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UNITED STATES ATOMIC ENERGY COMMISSION

USE OF A DENSITY (SPECIFIC VOLUME) METHOD
AS A SENSITIVE ABSOLUTE MEASURE OF ALLOY
COMPOSITION, AND ITS APPLICATION TO THE
ALUMINUM-URANIUM SYSTEM

By

L. R. Aronin

J. L. Klein

Price \$ 0.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

October 29, 1954

Nuclear Metals, Incorporated
Cambridge, Massachusetts

Technical Information Service Extension, Oak Ridge, Tenn.

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ABSTRACT

Mass density measurement (or its reciprocal, specific volume) is shown to be a highly sensitive and accurate method for calculating composition in the aluminum-uranium system. Theoretical considerations of application of density measurement to composition calculation are given for the general case of a simple binary alloy, and specific applications to the aluminum-uranium system are considered in detail for a structure consisting of primary aluminum and UAl_4 compound. Extraneous factors which could influence a density-composition correlation are considered analytically. These factors — voids, variations in composition and density of primary aluminum and UAl_4 compound, presence of UAl_3 as a non-equilibrium phase, and presence of a foreign phase such as uranium carbide — are shown to lead to negligible error under the experimental conditions of this work. Experimental application of the hydrostatic weighing method to obtain density values reproducible to one part in 10,000 is described. In the composition range investigated experimentally, 7 to 21 weight percent uranium, this reproducibility corresponds to an uncertainty of ± 0.03 weight percent uranium. Good experimental correlation is obtained between compositions calculated from density measurements and those measured by conventional chemical analysis.

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DATE MAR 8 1957 *AE*
For The Atomic Energy Commission
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Use of a Density (Specific Volume) Method as a Sensitive
Absolute Measure of Alloy Composition, and Its
Application to the Aluminum-Uranium System

L. R. Aronin and J. L. Klein

INTRODUCTION

A program has been under way for some time at Nuclear Metals, Inc.* to produce homogeneous castings of aluminum-uranium alloy in the neighborhood of 15 weight percent uranium. One requirement in this work has been to maintain the uranium content uniform to within plus or minus one percent (i.e., ± 0.15 percent uranium in a 15.0 weight percent alloy). This specification has presented a problem in uranium assay, since conventional methods of chemical analysis have an uncertainty of about plus or minus one percent, which is the same order as the desired control range. The wide difference in atomic number between aluminum and uranium leads to the possibility of the development of physical methods of high precision to measure uranium contents and act as an independent check on chemical analyses.

The use of density (or specific volume) determinations as a reliable means of analysis appears feasible for binary alloys, such as aluminum-uranium, which are composed of elements differing widely in atomic mass. Such measurements are readily performed, and, under proper restrictions, may provide a most sensitive means of surveying alloys for uniformity. This report covers the theoretical considerations of a density method for measuring composition of aluminum-uranium alloys, and the experimental application

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to the range of 7 to 21 weight percent uranium. In the early stages of the work density measurements were regarded primarily as a possible precision method of obtaining relative values of composition for studying homogeneity in castings. However, as the work progressed it became evident that the density method is capable of yielding precise absolute values of uranium content.

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THEORETICAL CONSIDERATIONS — GENERAL

Although the physical principles relating composition to density (where density is the ratio of mass to volume) are simple, successful application of the technique depends upon proper evaluation of those factors which are significant in both the theoretical and experimental determination of mass and volume. In this section are presented general expressions for the relationship of density and specific volume of solids to composition, applicable in principle to any binary system. The subsequent sections consider the specific case of aluminum-uranium alloys.

While density (gm/cm^3) is the commonly tabulated constant relating mass to volume, its reciprocal, specific volume (cm^3/gm), leads to simpler expressions in many instances. Accordingly, alternative expressions in terms of either density or specific volume are given below.

Requirements of Method

The following conditions are to be satisfied if the density method is to give a reliable measure of composition:

- (1) Compositions of phases present must be known.
- (2) Densities of phases present must be known.
- (3) Volume of solid must be the same as that measured, i.e., there can be no voids present.
- (4) "Foreign" phases — impurities or non-equilibrium phases — must not interfere.
- (5) Specimen densities must be determined by a reliable method possessing adequate sensitivity.

