Letter

# Thermal expansion of neptunium

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Neptunium metal exists in three allotropic forms. The structure of the room temperature or $\alpha$ phase is orthorhombic with lattice parameters $a = 4.723$ Å, $b = 4.887$ Å and $c = 6.663$ Å [1]. The $\beta$ phase is tetragonal and exists between 553 and 850 K with $a = 4.883$ Å and $c = 3.389$ Å at 555 K. The $\gamma$ phase is body-centered cubic with $a = 3.52$ Å at 873 K and is stable to 910 K, the melting point [2, 3]. Thermal expansion measurements of neptunium metal from 100 to 870 K are reported here, the first such reported measurements below room temperature.

Samples were prepared by casting and machining double-electrorefined neptunium into rods 5.0 cm in length and 0.635 cm in diameter. The results of a chemical analysis of the material performed before casting are given in Table 1. During the casting process the material was held in a tantalum crucible and then cast into a graphite mold. Differences in the composition of the dilatometer specimen from the analysis in Table 1 would then most likely arise in the tantalum and carbon values, but absorption of these elements would primarily be in the surface layer, which is removed during machining.

Thermal expansion measurements were made in a Theta dilatometer with a double pushrod for differential measurement, which minimizes errors introduced due to the thermal expansion of the measuring system. Samples were measured against an NBS fused silica standard reference material. Measurements with tungsten and borosilicate glass NBS standard reference materials against the fused silica standard indicate an accuracy of 5% or better in the coefficient of thermal expansion (CTE) over the temperature range 100 - 870 K.

Thermal expansion measurements were made on two samples. The density of each, determined by the immersion density method, was 20.41 g cm$^{-3}$ before and after thermal cycling. A thermal expansion measurement on sample 1 was made from 100 to 450 K followed by a measurement from 100 to 680 K. Three measurements were made on sample 2 from 100 to 680 K. One of the thermal expansion curves for sample 2 is shown in Fig. 1.

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TABLE 1

Chemical analysis of the neptunium samples

| *Element* | *Concentration* (ppm unless wt.% indicated) |
|---|---|
| Np | 99.97 wt.% |
| Ag | 3 |
| Al | 30 |
| Am | 0.2 |
| B | < 5 |
| Be | < 1 |
| Bi | < 1 |
| C | 20 |
| Ca | 100 |
| Cr | < 5 |
| Cu | < 1 |
| Fe | 5 |
| Mg | < 1 |
| Mn | < 1 |
| Mo | < 20 |
| Na | < 50 |
| Ni | < 5 |
| Pb | < 5 |
| Pu | 14 |
| Si | < 5 |
| Sn | < 5 |
| Zn | < 5 |
| $O_2$ | 75 |
| Ta | < 10 |
| W | < 20 |
| Ir | < 100 |
| U | < 10 |

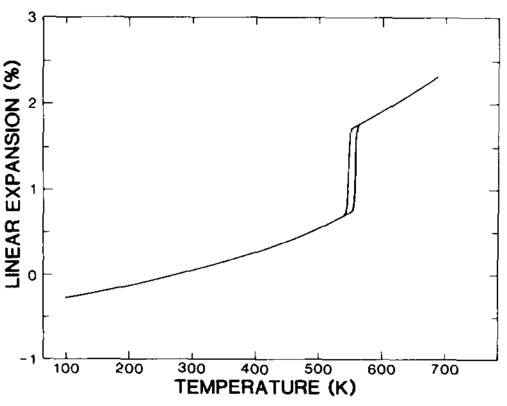


Fig. 1. Linear expansion of neptunium metal as a function of temperature from 100 to 680 K.

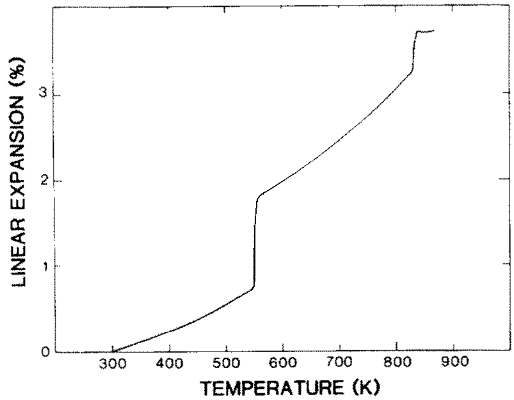


Fig. 2. Linear expansion of neptunium metal as a function of temperature from room temperature to 870 K.

Figure 2 shows results of a single measurement of the thermal expansion of sample 2 from room temperature to 870 K, where the sample began to sag.

