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**NASA TECHNICAL
MEMORANDUM**

NASA TM-78867

NASA TM-78867



(NASA-TM-78867) SOME PROPERTIES OF
LOW-VAPOR-PRESSURE BRAZE ALLOYS FOR
THERMIONIC CONVERTERS (NASA) 14 p HC A02/MF
A01 CSCL 10A

N78-22471

Unclas
16620

G3/44

**SOME PROPERTIES OF LOW-VAPOR-PRESSURE BRAZE
ALLOYS FOR THERMIONIC CONVERTERS**

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TECHNICAL PAPER to be presented at the
International Plasma Science Conference
sponsored by the Institute of Electrical and Electronics Engineers
Monterey, California, May 15-18, 1978

SOME PROPERTIES OF LOW-VAPOR-PRESSURE BRAZE

ALLOYS FOR THERMIONIC CONVERTERS

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SUMMARY

Binary eutectic alloys of Zr, Hf, Ru, Nb, Ir, Mo, Ta, Os, Re, and W fill the need for very-low-vapor-pressure ($<10^{-10}$ t at 1500 K and $<10^{-5}$ t at 2000 K) braze fillers for thermionics applications. These alloys have melting points from 1510 K; 600 K lower than unalloyed Zr which is the lowest melting metal to meet the above vapor pressure criterion (excluding Th).

The inherent advantages in using these alloys in the fabrication of thermionic energy converters calls for further investigation of their physical properties. To this end, property measurements were made for arc-melted, rod-shaped specimens nominally $1\frac{1}{16}$ inch in length to 0.225 inch in diameter. Density and d.c. electrical resistivity at 296 K were measured for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 19-wt percent W; Zr, 22.3-wt percent Nb; Nb, 66.9-wt percent Ru; Hf, 25.3-wt percent Re; Zr, 25.7-wt percent Ta; Hf, 22.5-wt percent W; and Nb, 35-wt percent Mo. Thermal conductivity was inferred from the electrical conductivity using the Wiedemann, Franz, Lorenz relation. Linear thermal expansion from 293 K to two-thirds melting point, under a helium atmosphere, was measured for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 22.3-wt percent Nb; Nb, 66.9-wt percent Ru; and Zr, 25.7-wt percent Ta.

INTRODUCTION

The screening and development of new electrode materials for lower temperature, out-of-core thermionics is a major focus of current thermionic energy conversion research (ref. 1). The diminiode, a miniature cesiated diode, is used at Lewis Research Center to screen and test these novel electrode materials (refs. 2 to 4).

Brazing and diffusion bonding are the two chief methods used at Lewis to attach the nonweldable electrode materials to Ta and Nb, 1 percent-Zr supports in the diminiode. A braze development program was begun to find electrode braze alloys of low vapor pressures in order to minimize intolerable vapor deposition contamination of the electrode surfaces. Binary eutectics of Zr, Hf, Ru, Nb, Ir, Mo, Ta, Os, Re, and W were selected as braze fillers since they would theoretically have vapor

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pressures of less than 10^{-10} torr at 1500 K and less than 10^{-5} torr at 2000 K (ref. 5). Thorium was omitted due to severe safety restrictions, but it also met the above vapor pressure criteria. Alloying was used to reduce melting points; for example, Zr-21.7-wt percent Ru has a melting point of 1510 K, 600 K below the melting point of Zr which is the lowest melting point metal considered above. Binary alloys of eutectic or melting-point-minimum composition were selected for homogeneous, instantaneous melting.

A prior report (ref. 6) gave current braze usage, melting points, composition, and hardness values for several of these braze alloys. This report provides the results of further property measurements.

Arc-melted, rod-shaped samples of nominal 2.7-cm ($1\frac{1}{16}$ in.) length with 0.57-cm (0.225-in.) diameters were prepared. Density was measured volumetrically and d.c. electrical conductivity was measured using a four terminal potentiometric method at 296 K for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 19-wt percent W; Zr, 22.3-wt percent Nb; Nb, 66.9-wt percent Ru; Hf, 25.3-wt percent Re; Zr, 25.7-wt percent Ta; Hf, 22.5-wt percent W; and Nb, 35 wt percent Mo. Thermal conductivity was inferred from the electrical conductivity using the Wiedemann, Franz, Lorenz relation (ref. 7).