Analytical Expressions

A general case is considered for a binary A-B alloy, such as shown in Figure 1. In brief, A and B represent the alloying elements; α and β , phases

present; x , weight fraction of B; ρ , density; v , specific volume; V , total volume; M , total mass. Quantities relating to α or β phases are denoted by appropriate subscripts.

The fundamental assumption is that the total volume of a sample is given by the sum of the volumes of the phases present. That is,

$$V = V_{\alpha} + V_{\beta} + V_{\epsilon} \quad (1)$$

and

$$V_{\epsilon} \approx 0 \quad (2)$$

In equations (1) and (2) V is total volume, V_{α} volume of alpha phase, V_{β} volume of beta phase, and V_{ϵ} volume associated with voids, impurities, non-equilibrium phases, and phase interface defects. It is assumed, as in equation (2), that V_{ϵ} is small enough to be ignored. In cases where $V_{\epsilon} \neq 0$, corrections can be made for specific cases as illustrated in subsequent discussions of aluminum-uranium alloys.

Since $V = \frac{M}{\rho}$, equation (1) may be written

$$\frac{M}{\rho} = \frac{M_{\alpha}}{\rho_{\alpha}} + \frac{M_{\beta}}{\rho_{\beta}} \quad (3)$$

From a mass balance (lever relationship)

$$\begin{aligned} M_{\alpha} &= \left(\frac{x_{\beta} - x}{x_{\beta} - x_{\alpha}} \right) M \\ M_{\beta} &= \left(\frac{x - x_{\alpha}}{x_{\beta} - x_{\alpha}} \right) M \end{aligned} \quad (4)$$

Substituting equations (4) in (3) and simplifying, an expression for alloy composition in terms of known phase densities and measured alloy density is obtained:

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$$x = \frac{\rho_{\beta} x_{\beta} - \rho_{\alpha} x_{\alpha}}{(\rho_{\beta} - \rho_{\alpha})} = \frac{\rho_{\alpha} \rho_{\beta} (x_{\beta} - x_{\alpha})}{\rho (\rho_{\beta} - \rho_{\alpha})} \quad (5)$$

If specific volume is used in place of density, equation (5) becomes

$$x = \frac{v_{\alpha} x_{\beta} - v_{\beta} x_{\alpha}}{(v_{\alpha} - v_{\beta})} = \frac{v (x_{\beta} - x_{\alpha})}{(v_{\alpha} - v_{\beta})} \quad (6)$$

Equation (5), giving composition in terms of density, is an hyperbola of the form $x(\rho) = C_1 - \frac{C_2}{\rho}$. It is readily apparent that equation (6), giving composition in terms of specific volume, is linear of the form $x(v) = C_1 - C_2 v$. Equations (5) and (6) are plotted schematically in Figure 2.

In the important case where A has essentially zero solid solubility for B (as in the aluminum-uranium system), $x_{\alpha} = 0$ and equations (5) and (6) reduce to

$$x = x_{\beta} \frac{\rho_{\beta}}{\rho} \frac{(\rho - \rho_{\alpha})}{(\rho_{\beta} - \rho_{\alpha})} \quad (7)$$

$$x = x_{\beta} \frac{(v_{\alpha} - v)}{(v_{\alpha} - v_{\beta})} \quad (8)$$

Sensitivity

The sensitivity of the method is obtained by differentiating equations (5) and (6) with respect to ρ and v , respectively:

$$dx = \frac{\rho_{\alpha} \rho_{\beta}}{\rho^2} \frac{(x_{\beta} - x_{\alpha})}{(\rho_{\beta} - \rho_{\alpha})} d\rho \quad (9)$$

$$dx = - \frac{(x_{\beta} - x_{\alpha})}{(v_{\alpha} - v_{\beta})} dv \quad (10)$$

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APPLICATIONS OF THEORY TO ALUMINUM-URANIUM ALLOYS
IN RANGE 0-68.8 WEIGHT PERCENT URANIUM

The aluminum-uranium phase diagram^(1,2) is shown in Figure 3. For this investigation the region of interest has been the two-phase field, aluminum and UAl_4 compound, and the region of the eutectic composition (13 weight percent uranium).

