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PuAl alloys density measurements using gas pycnometer: First results

Odile Ast *, Marc Perez, Sebastien Carlet

CEA Valduc, DRMN, 21120 Is Sur Tille, France

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Abstract

Plutonium alloys density is an important data to determine some metallurgical parameters like martensitic (α') phase fraction (in relation with delta phase stability studies) and to quantify swelling (in relation with self radiation phenomena studies). Density is usually obtained by Archimedes technique. Density measurements on plutonium alloys using gas pycnometer have recently been developed in order to improve accuracy. This paper presents results for delta plutonium alloys (Pu 1.8–5.8 at% Al). The measurements by Archimedes technique and gas pycnometer give the same mean density but the accuracy is divided by 10 for the gas pycnometer method. The first results obtained with gas pycnometer are in agreement with literature.
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Keywords: Actinide compounds; Density; Archimede; Pycnometer

1. Introduction

The gas pycnometer is one of the non-destructive techniques for density measurements. This device allows measurements of volume with high precision (accuracy of an order of 5×10^{-5}), so it is interesting to see if it is possible to determine swelling of delta plutonium alloys. The application on plutonium measurements entails some problems, caused by radioactive self heating. A specific procedure has then been defined to perform measurement on delta plutonium aluminum alloys (1.8–5.8 at%).

2. Experimental technique

Generally, Archimedes technique is used to measure samples density [1]. This technique requires careful attention and is sensitive to many parameters: bubble surface tension, chemical changes, calibration of the fluid density. The accuracy is limited (0.02 g/cm^3) [1]. The gas pycnometer technique has been developed in glove box to improve accuracy of density measurements. The pycnometer allows determination of a sample volume by measuring the variation of helium pressure in a calibrated volume. The principle of this process is based on Boyle and Mariotte law (Eqs. (1) and (2)).

The process frequently used, shown in Fig. 1, is described hereafter. The expansion chamber contains a quantity of helium of about 1 cm^3 measured accurately. After the calibrated ball (with a certified volume) has been introduced in the sample chamber, the variation of pressure, ΔP, is measured accurately between the expansion chamber and the sample chamber (Eq. (1)).

This operation is then repeated without the ball (Eq. (2)).

$$V_{\text{precision ball}} = V_{\text{ch}} - V_{\text{exp}} \times \left(\frac{P_1^*}{P_2^*} - 1 \right) \quad (1)$$

$$V_{\text{empty}} = -V_{\text{exp}} \times \left(\frac{P_1^0}{P_2^0} - 1 \right) + V_{\text{ch}} \quad (2)$$

where P_1^0 is the equilibrated charge pressure (empty sample cup), P_2^0 the equilibrated pressure after expansion (empty sample cup), P_1^* the equilibrated charge pressure (calibrated ball in chamber), P_2^* the equilibrated pressure after expansion (calibrated ball into chamber), V_{ch} the volume of the sample chamber, V_{exp} the volume of the expansion chamber, and V_{empty} is the volume of the empty sample chamber (equal to 0).

These equations make possible the determination of the volumes of the expansion and sample chambers. The volume of the studied sample is deduced from Eq. (1), by replacing the ball by the sample. The density of the sample is achievable by knowing its mass.

Density measurements on plutonium alloys are more difficult to carry on since radioactive self heating involves an expansion of the sample chamber volume and creates temperature instability (Fig. 2). The total dispersion (blue dots) shows the instability of the gas pycnometer. This curve smoothens the imperfections, while, the pink curve concerns the moving dispersion. The first point of the moving dispersion is calculated from the first five volume measurements, the second point is obtained from the five following volume measurements and so on. This calculation is used to detect the anomalies of the specimen measurements (like radioactive self heating). This curve leads to define the range in which the system (gas/sample) is in a steady state. This steady state is obtained after 200 measurements. The average dispersion is then calculated with the values obtained from the 200th to the 400th measurements and is about 2×10^{-5} cm^3.

In order to stabilize the system with plutonium alloys, it is necessary to perform at least 400 measurements; so the only disadvantage of

* Corresponding author. Tel.: +33 3 80 23 48 51
E-mail address: odile.ast@cea.fr (O. Ast).