Linear thermal expansion from 293 K to two-thirds melting point, under a helium atmosphere, was measured by a NASA contractor for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 22.3-wt percent Nb; Nb, 66.9-wt percent Ru; and Zr, 25.7-wt percent Ta using dual rod differential dilatometry and a coil-and-core linear variable displacement transformer (LVDT) electronic displacement measuring device.

Retrospective bibliographic searches were performed by the Center for Information and Numerical Data Analysis and Synthesis (CINDAS) at Purdue University for the properties of electrical resistivity, linear thermal expansion coefficient, and thermal conductivity for these alloys. No useful data could be found. Therefore, it is likely that these are the first determination for these materials.

SAMPLE PREPARATION

Previous work had shown that the physical properties of these refractory metal braze alloys were significantly affected by impurity levels (ref. 6). Arc-melted samples which generally have a lower level of impurities, especially interstitials such as oxygen, hydrogen, and nitrogen, appeared to be cleaner than samples hot-press sintered from powder.

Therefore, samples used in this study were formed by arc melting and remelting on a water-cooled copper hearth in an argon atmosphere. Except for Zr, 25.7-wt percent Ta and Zr, 19-wt percent W, small pieces of metal were melted rather than powder.

Chemical analysis was done on about half of these braze samples. Of nine alloys that have been analyzed, seven were within 2 percent of nominal; one was 5 percent off; the other, 11 percent off (ref. 6). Exact values are given where an analysis was made. The approximately 30-gm arc-melted buttons of the braze-filler alloys were remelted and cast in funnel-shaped molds. Then the rods were sawed from the cast mushrooms. The rods were then rough ground with a boron-nitride wheel.

Fluorescent penetrant dye was used to screen out samples with extensive cracks. Finishing was done by centerless grinding to a tolerance of ± 0.0005 cm (0.0002 in.) on a nominal 0.572 -cm (0.225 -in.) diameter. Length was approximately 2.7 cm ($1\frac{1}{16}$ in.) except for Hf, 25.3-wt percent Re which had cracked and was finished at 1.7 cm.

APPARATUS AND TESTS

The four-terminal d.c. current-voltage method was used to measure the resistivity of each sample. Except where noted, data were taken in air at 296 ± 1 K. The cylindrical specimen was cradled in a Lucite box. Point contacts nominally 2 centimeters apart (measured to ± 1 percent) were used to allow measurement of the potential drop with a nanovoltmeter (accurate to ± 2 percent full scale with overlapping full scales of 3, 10, 30, 100, etc.). A constant current source was set at 5 amperes d.c. using a 0.01Ω resistor accurate to ± 1 percent. Brass blocks carried the current to the flat ends of the cylinders. Voltage drops from 1 to 50 mV were measured.

Cross-sectional area and length were obtained accurately from the measured dimensions of the cylindrical specimens. Density was determined by dividing the observed weight on a microbalance by the calculated volume. Errors of less than 2 percent, including buoyancy effects, are expected from using this volumetric method (ref. 8).

The linear thermal expansion of each specimen was measured by a NASA contractor using dual rod differential dilatometry. In this method, a reference sample (in this case fused silica) is heated simultaneously with the material being measured. Fused silica or alumina extension rods translate sample displacement out of the hot zone to the measurement system. One extension rod pushes the core and the other the coil of an LVDT, thereby giving a voltage output proportional to the difference in thermal expansion. Expansion of the extension rods was effectively canceled out since the reference and specimen were of equal lengths. The rods push against the sample and the reference at a constant force.

Samples were heated in a helium atmosphere (0.1 ppm impurities allowed) at a rate of 5 K/minute with a 25-gram spring load. A dual trace strip chart recorder plotted relative expansion and thermocouple (K type) readings simultaneously. A fused silica reference sample was

used. Calculations were taken from the data at approximately 100 K intervals or more if needed for a smooth graph of $\Delta l/l_0$ against temperature.

RESULTS AND DISCUSSION

Electrical Resistivity, Density, and Thermal Conductivity

Table I gives the values obtained for density, electrical resistivity, and thermal conductivity. Nominal compositions for the alloys tested are given in the first column with measured values below in parentheses where known. Literature melting point and electrical conductivity, $(1/\rho)$ are also indicated. One sample was used for each composition.

Resistivity was calculated from the relation

$$\rho = \frac{RA}{l}$$

where R is the sample resistance in ohms, A is its cross sectional area in cm^2 , and l is the distance between voltage probes in cm (typically 2 cm). Each sample was measured six times (except for Hf, 25.3-wt percent Re) and the results were averaged for Table I. Placement of voltage contacts was varied between readings to average out anisotropic effects. Room temperature was 296 ± 1 K except for Hf, 25.3-wt percent Re at 302 K. Accuracy of these measurements was about ± 5 percent, mostly due to limitations of the potentiometer.