Expressions for Alloys with Natural Uranium

When the general nomenclature of the preceding section is applied to the aluminum-uranium system,*

$$\begin{aligned}\rho_a &\equiv \rho_{Al} = 2.7000 \text{ gm/cm}^3 \\ v_a &\equiv v_{Al} = 0.37037 \text{ cm}^3/\text{gm}\end{aligned}$$

at 25°C by direct measurement;

$$\begin{aligned}\rho_\beta &\equiv \rho_c \equiv \rho_{UAl_4} = 6.062 \text{ gm/cm}^3 \\ v_\beta &\equiv v_c \equiv v_{UAl_4} = 0.1650 \text{ cm}^3/\text{gm}\end{aligned}$$

for natural uranium by calculation from x-ray results;⁽²⁾

$$\begin{aligned}x_a &= 0 \\ x_\beta &\equiv x_c = \frac{238.13}{238.13 + 4(26.98)} = 0.6882\end{aligned}$$

for natural uranium.

Substituting the values above in equations (7) and (8), the expressions for weight fraction of uranium in terms of measured density or specific volume of the alloy become

* Physical atomic weights are used throughout this paper. The ratio of physical to chemical atomic weight is 1.000272.

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$$x = 1.2408 - \frac{3.3502}{\rho} \quad (11)$$

$$x = 1.2408 - 3.3502 v \quad (12)$$

for natural uranium.

Working graphs of equations (11) and (12) are plotted in Figures 4 - 7. Figures 4 and 6 cover the range of 0 - 68.8 weight percent uranium. Figures 5 and 7 have expanded scales to permit close readings in the range of 13-17 percent uranium.

Effect of U²³⁵ Enrichment

When enriched uranium is used, the constants in equations (11) and (12) are altered slightly. If the enrichment factor is denoted by f , equation (12) becomes

$$x = \frac{(238.12 - 3.01f)(0.37037 - v)}{(71.08 - 1.11f)} \quad (13)$$

For the special case where $f = 0.935$, equation (13) becomes

$$x = 1.2443 - 3.3597 v \quad (14)$$

for 93.5 percent enriched uranium.

Of course, if a value of $f = 0.007$ (natural uranium) is substituted in equation (13), the result is identical to equation (12).

When enriched uranium is used, a given measured value of density corresponds to a slightly higher uranium content than would be given for natural uranium. For an enrichment factor of $f = 0.935$, the fractional increase in composition corresponding to a given measured density is

$$\frac{dx}{x} = +0.0029 \quad .$$

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For example, the density value corresponding to a natural uranium content of 15.00 percent is the same as the density value for 15.04 percent of uranium enriched 93.5 percent.

Sensitivity

The sensitivity of the method when applied to the aluminum-uranium system in the range of interest is given by substituting the appropriate values in equation (10):

$$dx = - \frac{0.6882}{(0.3704 - 0.1650)} dv = -3.35 dv \quad (15)$$

By the experimental techniques (to be described) for this investigation, the uncertainty, dv , in measured specific volume is of the order of $\pm 3 \times 10^{-5}$ cm^3/gm . Hence, the method is sensitive to differences of ± 0.01 weight percent uranium.

SPECIAL CONSIDERATIONS FOR ALUMINUM-URANIUM ALLOYS

Voids

The most serious source of possible error in a density-analysis correlation would arise from the presence of porosity or internal voids in the specimen. Since specific volume is defined as the ratio of volume to mass,

$$v = \frac{V}{M}$$

then

$$dv = \frac{dV}{M}$$

From equation (8) for a system where $x_{\alpha} = 0$,

$$dx = - \frac{x_{\beta} dv}{(v_{\alpha} - v_{\beta})} = -x_{\beta} \frac{dV}{M(v_{\alpha} - v_{\beta})} \quad (16)$$

Also, since $\frac{dv}{v} = \frac{dV}{V}$, and from equation (8)

$$\frac{dx}{x} = - \frac{dv}{(v_{\alpha} - v)}$$

then (in terms of absolute values)

$$\left| \frac{dx}{x} \right| > \left| \frac{dv}{v} \right| \text{ or } \left| \frac{dV}{V} \right|$$

Therefore, the uncertainty in composition is directly proportional to the volume of voids; the fractional error in calculated composition is greater than the fractional volume of voids (ratio of volume of voids to total volume of sample). It is possible, however, to take adequate precautions against this source of error, as described in the section on Experimental Methods.