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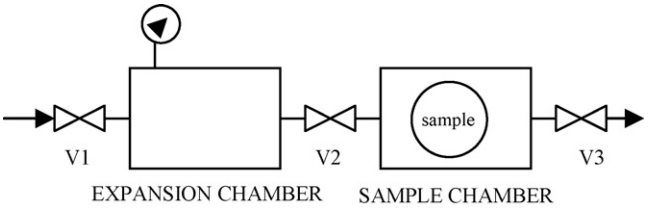

Fig. 1. Schematic diagram explaining the gas pycnometer process.

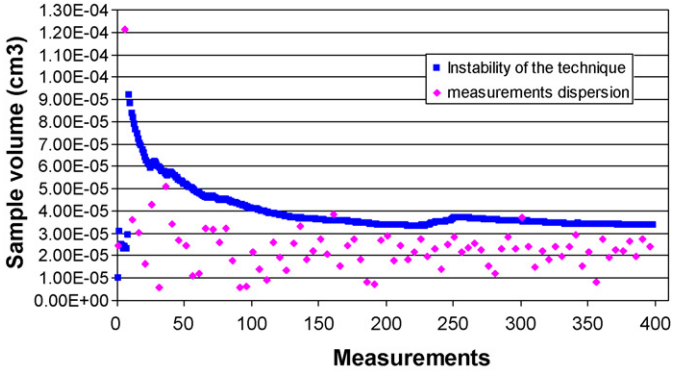

Fig. 2. Instability of the technique due to plutonium features.

this technique is that it is time consuming. The pycnometer was then modified in order to make possible the automatic acquisition of 400 data.

Moreover, the temperature is measured near the expansion chamber, rather far from the sample chamber. These chambers are in aluminum alloys whose expansion coefficient is about $2.2 \times 10^{-5}\,^{\circ}C^{-1}$. With that type of device, the temperature of the plutonium sample is unknown. This difficulty is in establishing a reference line to determine the volume of the sample chamber versus temperature. Many measurements have been performed at three different temperatures to determine the evolution of the volume of the two chambers in the range of temperature generally obtained with plutonium samples. The volume of the sample chamber is a linear function of temperature (Fig. 3), whereas the volume of the expansion chamber is nearly constant (Fig. 4), considering an accuracy of this volume in the order of 5×10^{-5} cm^3.

This reference line is used to improve the accuracy by determining the sample chamber volume precisely. The total accuracy is a sum of different parameters: accuracy of the measurement (3σ), accuracy of the reference line.

The next step of this study consists in determining the repeatability of the technique by measuring several times the volume of the same sample. The study showed that the accuracy due to the repeatability is negligible compared to the total accuracy (10^{-4} compared to 5×10^{-3} g/cm^3). Concerning plutonium

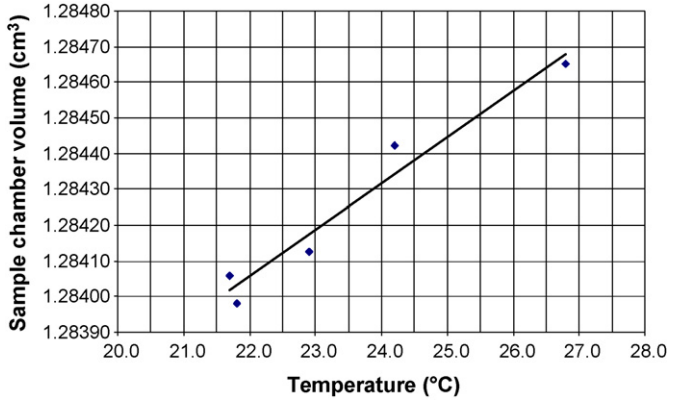

Fig. 3. Expansion of the sample chamber vs. temperature.