In general, the resistivities of these alloys were about ten times the resistivity of the less resistive metal and about three times that of the more resistive component. Two exceptions were Zr, 19-wt percent W and Nb, 35-wt percent Mo. There is a good possibility, especially since powdered Zr was used for Zr, 19-wt percent W, that impurities caused the increase for Zr, 19-wt percent W.

Densities were between those of the two constituent metals.

Thermal conductivity was estimated using the Wiedemann, Franz, Lorenz relation (ref. 7)

$$\sigma_T = \sigma_E TL$$

where

σ_T thermal conductivity

σ_E electrical conductivity

T degrees K

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L the Lorenz constant which is theoretically defined as

$$L = 2.45 \times 10^{-8} \text{ W}\Omega/(\text{K})^2$$

Thermal Expansion

Linear thermal expansion or contraction values for the alloys tested are shown in figures 1 to 5, inclusive. Each sample was first heated (circles) and then cooled (squares). Heating data points were used to draw the curves as temperature control was better during heating than during cooling. Also, there were some net changes in sample lengths due, most likely, to voids, inhomogeneities, and other imperfections (ref. 10). Despite the use of an ultrapure helium atmosphere, some surface contamination of the samples was seen in a darkening and dulling of the surface finish. This may be directly related to time and temperature since Zr, 25.7-wt percent Ta had the darkest surface.

The data, overall, have an estimated accuracy of ± 5 percent. Table II gives the average coefficients of expansion that have been obtained for sections of the expansion curves that are approximately linear. Net expansion changes of more than 100 ppm, as seen for Zr, 13-wt percent W; Zr, 66.9-wt percent Ru, and Zr, 25.7-wt percent Ta, are probably due to some physical imperfections in the samples.

In general, the thermal expansion curves of these refractory metal alloys were linear, with a slight increase in slope with temperature rise. A noticeable exception was the Zr, 13-wt percent W alloy. Here, a -0.125 percent jump occurred at around 1100 K. This mimics an identical break of -0.2 percent seen in the linear thermal expansion curve of pure Zr (ref. 9) due to an α to β transition. A net growth of 1280 ppm also occurred for the Zr, 13 W material. This large change seems to be due to a spurt of growth at about 900 K upon heating. It is probably due to an imperfection in the sample such as voids or inhomogeneities (ref. 10).

It can also be observed that the expansion of these alloys is close to their constituent metals. This should make them useful in critical brazing applications. Reference 9 gives expansion curves for all the above metals except Ru. The total expansion of the Zr, 22.3-wt percent-Nb braze was within 500 ppm of pure Nb data for its entire length. The Nb, 66.9-wt percent-Ru braze is very close to Ru in expansion and seems identical to the Nb data shown. The Zr-25.7-wt percent-Ta braze is within 500 ppm of Zr and Ta at temperatures below 900 K.

SUMMARY OF RESULTS

Density and d.c. electrical conductivity at 296 K were measured for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 19-wt percent W; Zr, 22.3 wt percent Nb; Nb, 66.9-wt percent Ru; Hf, 25.3-wt percent Re; Zr, 25.7-wt

percent Ta; Hf, 22.5-wt percent W; and Nb, 55-wt percent Mo. Thermal conductivity was inferred from the electrical conductivity using the Wiedemann, Franz, Lorenz relation. Linear thermal expansion from 293 K to two-thirds melting point, under a helium atmosphere was measured for Zr, 21.7-wt percent Ru; Zr, 13-wt percent W; Zr, 22.3-wt percent Nb; Nb, 66.9-wt percent Ru; and Zr, 25.7-wt percent Ta.

Resistivities of 55 to 181 (10^{-6} Ω cm) were observed with the alloys having resistivities about ten times that of the less resistive constituent metal and about three times that of the more resistive constituent metal. Two exceptions, with greater resistivities were Zr, 19-wt percent W and Nb, 35-wt percent Mo.

Coefficients of linear thermal expansion were from 6 to 10.5 (10^{-6} /K). Alloys had approximately linear thermal expansion curves with slowly increasing slopes with the exception of Zr, 13-wt percent W which showed a -0.125 jump at about 1100 K, following the α to β transition of Zr. All of the brazes had linear thermal expansion near that of their constituent metals.