Effect of Possible Variations in Composition and Density of UAl_4

Experimental determination of alloy density and density of the aluminum used in alloying may be readily obtained with massive samples.

However, chemical separation from the alloy would be required to obtain UAl_4 compound, and therefore x-ray lattice parameters reported by Borie⁽²⁾ have been used to compute a value of 6.06_2 gm/cm^3 for the density of stoichiometric UAl_4 . These "ideal" values of density and composition for UAl_4 compound have given results that correlate well with chemical analysis. The work of Borie suggests, however, that the intermetallic compound may exist over a range of composition, with either some uranium sites unoccupied, or with the substitution of some aluminum atoms on uranium sites. Of these possibilities, the latter would appear much more probable. The effect of such departure from stoichiometric composition may be computed.

Borie has determined that the UAl_4 unit cell is orthorhombic and contains four formula weights. Lattice parameters given are: $a = 4.41 \text{ \AA}$, $b = 6.27 \text{ \AA}$, and $c = 13.71 \text{ \AA}$. If the number of sites occupied by uranium atoms per quarter cell is designated by γ , the specific volume of compound becomes

$$v_c = \frac{N V_o}{4 \{ A_U \gamma + [4 + (1 - \gamma)] A_{Al} \}} \quad (17)$$

where N = Avogadro's number = 6.024×10^{23} atoms/mole
(physical scale)

V_o = volume of unit cell = $37.91 \times 10^{-23} \text{ cm}^3$

A_U = 238.13

A_{Al} = 26.98.

Solved for γ , equation (17) becomes

$$\gamma = \frac{0.2704}{v_c} - 0.6389 \quad (18)$$

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The weight fraction of uranium in the compound is

$$x_c = \frac{A_U \gamma}{A_U \gamma + A_{Al}[4 + (1 - \gamma)]} \quad (19)$$

If equation (18) is substituted in (19), then

$$x_c = 1.1278 - 2.6656v_c \quad (20)$$

If x_c is substituted for x_p and v_c for v_p in equation (8), the expression for weight fraction of uranium in the alloy becomes

$$x = \frac{(1.1278 - 2.6656v_c)(0.37037 - v)}{(0.37037 - v_c)} \quad (21)$$

In the case where $\gamma = 1$, $v_c = 0.1650$ and equation (21) reduces to equation (12).

After chemical separation of the compound from the alloy, Borie obtained experimental values of $5.7 \pm 0.3 \text{ gm/cm}^3$ for the density of UAl_4 ($0.175 \pm .009 \text{ cm}^3/\text{gm}$ for specific volume). Figure 8 is a plot of equation (21) for three values of specific volume of UAl_4 in the range of 13-17 percent uranium. The three straight lines plotted converge, of course, at zero weight percent uranium. It will be noted that in the range of composition covered by Figure 8, a variation of $\pm .009 \text{ cm}^3/\text{gm}$ in v ($\pm 0.3 \text{ gm/cm}^3$ in ρ) will affect the correlation with chemical analysis by approximately ± 0.15 weight percent. Inasmuch as use of the x-ray density value gave excellent experimental agreement with chemical analysis in the present work, it would appear unlikely that the compound differed significantly from ideal UAl_4 in the chill castings used.

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Effect of Non-Equilibrium Phase -- Possible Presence of UAl_3

In some instances the presence of the intermetallic compound, cubic UAl_3 , has been reported in alloys containing less than 68.8 weight percent uranium. From the equilibrium diagram, Figure 3, it will be noted that UAl_4 is formed during equilibrium cooling by a peritectic reaction between liquid of approximately 17 weight percent uranium and solid UAl_3 . The presence of impurities is said to retard the peritectic and result in retained UAl_3 . Both x-ray diffraction and metallographic examination were used in this investigation on alloys covering a range of 7 to 21 percent uranium in an attempt to detect the presence of UAl_3 . Neither method revealed any UAl_3 in these alloys. It is suggested that in chill casting from a homogeneous liquid that is relatively free of impurities, the cooling rate is so rapid that the peritectic equilibrium reaction is by-passed, and UAl_4 precipitates directly from the liquid. Such a mechanism could also explain the inverse segregation noted in these chill castings.