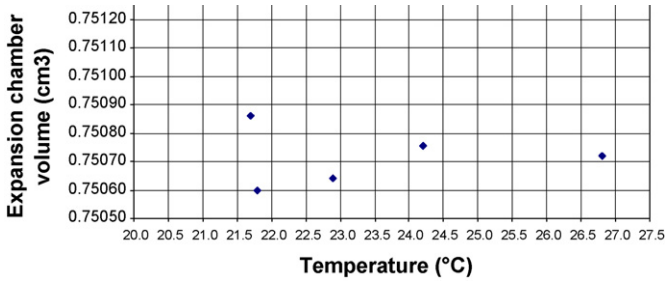

Fig. 4. Evolution of the expansion chamber volume vs. temperature.

alloys, it would be different in relation with the radioactive self heating; these experiments have not been done yet but will be carried on in 2007.

3. Density of delta plutonium aluminum alloys

The different alloys studied are PuAl alloys with different aluminum contents: 1.8, 2.3, 3, 5.8 at%. After casting, all these alloys have been heat treated for 10 h at 450 °C. The PuAl alloys phase diagram [2] shows the stability limit of the delta phase at about 2 at% of aluminum (Fig. 5).

Metallurgical characterizations have also been performed to check the quality of the casting. The mass used for hardness measurements is 100 g.

Hardness increases with solute content, in the range from 2 to 10 at% Al for which the samples are delta monophased (Fig. 6).

There is a minimum of hardness for an aluminum content of 2 at%. This trend seems to be due to an $(\alpha + \delta)$ biphase presence. These results are in agreement with Miller and White [3,4] (Fig. 7).

The density measurements have been performed using Archimedes and gas pycnometry techniques on the same sample.

Table 1 summarizes all the results. Both methods have given the same mean density, but the accuracy is improved by gas pycnometry (0.002 compared to 0.02 by Archimedes technique). Dividing the accuracy by 10 is very promising to measure precisely swelling on plutonium alloys.

Density decreases as solute content increases, excepted for the PuAl 1.8 at% alloy.

For the lowest aluminum content, the density obtained by pycnometry is lower than Archimedes measurement. Different assumptions have been emitted:

- We have to do again the measurements at least three times (to improve the statistic) and add this dispersion on the total accuracy calculation. To obtain valuable data it is necessary to remove the sample of the chamber, replace it and wait for

Table 1
Comparison of density obtained by Archimedes and pycnometer methods

PuAl alloys	Density (g/cm^3) using gas pycnometer	Density (g/cm^3) using Archimedes technique
PuAl 5.8 at%	15.485 ± 0.003	15.483 ± 0.006
PuAl 3 at%	15.642 ± 0.003	15.661 ± 0.014
PuAl 2.3 at%	15.699 ± 0.002	15.731 ± 0.009
PuAl 1.8 at%	16.244 ± 0.002	16.259 ± 0.012