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TABLE I. - PROPERTIES OF SOME REFRACTORY BRAZE ALLOYS (296 K)

Nominal ^a composition, wt %	Literature melting point, K	Density, gm/cm ³ (±2%)	Electrical resistivity, 10 ⁻⁶ Ω cm (±5%)	Electrical conductivity 10 ⁴ /(Ω cm) (±5%)	Approximate ^b thermal conductivity, (W/cm-K)
Zr, 21.7 Ru	1510	7.51	61.6	1.62	0.117
Zr, 18.3 W (13 W)	1930	7.25	70.2	1.42	.103
Zr, 18.3 W (19 W)	1930	7.59	139.0	.72	.052
Zr, 22 Nb (22.3 Nb)	2020	6.93	82.2	1.22	.088
Nb, 66.9 Ru	2040	10.80	88.3	1.13	.082
Hf, 24.3 Re (25.3 Re)	2110	14.61	c _{180.5}	c ₅₅	c _{.040}
Zr, 25 Ta (25.7 Ta)	2120	7.81	149.9	.67	.048
Hf, 22.5 W	2200	13.77	55.0	1.62	.132
Nb, 35 Mo	2560	9.12	173.4	.58	.042

^a Composition values are nominal. Values in parentheses give measured composition.

^b Calculated using $\sigma_T = \sigma_{ETL}$; $L = 2.45 \times 10^{-8} \text{ W}\Omega/(\text{K})^2$.

^c Measured at 302 K.

TABLE II. - AVERAGE COEFFICIENTS OF LINEAR THERMAL EXPANSION OF ALLOYS

Material	Total temperature range, K	Temperature range (K) for linear fit	Approximate linear coefficient of expansion, $(10^{-6})/K$	Comments	Net change in length, ppm
Zr, 21.7 Ru	293-1073	293-1073	6.82±0.25	Slope calculated by a least squares fit. Limits give 95 percent confidence interval on slope.	0
Zr, 13 W	293-1373	273-773 1100-1200 1273-1373	6.0 ~1250 ppm shift 8.8	Contraction reflects $\alpha \rightarrow \beta$ transition in Zr.	+1280
Zr, 22.3 Nb	293-1373	273-773 773-1073 1073-1373	7.0 8.0 8.9	Slope uniformly increases $\sim 1 \times 10^{-6}/K$ per 350 K	-90
Nb, 66.9 Ru	293-1373	373-773 773-1073 1073-1373	7.5 8.4 10.0		+370
Zr, 25.7 Ta	293-1473	273-673 673-973 973-1273 1273-1473	6.9 8.5 10.2 10.5		+280