Even though no UAl_3 was found, it is of interest to estimate the magnitude of error in a density-analysis correlation if UAl_3 were present. From Kaufmann and Gordon,⁽¹⁾ the x-ray density for UAl_3 is 6.80 gm/cm^3 . If, in the worst case, it is assumed that all of the uranium occurs as UAl_3 , a density-analysis correlation can be computed for this situation by substituting the proper numbers for x_p and ρ_p in equation (7). Such a calculation shows that if the uranium were actually present as UAl_3 , and it had been assumed to be

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present as UAl_4 , the calculated uranium content for alloys near the eutectic would be about 0.05 weight percent high. Hence, it is readily apparent that the presence of small amounts of UAl_3 cannot influence results significantly.

Effect of Presence of Uranium Carbide

The effect of impurities on a density-analysis correlation is illustrated by a calculation on the effect of carbon, which is a principal impurity in uranium. Biscuit uranium, used as melting stock, contains the order of 50 ppm carbon. Since the alloys used in this investigation were obtained by dissolving solid uranium in molten aluminum at a maximum temperature of $900^{\circ}C$ ($1650^{\circ}F$), very little carbon was picked up from the graphite crucible. For the purposes of this calculation, therefore, a nominal carbon content of 100 ppm will be assumed.

Three carbides of uranium may occur: ⁽³⁾

<u>Formula</u>	<u>Density, ρ, gm/cm³</u>	<u>Specific Volume, v, cm³/gm</u>
UC	13.6	0.0735
U_2C_3	12.88	0.0776
UC_2	11.68	0.0856

Assume:

1 gram of alloy, and
carbide present as UC_n .

Let:

x = wt. fraction of uranium

y = " " " carbon

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and substituting numerical values

$$dx = \left[3.35v_{\epsilon} \left(\frac{19.8 + n}{n} \right) - \frac{4.8}{n} - 1.24 \right] dy . \quad (24)$$

The worst case is that in which $n = 1$ and $v_{\epsilon} = 0.0735$, i.e. when all carbon is present as UC.

Equation (24) then becomes

$$dx = -0.9 dy, \text{ or } dx \approx -dy. \quad (25)$$

If $dy = 100 \text{ ppm} = 10^{-4}$, then $dx = -0.01$ weight percent U. That is, the presence of 100 ppm carbon gives an apparent uranium content 0.01 weight percent higher than the true value.

If the other extreme, UC_2 ($n = 2$ and $v_{\epsilon} = 0.0856$), is chosen, the error is about 0.005 weight percent uranium. In either case the error is insignificant.

Effect of Variations in Aluminum Density

Density of the aluminum base metal will vary with purity. For example, high purity (99.9 percent or 99.99 percent) aluminum in the wrought condition has a density* of 2.7000 gm/cm^3 , whereas the density of 2S aluminum is quite variable and may be as high as 2.7100 gm/cm^3 . Sensitivity of calculated composition to variation in aluminum density is obtained by differentiating equation (7) with respect to ρ_{α} , which gives

$$dx = \frac{(\rho - \rho_{\beta})}{(\rho_{\beta} - \rho_{\alpha})^2} \frac{\rho_{\beta}}{\rho} x_{\beta} d\rho_{\alpha} . \quad (26)$$

In the neighborhood of 15 weight percent uranium, an extreme variation in aluminum density from 2.70 to 2.71 corresponds to

*Uncorrected for air buoyancy — see Appendix.

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$\rho = \pm 0.005 \text{ gm/cm}^3$, and in this case

$$dx = \frac{(3.10 - 6.06)}{(6.06 - 2.70)^2} \left(\frac{6.06}{3.10} \right) (.688)(.005) ,$$

or $dx \approx 0.2$ weight percent uranium. Thus, it is quite apparent that the density of aluminum melting stock must be known fairly closely.

In this work, 99.9 percent pure aluminum was used. Pig aluminum, as received from the mill, is considerably porous, and therefore, its density was determined experimentally after hot working to seal voids. By this technique an aluminum density was measurable to within $\pm .0003 \text{ gm/cm}^3$. This variation, when introduced in equation (26), gives an uncertainty of ± 0.01 weight percent in the neighborhood of 15 percent uranium.