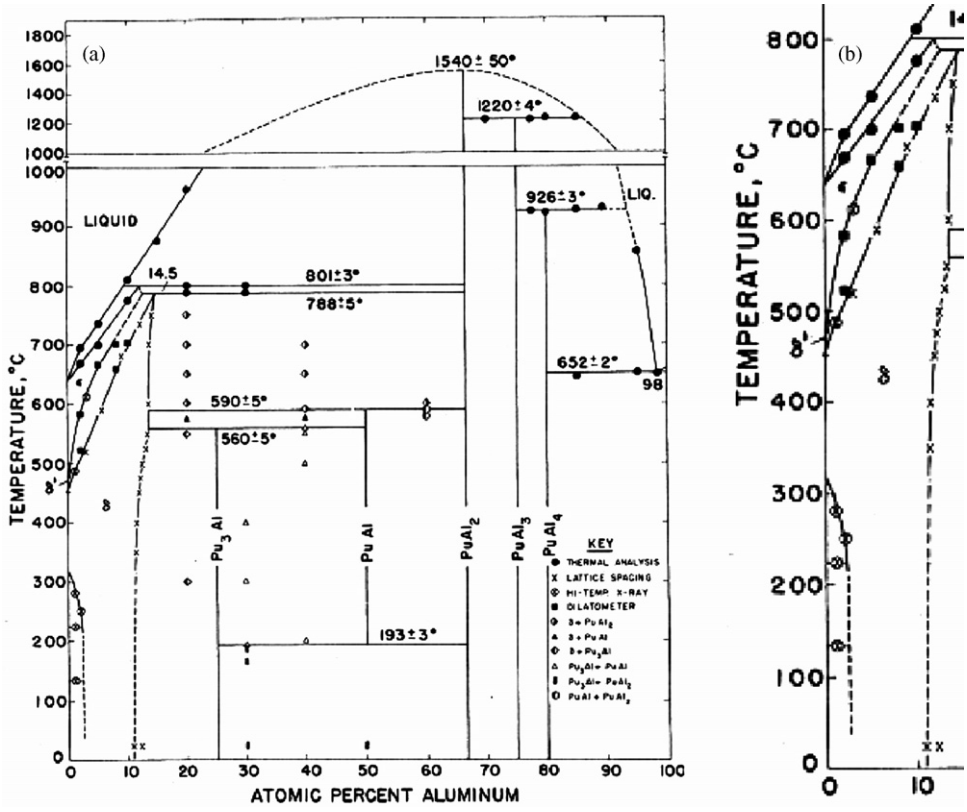

Fig. 5. PuAl alloys phase diagram [2].

the stabilization of the system for each measurement. It is the only way to determine the right volume and it takes a long of time.

Like hardness, density rises with the aluminum content as long as the aluminum content is lower than 2 at%. The density of PuAl 1.8 at%, obtained with this technique that we have measured, is higher than literature data.

For this low Al content, the sample is not monophased but is a mixture of α and δ phases, as confirmed by Electron Probe Micro Analyzer (EPMA) results that show strong aluminum coring (Fig. 8). In some area, the aluminum content is lower than the

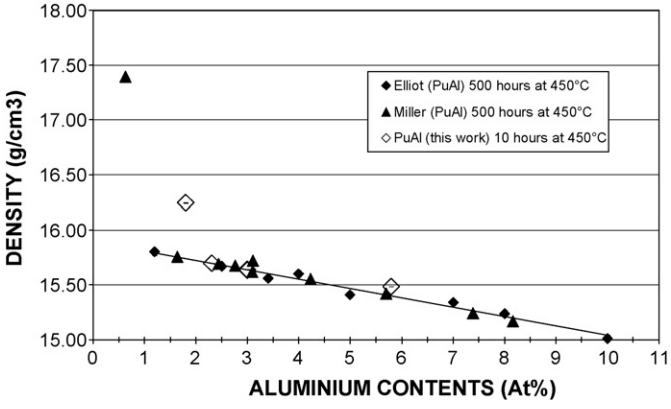

Fig. 7. Density vs. aluminum contents (at%): comparison with literature data.

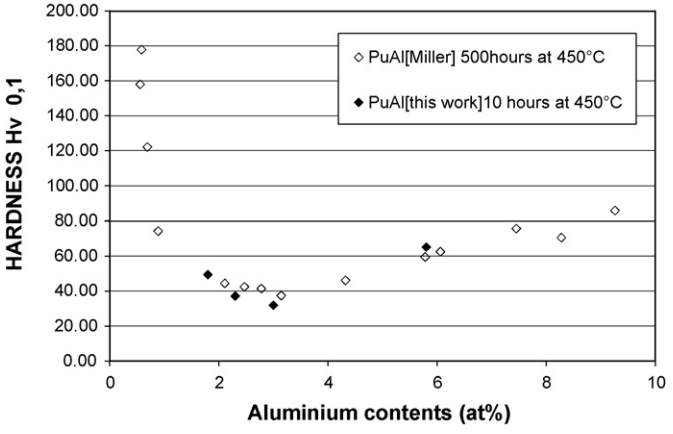

Fig. 6. Hardness vs. aluminum content (at%).