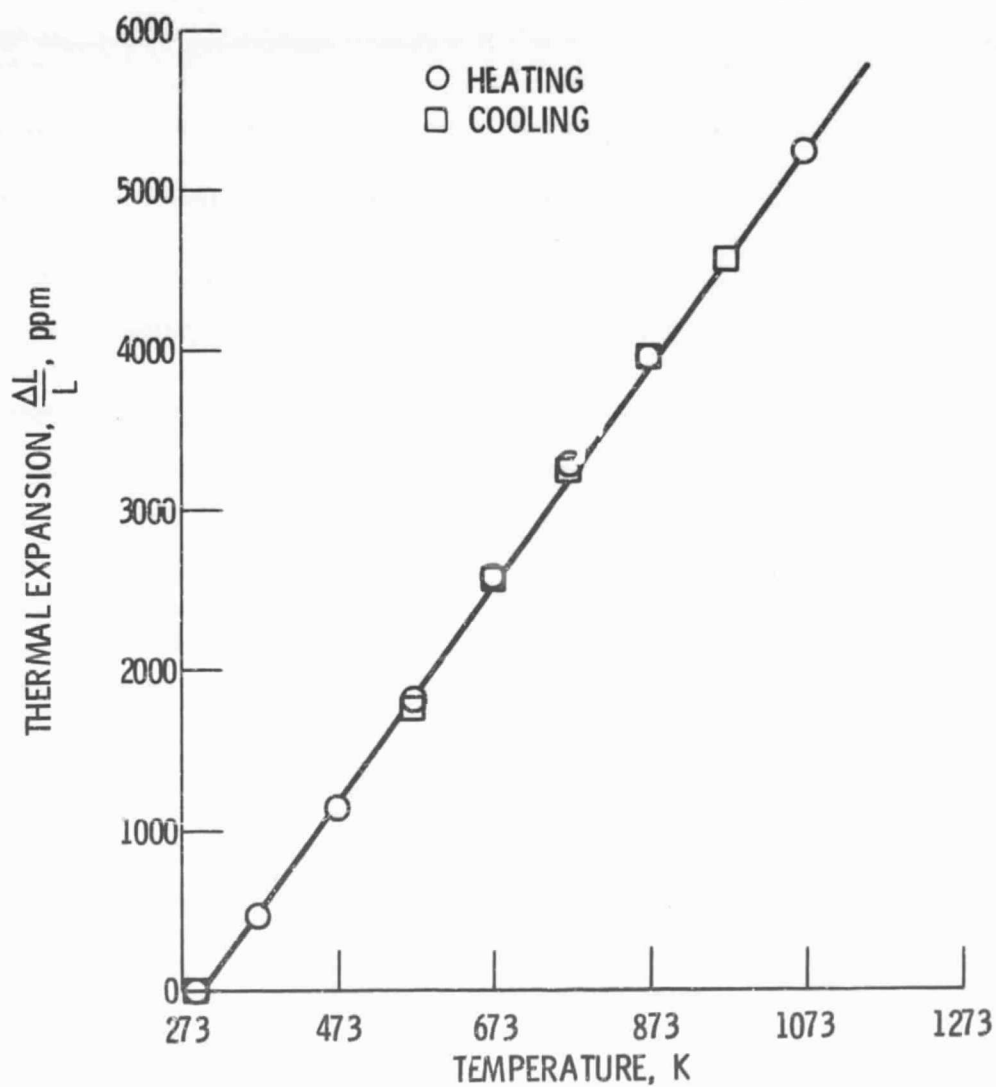


Figure 1. - Thermal expansion curve for zirconium - 21.7 ruthenium.