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EXPERIMENTAL METHODS

Specimens

All alloys from which samples were taken were melted and chill cast in vacuum. Two types of castings were used: (1), 1-1/2 inch square billets, approximately 7 inches long, in which compositions covered the range from 7 to 21 weight percent uranium in about two percent steps; (2), cylindrical tubes having about a 1-1/4 inch wall thickness, in which the uranium content was approximately 15 - 16 percent. Melting stock was 99.9 percent Alcoa aluminum, and cropped Mallinckrodt uranium biscuit estimated to be 99.94 percent pure. Low temperature (900°C max.) induction melting in a degassed graphite crucible was done in a vacuum of approximately 100 microns, and the molten metal was bottom poured into degassed graphite molds in the same vacuum chamber.

Castings were machined to sound surfaces and radiographed to detect voids. Samples having a volume of about two cubic centimeters were selected from sound portions. Microporosity was eliminated by hot pressing to seal voids—specimens were reduced about 50 percent in thickness at 450°C between anvils covered with tantalum to avoid sticking. After being ground through 2/0 metallographic paper and cleaned in distilled water and acetone, specimens were ready for density measurement.

Techniques

Various methods for experimental determination of density of solids are described in some detail by Hidnert and Pepper.⁽⁴⁾ A

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hydrostatic weighing method, in which the volume of sample is determined by loss in weight in liquid, was used in this investigation.

If buoyancy of air is neglected, density and specific volume are given simply as

$$\rho = \rho_L \left(\frac{W_g}{W_g - W_L} \right) \quad (27)$$

$$v = \frac{1}{\rho} = v_L \left(\frac{W_g - W_L}{W_g} \right) \quad (28)$$

where ρ = measured density of solid in gm/cm³

ρ_L = density of immersion liquid (~ 1 gm/cm³ for water)

W_g = weight of specimen in air

W_L = weight of specimen in liquid.

Inasmuch as densities of alloys measured here did not differ greatly from that of aluminum, and aluminum densities were computed from equation (27), errors introduced by neglecting buoyancy of air were essentially cancelled. A complete discussion of this point is given in the Appendix — in the general case air buoyancy may not be neglected.

The hot pressed, polished, and cleaned samples described above were weighed first in air and then in distilled water. Steps and precautions in weighing techniques were as follows:

(1) Weighings were performed on a "chainomatic" analytical balance having a sensitivity of 0.25 mg/mm. Weights in air were obtained to the nearest 0.1 mg. by the method of swings after the

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samples had been thoroughly dried in a vacuum dessicator. Chain and rider were calibrated with standardized weights. Samples were weighed individually and in groups of three as a cross-check.

(2) To assure thorough wetting of all surfaces, samples were immersed in distilled water which was then placed in a vacuum chamber. A combination of evacuation and simultaneous mechanical agitation served to dislodge air bubbles clinging to sample. Buoyancy resulting from such bubbles can lead to large errors. Water and samples were allowed to attain ambient balance temperature before weighing to avoid convection currents, which could affect results.

(3) Samples were transferred while completely wet to a weighing cage immersed in a 150 ml. beaker of de-aerated distilled water to which had been added a few drops of aerosol wetting agent to stabilize surface tension.* The immersed cage was suspended from the balance arm by a fine (40 gage) wire. Weight of empty cage plus suspension wire automatically corrected for surface tension on the suspension wire at the surface of the water. Care was exercised during weighing to avoid wetting the fine suspension wire above the air-water interface. When the precautions listed were observed, it was possible to reproduce weight in water measurements to 0.1 mg.

Although prolnced exposure to water may cause corrosion of aluminum-uranium alloys, no trouble was encountered in this investigation in the times required for the wet weighings.

*It was established that amount of wetting agent could be varied from two to twenty drops per 100 ml. of water without affecting results. Wetting agent is added after evacuation, otherwise foaming will result.

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(4) Water temperature was measured to the nearest 0.1°C during each weighing. Density values for water were obtained from standard tables. Final calculated densities of specimens were adjusted to a standard temperature of 25°C — the volume coefficient of thermal expansion of pure aluminum was used, inasmuch as actual water temperatures differed only slightly from 25°C , and in the highest uranium alloy studied (21 percent uranium) the volume of aluminum phase is greater than 80 percent of the total volume.

