ga standard. In calculating concentrations, from intensity data from two different areas of a cored Pu-Ga alloy with Ziebold's formula and his (Hakkila's), the same results were obtained.

It should be noted here that this result was not unexpected because it is easily seen that equation (1) when written in the form

$$K = \frac{C}{\alpha + C - \alpha C} \quad (3)$$

can be approximated by

$$K = \frac{C}{\alpha} \quad (4)$$

for $C < 1.5$ w/o.

This paper extends Hakkila's work to the entire solid solution range of δ - stabilized plutonium, i.e., 2.5 a/o - 8.0 a/o or .74 w/o - 2.47 w/o, in an attempt to become better acquainted with the microprobe problems involved in working with plutonium-gallium alloys, to establish the accuracy of analysis of gallium in plutonium, and to determine the reproducibility of the constant α .

EXPERIMENTAL PROCEDURE

Plutonium with a reported heavy metal impurity of less than 100 ppm was alloyed with gallium. The metals were melted at 1000°C in an induction furnace and cast into $\frac{1}{2}$ " diameter rods. Samples were cut and annealed at 600°C for 100 hours and then at 475°C for 144 hours. Two gallium chemical analyses were taken on each sample. The maximum deviation between any two analyses was 0.03 w/o absolute. After mounting, sample #'s 3, 4, 5, and 6 were mechanically polished utilizing standard techniques, ending up with 1μ diamond paste. Samples 1 and 2 were polished with 600 grit paper and then chemically polished.

In order to avoid contamination of the microprobe, the samples were ultrasonically cleaned in Dow Chlorothane Nu* and washed with ethyl alcohol. A film of Kodacel A-30[†] was placed over the plutonium surface, flooded with alcohol and stripped off. The plutonium was then masked off and clear lacquer sprayed over the entire mount. The masking was removed and the sample placed in a Materials Analysis Corporation Microprobe Model 400[#].

In order to eliminate interference from the second order $L_{\beta 1}$ and $L_{\beta 3}$ plutonium lines, an accelerating potential of 19 KV was used. Specimen current was maintained at 0.04 μ a while counting. The intensities of twenty areas were determined for a 30 second interval at 1.300Å and 1.380Å for background and at 1.342Å for the Ga $K\alpha$. The counts per sec were evaluated by

$$\text{Counts/Sec} = \frac{N_{1,342} - (N_{1,380} + N_{1,300})}{60}$$

where $N_{1,342}$, $N_{1,380}$, and $N_{1,300}$ are the number of counts at the designated wavelengths. The gallium standards were evaluated in the same manner as the alloys.

*Dow Chemical Company, Midland, Michigan

[†]Eastman Kodak Company, Rochester, New York

[#]Materials Analysis Company, Palo Alto, California

RESULTS AND DISCUSSION

Table 1 lists the intensity data of the six alloys plus the gallium standards. The relative intensities K (averaged from the 20 areas), and the corresponding constants α (calculated from equation 1), are also shown.

The observed standard deviation, based on the total number of counts, for samples 1 and 6, were calculated to be 105 and 111 counts as compared to an expected deviation of 101 and 104.

The sample size required for a 99% confidence limit of a ± 0.05 w/o absolute deviation from the true concentration was determined to be 19.

Equation 1 is plotted in Figure 1 for a value of $\bar{\alpha} = 0.52$.

It is observed that there is a good correlation between the data and the functional relationship noted in Equation 1.

Note also that the plotted function is linear in the concentration range studied which confirms Hakkila's assumption of linearity, i.e., a single standard in this solid solution range establishes the approximate calibration curve for that region.

The calculated value of α is somewhat surprising. Values less than 1 are usually indicative of large fluorescence effects². Scott⁵ reports, however, that the absorption correction should be dominant in the case of Pu-Fe alloy which might be expected to exhibit the same behavior as Pu-Ga alloys. A theoretical

calculation of α was made based on a method proposed by Ziebold² yielding $\alpha = 0.77$ as compared to an experimentally determined value of 0.55. It is obvious that the use of $\alpha = 0.77$ will result in an unacceptable error in C. It should not be assumed, however, that Hakkila's measured value and the author's are in disagreement. There is apparently another correction factor in the Pu-Ga system which cannot be predicted. In all alloys studied there was an unusually high background from 1,200Å to 1,500Å which bracketed the Ga-K α peak. This background was traced to the plutonium. Waterbury⁶ stated that high background was not observed in Hakkila's study. This would effectively increase his observed K value for corresponding concentrations which would account for his lower value of α .

CONCLUSIONS

1. The electron microanalyzer is a quick, accurate tool for analyzing small amounts of gallium in plutonium.
2. The relative X-ray intensity versus elemental concentration curve for the delta stabilized region may be approximated by a straight line thru the origin with a slope of $\frac{1}{\alpha}$.
3. Accuracies of ± 0.05 w/o can be obtained with a sample size of 19.
4. A calibration curve of relative intensity versus concentration is the only acceptable way of obtaining accurate gallium analyses with the microprobe.

TABLE 1

Relative Intensity Data for Plutonium-Gallium Alloys

Sample #	w/o Ga	a/o Ga	Intensity (Count/Sec)	K	α	Comments
1	0.56	1.90	<u>22.4*</u>	1.07×10^{-2}	0.52	*Average of 20 areas
2	0.76	2.57	<u>31.5</u>	1.50×10^{-2}	0.50	"
3	1.15	3.86	<u>44.4</u>	2.15×10^{-2}	0.53	"
4	1.53	5.07	<u>60.8</u>	2.95×10^{-2}	0.51	"
5	1.85	6.08	<u>64.1</u>	3.45×10^{-2}	0.53	"
6	2.12	6.90	<u>73.8</u>	3.97×10^{-2}	0.52	"
Ga Std 1	100.00		<u>2096.*</u>			Used with #'s 1 & 2. Average of 20 areas
Ga Std 2	100.00		<u>2062</u>			Used with #'s 3 & 4. Average of 20 areas
Ga Std 3	100.00		<u>1858</u>			Used with #'s 5 & 6. Average of 20 areas

Accelerating Potential 19 KV - Specimen Current $0.04\mu\text{a}$

Figure 1. Relative intensity K_{α} of gallium K_{α} lines as a function of gallium concentration C , in plutonium-gallium alloys. Error bars indicate 99% confidence level for a sample size of 19.

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