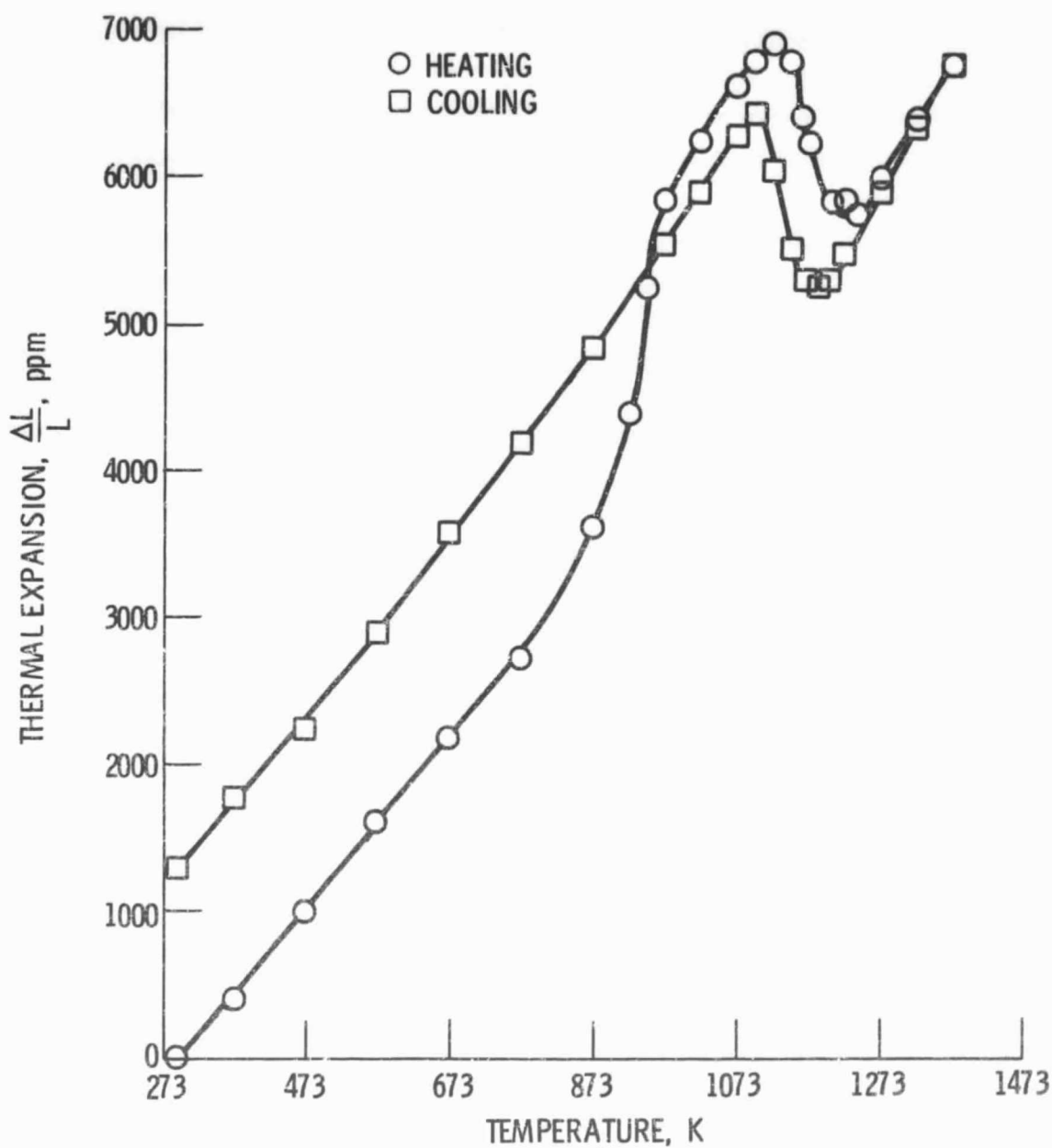


Figure 2. - Thermal expansion curve for zirconium - 13 tungsten.