(5) Reproducibility of technique and experimental conditions was monitored by running standard samples with each batch of unknowns.

Precision and Sensitivity

If equation (28) is differentiated with respect to measured weight,

$$dv \leq 2 \frac{dW}{W_g} v_L \quad \text{where } dW = dW_g = dW_L,$$

or

$$dv \leq 2 \frac{dW}{V} v \quad \text{when } v_L \approx 1 \text{ (water).}$$

Experimentally, $dW = 10^{-4}$ gm., $V \approx 2 \text{ cm}^3$, and $v \approx 0.3 \text{ cm}^3/\text{gm}$ for 15 percent uranium. The absolute uncertainty in specific volume is then

$$dv = \left(\frac{2 \times 10^{-4}}{2} \right) (0.3) = 3 \times 10^{-5} \text{ cm}^3/\text{gm}.$$

The fractional error in specific volume (or density) is given by $\frac{dv}{v}$ and equals 10^{-4} . As shown earlier, this precision leads to a sensitivity in composition of 0.01 weight percent uranium.

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Chemical Analysis

After density values were obtained, samples were submitted for chemical analysis. Complete specimens were dissolved for analysis in preference to drillings to avoid possible errors from segregation in the specimens. An alkaline peroxide spectrophotometric method,⁽⁵⁾ reliable to $\pm$ one percent of the uranium present, was used. It is quite evident, of course, that a meaningful correlation between compositions determined by density and compositions determined by chemical analysis depends not only on good experimental technique in determining densities, but on a reliable and accurate method of chemical analysis, such as used here.

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RESULTS AND DISCUSSION

Experimental results fall into two groups:

- (1) Six specimens from each of the seven 1-1/2" square castings varying from 7 to 21 weight percent uranium.
- (2) About 90 specimens which represent a statistical sampling of a number of hollow cylinder castings in the neighborhood of 15 weight percent uranium.

Results for the first group are given in Figure 9 as the composition difference between chemical analysis and density prediction plotted as a function of uranium content. Results for the second group are plotted in Figure 10 as a statistical analysis — number of samples versus difference between chemical analysis and density prediction. In Figure 10 each point represents a total analysis difference spread of 0.05 weight percent uranium — for example, the 19 samples at 0.00 percent difference represent 19 samples that lie within the bracket minus 0.02 to plus 0.02 percent, inclusive.

Figures 9 and 10 also show estimated limits of precision for both methods of determining composition. An excellent correlation is evident, for almost all specimens in both plots lie well within the combined uncertainties of the chemical and density methods. The correlation is limited, primarily, by the accuracy of chemical analysis, which, as stated previously, is of the order of $\pm$ one percent of the uranium present.

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ACKNOWLEDGMENTS

The authors are indebted to W. L. Lees for helpful discussions, to E. B. Read and C. Albright for chemical analyses, and R. C. Pugh and C. Latham-Brown for many of the density measurements.

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APPENDIX

In the text it was pointed out that if density is calculated from loss of weight in liquid and computed by equation (27), an error results from neglect of buoyancy of air. In general, the air buoyancy cannot be ignored; in this work, however, negligible error arises by use of equation (27), as shown below.

Let:

- ρ = $\rho_l W_g / (W_g - W_l)$, uncorrected specimen density.
- v = $1/\rho$.
- ρ_t = true specimen density.
- v_t = $1/\rho_t$.
- ρ_g = density of air.
- ρ_l = density of weighing liquid.
- ρ_b = density of brass weights of analytical balance.
- W_g = mass of brass weights for weighing specimen in air.
- W_l = mass of brass weights for weighing specimen in liquid.
- V = volume of specimen.
- V_b = volume of brass weights, W_g .
- V'_b = volume of brass weights, W_l .