Results for the coefficient of thermal expansion for the $\alpha$ and $\beta$ phases are shown in Table 2; literature values are listed for comparison where available. Results for transformation temperatures and the associated hysteresis are shown in Table 3. These were reproducible to within 1%. Comparison of these values with those of ref. 3 is good for the $\alpha$ phase within the

TABLE 2

Coefficient of thermal expansion (CTE) results for $\alpha$ and $\beta$ neptunium, compared with results of ref. 3

| *Phase* | *Temperature range* (K) | *CTE* ($10^{-6}$ K$^{-1}$) | |
|---|---|---|---|
| | | *This work* | *Ref. 3* |
| $\alpha$ | 100 - 300 | 16.2 ± 0.8 | — |
| $\alpha$ | 300 - 525 | 27.0 ± 1.4 | 27.5 |
| $\beta$ | 550 - 870 | 60.5 ± 2.2 | 41 |

TABLE 3

Transformation temperature results for the $\alpha \rightarrow \beta$, $\beta \rightarrow \alpha$, $\beta \rightarrow \gamma$ and $\gamma \rightarrow$ liquid transformations in neptunium

| *Transformation* | *This work* | | | *Ref. 3* |
|---|---|---|---|---|
| | *Onset* (K) | *Completion* (K) | *Midpoint* (K) | *Midpoint* (K) |
| $\alpha \rightarrow \beta$ | 551 ± 2 | 558 ± 2 | 555 ± 5 | 546 ± 5 |
| $\beta \rightarrow \alpha$ | 545 ± 2 | 538 ± 2 | 542 ± 5 | 536 ± 5 |
| $\beta \rightarrow \gamma$ | 830 ± 2 | 840 ± 2 | 832 ± 5 | 850 ± 10 |
| $\gamma \rightarrow$ liquid | 870 ± 5 | — | — | 913 ± 5 |

errors listed, but the values for the $\beta$ phase reported here are considerably higher. However, Zachariasen [2] reported a CTE value of $64 \times 10^{-6}\ K^{-1}$ for the 100 and 010 crystal directions and CTE $\approx$ 0 for the 001 direction from X-ray diffraction data in the interval 555 - 700 K. X-ray diffraction analysis of samples from one of the dilatometer specimens after the thermal expansion measurements indicates some preferred orientation present in the sample. The 010 reflection is particularly intense, indicating many grains with this orientation parallel to the face of the rod. Optical microscopy of this specimen, shown in Fig. 3, indicates very large grains and many twins. The minimum grain size is 200 $\mu$m. This microstructure is typical of the cast material. The twins are probably mechanical twins formed during cooling. Specimens that were quenched from the $\beta$ phase through the $\beta \rightarrow \alpha$ phase transformation in an attempt to randomize the grains showed no significant change in microstructure and very little decrease in the CTE for the $\beta$ phase.

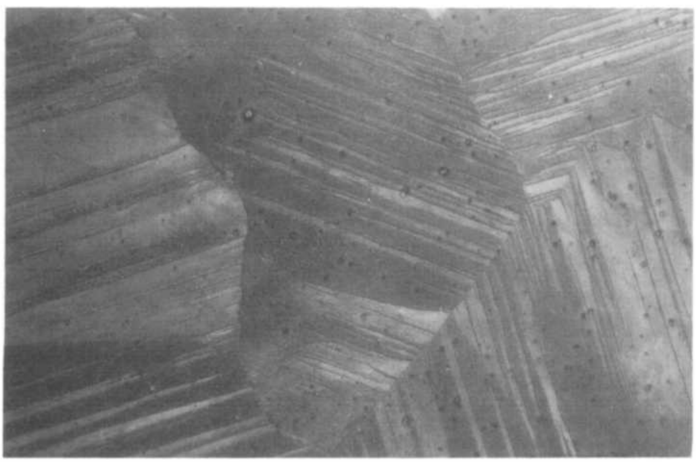

Fig. 3. Optical micrograph of neptunium (magnification, 100× ).

TABLE 4

Instantaneous values of the CTE for both $\alpha$ and $\beta$ phases at selected temperatures

| *Phase* | *Temperature* (K) | *CTE* ($10^{-6}\ K^{-1}$) |
|---|---|---|
| $\alpha$ | 100 | 11.1 |
| | 200 | 16.2 |
| | 300 | 21.3 |
| | 400 | 26.3 |
| | 500 | 31.4 |
| | 525 | 32.7 |
| $\beta$ | 550 | 42.8 |
| | 650 | 46.7 |
| | 750 | 58.5 |
| | 850 | 78.1 |

Instantaneous values of the CTE for selected temperatures are given in Table 4. These were reproducible to within 3% between temperature cycles of a single sample and 10% for the two different samples. Densities for the $\beta$ and $\gamma$ phases calculated from the thermal expansion data referenced to the room temperature value of 20.41 g $cm^{-3}$ are 19.30 g $cm^{-3}$ at 575 K and 18.30 g $cm^{-3}$ at 840 K.

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1 W. H. Zachariasen, Crystal chemical studies of the 5f series of elements. XVII. The crystal structure of neptunium metal, *Acta Crystallogr.*, *5* (1952) 660 - 664.
2 W. H. Zachariasen, Crystal chemical studies of the 5f series of elements. XVIII. Crystal structure studies of neptunium metal at elevated temperatures, *Acta Crystallogr.*, *5* (1952) 664 - 667.
3 H. A. C. McKay, J. S. Nairn and M. B. Waldron, The chemistry and metallurgy of neptunium, *Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958*, United Nations, Geneva, 1958, Paper P304, Vol. 28, pp. 299 - 306.