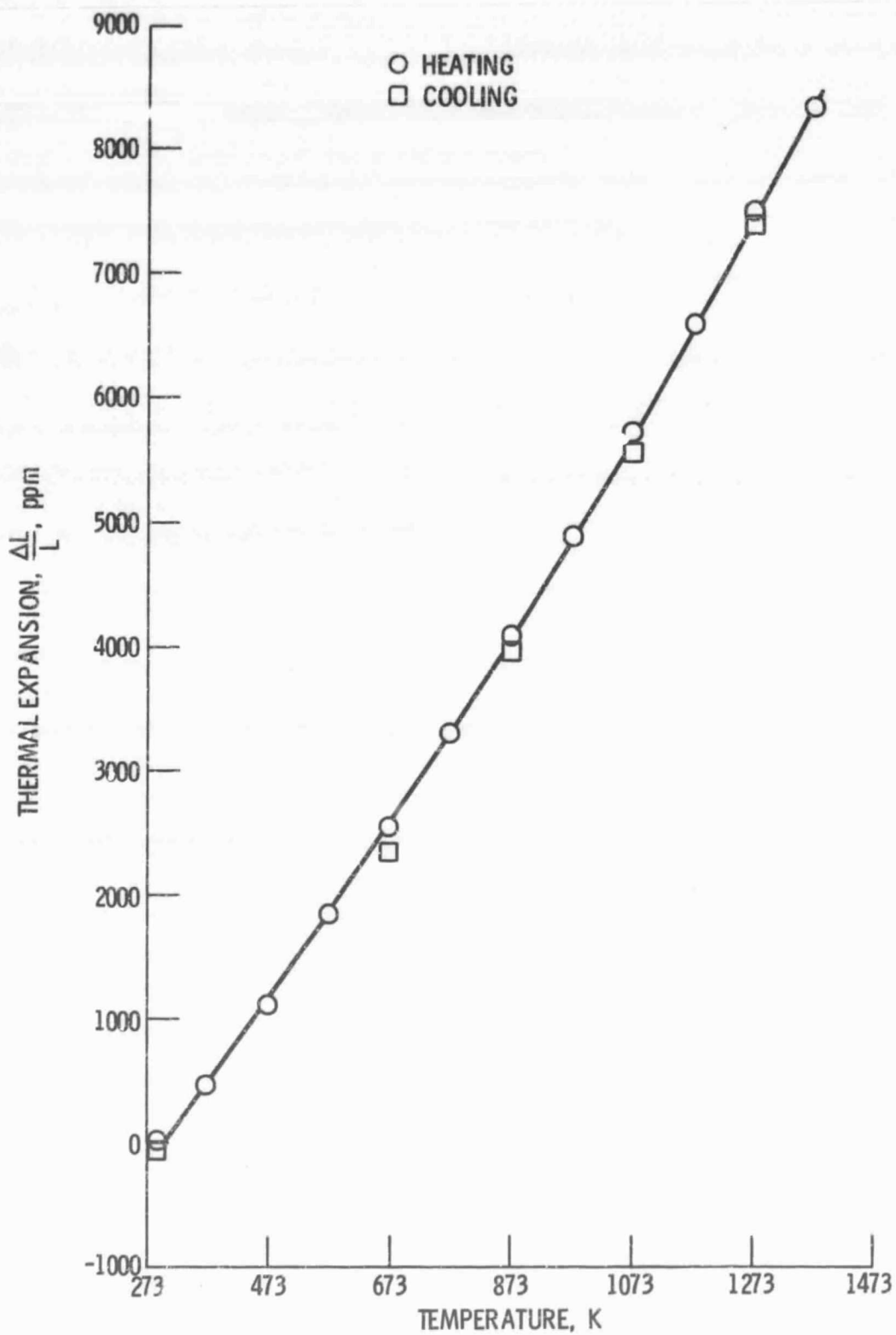


Figure 3. - Thermal expansion curve for zirconium - 22.3 niobium.

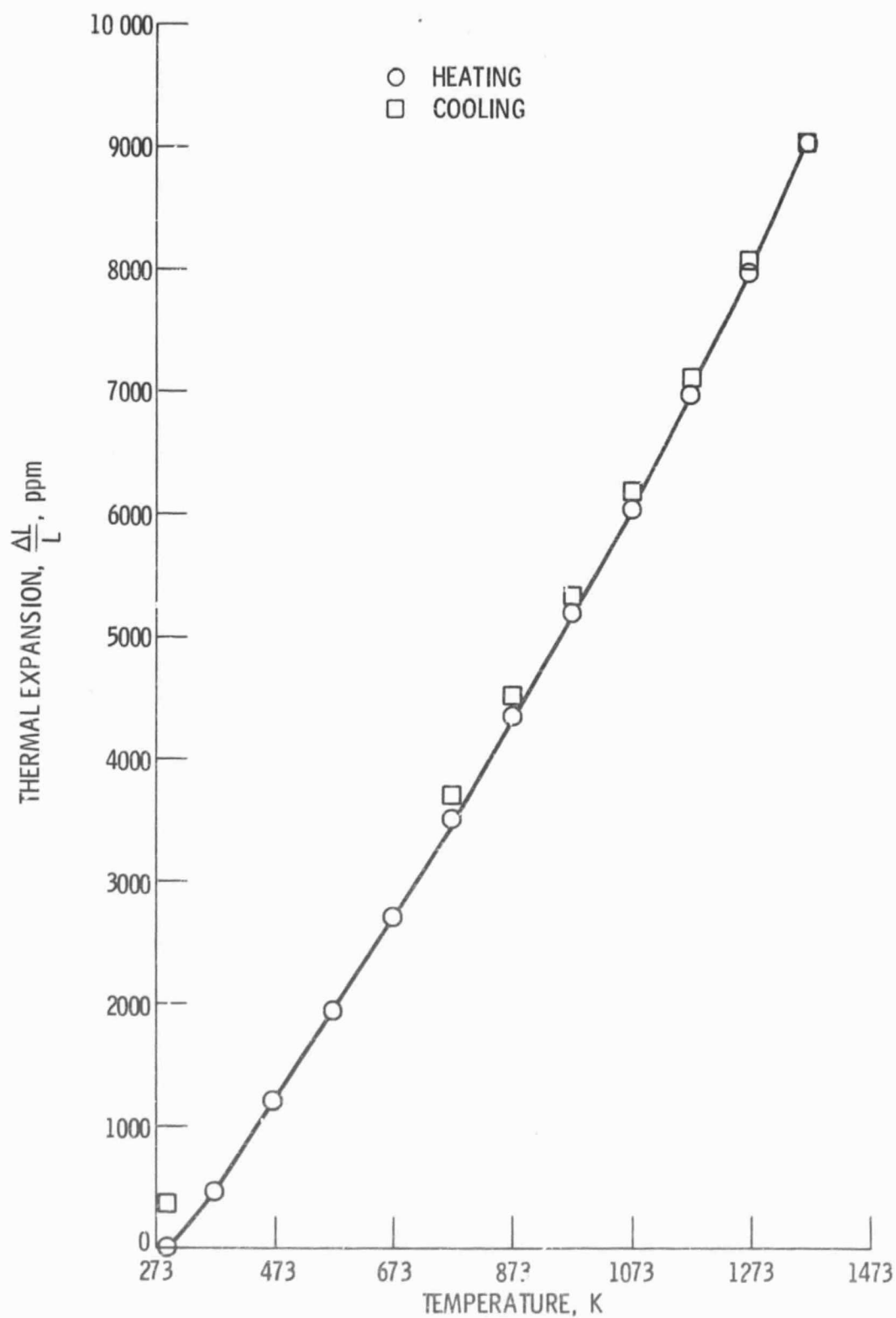


Figure 4. - Thermal expansion curve for niobium - 66.9 ruthenium.