Equilibrium of forces for weighing in air and liquid, respectively, gives

$$V(\rho_t - \rho_g) = V_b(\rho_b - \rho_g) \quad (1A)$$

$$V(\rho_t - \rho_l) = V'_b(\rho_b - \rho_g) \quad (2A)$$

Dividing equation (1A) by (2A) and simplifying,

$$\rho_t = \frac{\rho_l V_b - \rho_g V'_b}{(V_b - V'_b)} \quad (3A)$$

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Since

$$V_b = W_g / \rho_b \quad \text{and} \quad V'_b = W_\ell / \rho_b$$

equation (3A) may be expressed as

$$\rho_t = \frac{\rho_\ell W_g}{(W_g - W_\ell)} \left(1 - \frac{\rho_g W_\ell}{\rho_\ell W_g} \right)$$

or

$$\rho_t = \rho \left(1 - \frac{\rho_g W_\ell}{\rho_\ell W_g} \right) \quad (4A)$$

Since $W_\ell / W_g < 1$, and ρ_g / ρ_ℓ is of the order of 10^{-3} , negligible error results from setting

$$W_g \approx \rho V \quad \text{and} \quad W_\ell \approx V(\rho - \rho_\ell)$$

in the second term in brackets in equation (4A). The result then simplifies to

$$\rho_t = \rho \left[1 - \frac{\rho_g}{\rho_\ell} \left(1 - \frac{\rho_\ell}{\rho} \right) \right] \quad (5A)$$

or

$$\rho_t = \rho(1 - \mathcal{J}) \quad (6A)$$

where

$$\mathcal{J} = \frac{\rho_g}{\rho_\ell} \left(1 - \frac{\rho_\ell}{\rho} \right)$$

In the case where density of high purity aluminum is determined by loss in weight in water,

$$\begin{aligned} \rho &= 2.7000 \text{ gm/cm}^3 \\ \rho_g &= 0.0012 \text{ gm/cm}^3 \text{ at } 25^\circ\text{C and } 760 \text{ mm mercury} \\ \rho_\ell &= 1 \end{aligned}$$

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Then

$$\delta = .000750$$

In the 21 percent uranium alloy, the highest uranium content used in this work, $\delta = .000766$.

Since $\delta \ll 1$, specific volume may be expressed simply as

$$v_t = 1/\rho_t = v(1 + \delta) \quad (7A)$$

For the aluminum-uranium system, true composition is given from equation (8) in the text as:

$$x_t = x_\beta \left[\frac{(v_\alpha)_t - v_t}{(v_\alpha)_t - v_\beta} \right] \quad (8A)$$

where the subscript "t" designates true values (since v_β was calculated from x-ray lattice parameters, the true value was used in the text).

The error caused by ignoring the buoyancy of air is $\Delta X = x_t - x$, which may be computed by substituting equation (7A) in equation (8A) and subtracting equation (8). The result simplifies to

$$\Delta X = -x \left[\frac{v_\beta \delta}{v_\alpha - v_\beta} \right] \quad (9A)$$

In this work the largest error in computed uranium content arising from neglect of air buoyancy occurs in the 21 percent uranium alloy. Substituting values,

$$\Delta X = -(0.21)(0.165)(.00076)/(0.370 - 0.165),$$

or

$$\Delta X \approx -0.01 \text{ weight percent uranium.}$$

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Fig.1. Schematic Binary Phase Diagram.

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Fig.2. Schematic Relations for General Binary Alloy. Composition vs. (a) Density, (b) Spec. Vol.

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Fig. 3. Aluminum-Uranium Phase Diagram.

Fig. 4. Composition vs. Density of Al-U Alloys from 0 to 68.8 Wt. Percent Uranium.

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Fig. 5. Composition vs. Density of Al-U Alloys from 13 to 17 Weight Percent Uranium.

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Fig 6. Composition vs. Specific Volume of Al-U Alloys from 0 to 68.8 Wt. Percent Uranium.

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Fig. 7. Composition vs. Specific Volume of Al-U Alloys from 13 to 17 Wt Percent Uranium.

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Fig.8. Composition vs. Specific Volume of Al-U Alloys for Different Compound Densities in Range 13 to 17 Wt. Percent Uranium.

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Fig. 9. Deviation of Chemical Analysis Results from Values Predicted by Density Measurements in Range 7 to 21 Weight Percent Uranium.

Fig.10. Statistical Analysis of Difference between Chemical Analyses and Values Predicted from Density Measurements in Region of 15 Wt. % U.