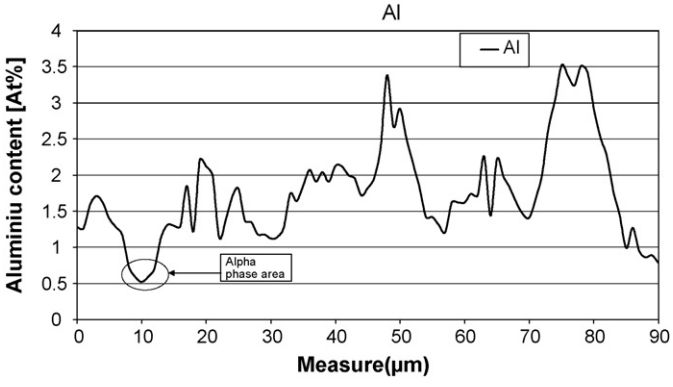

Fig. 8. Aluminum profile vs. distance for PuAl 1.8 at%.

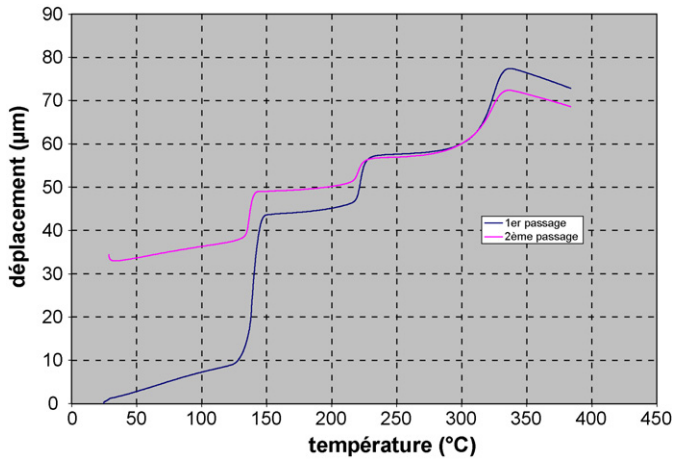

Fig. 9. Dilatometry curves performed to PuAl 1.8 at%.

threshold of the delta phase stability. In the work of Miller, a heat treatment of 500 h at 450 °C has been performed to obtain an homogeneous aluminum distribution and then to remove the alpha phase. The density and hardness enhancements are due to the alpha phase, whose hardness and density are about 220 Hv and 19.8 g/cm^3, respectively. Alpha phase volume% has been estimated by using the mixture law:

$$\mathrm{Hv}_{(\text{for } 1.8 \text{ at}\%)} = \%\alpha \times 220 + \mathrm{Hv}_{\delta} \times (1 - \%\alpha)$$

$$\mathrm{Density}_{(\text{for } 1.8 \text{ at}\%)} = \%\alpha \times 19.8 + \rho_{\delta} \times (1 - \%\alpha),$$

where Hv_{δ} = hardness of the homogenized delta phase, with aluminum content of 1.8 at%, ρ_{δ} = density of the homogenized delta phase, with aluminum content of 1.8 at%.

The hardness and the density of the homogenized δ PuAl 1.8 at% have been determined from Miller data.

The alpha phase volume%, obtained by these equations, is about 12%. A dilatometry measurement has been performed to determine precisely the alpha phase volume%. The dilatometry curve, shown in Fig. 9, has given an $(\alpha + \alpha')$ phases volume% equal to 11.7% which is in agreement with hardness and density measurements. However, it is not possible to discriminate these two phases by just knowing hardness and density. Alpha prime phase has been induced by samples machining. The second run has given an alpha phase volume% equal to 4%.

4. Conclusion

This paper shows that accuracy of density measurements has really been improved using gas pycnometer: accuracy has been divided by 10. First results obtained on PuAl alloys are in agreement with literature. Singular behavior of PuAl 1.8 at% has been explained by the high content of $(\alpha + \alpha')$ phases.

The outlook concerns the modeling of plutonium alloys temperature in order to obtain the real density. Accuracy must be still improved to perform swelling measurement (comparison with dilatometry results). After the complementary study, if we consider that the total accuracy is about 10^{-4} and if the volume of the sample is about 0.750 cm^3, we will be able to measure a swelling of about 10^{-4}.

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