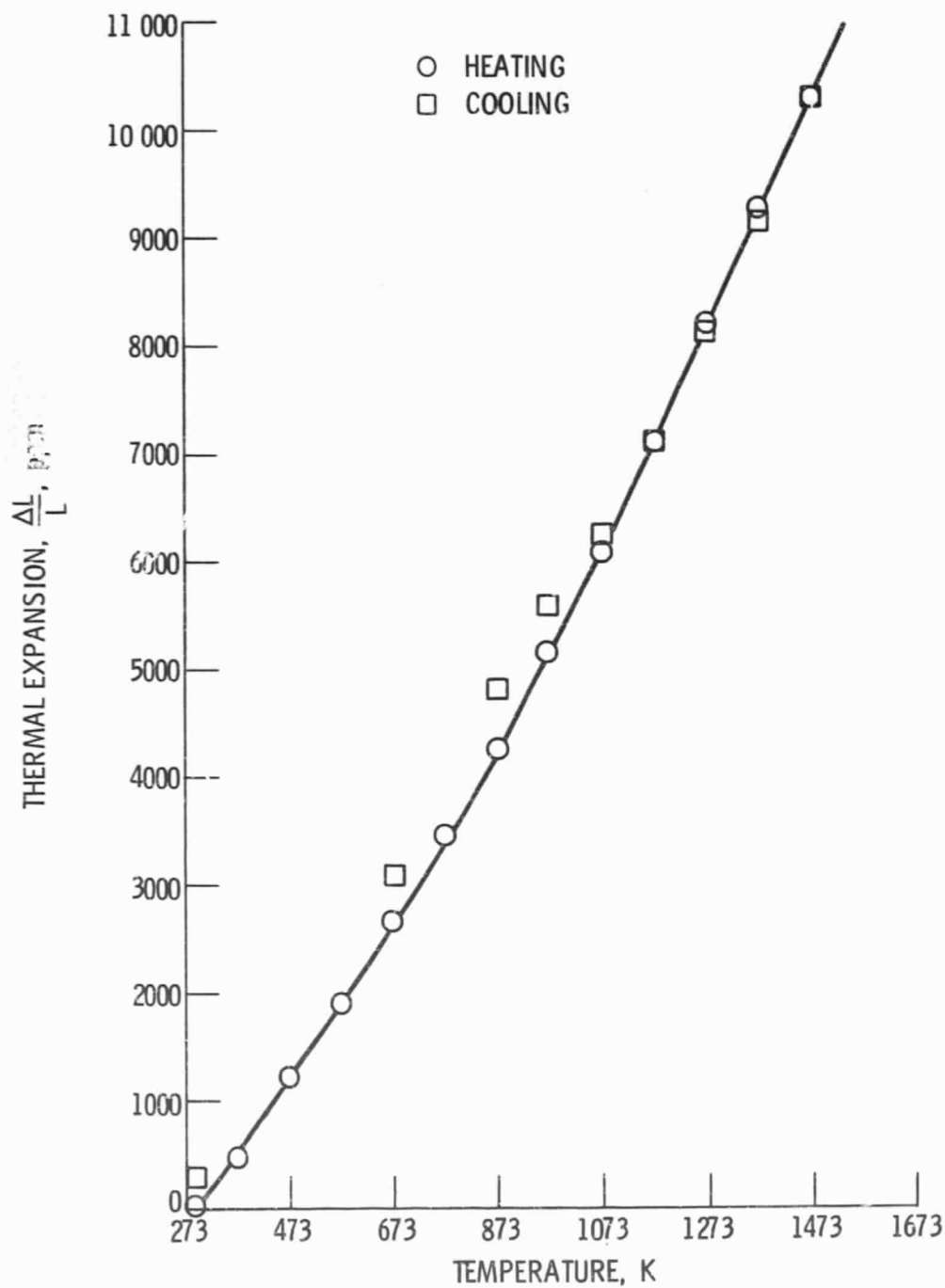


Figure 5. - Thermal expansion curve for zirconium - 25.7 tantalum.

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