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Thermal Expansion of Pyros from 20 to 1273 K[1]

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Pyros, which is a Ni-base alloy (82% Ni, 8% Cr, 4% W, 3% Mn, and 3% Fe), has been used extensively in France since 1926 as a temperature sensor and as a reference material for thermal expansion measurements. In this paper we present recent data on the expansion and expansivity of Pyros from 20 to 1273 K. Expansivity results, obtained by taking the derivative of a cubic-spline polynomial fitting performed to the $\Delta L/L$ experimental data, show that Pyros is a stable material in the 20 to 1273 K temperature range. Furthermore, since the expansivity values are similar to those of steels, Pyros should be of special interest to laboratories which are concerned with expansion measurements on steels. Therefore, we suggest that Pyros be considered as a suitable reference material for thermal expansion measurements on steels, and until more accurate results are obtained, we propose our results as reference data between 20 and 1273 K.

KEY WORDS: expansivity; high temperatures; low temperatures; Ni alloy; Pyros; reference material; thermal expansion.

1. INTRODUCTION

Research studies undertaken since 1894 by Imphy Steelworks and the Bureau International des Poids et Mesures on nickel steels [1] resulted in the development of a Ni-base alloy named Baros (90% Ni and 10% Cr). Results obtained in 1914, using the dilatometer described in Ref. 2, had shown that this alloy would be an excellent reference material for the study of iron alloys. The expansivity of Baros was found to be reversible, except

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for a small anomaly at about 820 K, and similar to that of steels. Furthermore, since expansivity could be expressed by the linear relationship between 273 and 1173 K [3],

$$\alpha = \frac{1}{L_{273}} \frac{dL}{dT} = 4.33 \times 10^{-9}\,\theta + 12.80 \times 10^{-6} \tag{1}$$

where θ is in °C. Baros could also be used for temperature measurements instead of thermocouples, which were not of practical use at that time. It was first used as such in the optical lever differential dilatometer developed by Chevenard in 1916 [3].

Pyros, a Ni–Cr–W alloy with additions of Mn and Fe [4], also developed by Imphy Steelworks, succeeded Baros as a pyrometer and as a reference material, essentially because it could be repeatedly used at temperatures as high as 1373 K. The expansivity of Pyros, which was also found to be similar to that of steels but more reversible than that of Baros, was expressed by the following relationship between 123 and 1273 K [4]:

$$\alpha = \frac{1}{L_{273}} \frac{dL}{dT} = A\left[\frac{e^{B/T}(B/T)^2}{(e^{B/T}-1)^2} + \frac{e^{B/2T}(B/2T)^2}{(e^{B/2T}-1)^2}\right] + 2CT \tag{2}$$

where T is in K, $A = 5.625 \times 10^{-6}$, $B = 336$, and $C = 3.94 \times 10^{-9}$. Pyros was used first as a pyrometer in the thermal analysis apparatus developed by Chevenard in 1919 [5] and then as a pyrometer and as a reference material in another version [6] of the optical lever differential dilatometer [3].

2. EXPERIMENTAL PROCEDURE

The thermal expansion of Pyros (cast No. 56: 82% Ni, 8% Cr, 4% W, 3% Mn, and 3% Fe) from 20 to 1273 K was obtained using two different dilatometers. Eleven samples were taken from various positions along the stock. Five samples were used for low-temperature measurements, whereas the other six were tested at high temperatures.

2.1. Low-Temperature Measurements (20 to 300 K)

Dilatometric results from 20 to 300 K were obtained with a tube-type vitreous silica differential dilatometer. The apparatus realized in the laboratory [7] and interfaced with a microcomputer to measure automatically the thermal expansion of solids from 4.2 to 350 K [8] was calibrated with NBS (U.S. National Bureau of Standards) certified copper and tungsten [9]. Measurements were performed relative to SRM 736

(OFHC copper) and the thermal expansion data used in the 20 to 300 K temperature range were those of the NBS [10]. Temperature measurements, with an accuracy of 0.2 K, were made by placing the hot junction of a calibrated thermocouple (Au–0.03 at % Fe and Chromel wires) into the drilled hole of a copper dummy specimen filled with a thermal bonding agent based on silicones and fillers [11]. The dummy specimen was placed in the vicinity of the sample and the reference material, and helium exchange gas was used in the dilatometer chamber. Cylindrical specimens 50 mm in length and 6 mm in diameter were cycled between 20 and 300 K using a cooling and heating rate of 1 K. min^{-1}. Data points collected at 0.5 K temperature intervals during cooling and heating were averaged, giving a unique set of thermal expansion data per sample.

2.2. High-Temperature Measurements (293 to 1273 K)

High-temperature dilatometric measurements were obtained with a vitreous silica single push-rod dilatometer (Adamel Lhomargy Model Di. 23) in which expansion is measured by means of a differential transformer (LVDT) with a sensivity to relative length changes $\Delta L/L$ of 5×10^{-6}. The apparatus was calibrated with NBS certified fused silica [12] and borosilicate glass [13]. Data used for the thermal expansion of the vitreous silica support system were those of the NBS [12] from 293 to 1000 K and those of Otto and Thomas [14] above 1000 K. Temperature measurements, with an accuracy of 0.5 K, were realized by placing the hot junction of a type S calibrated thermocouple (Pt vs Pt–10% Rh) into the drilled hole of a Pyros sample (25 mm in length and 6 mm in diameter). Heating and cooling rates were 3.5 K. min^{-1} and purified argon (<6 ppm O_2) exchange gas was used in the dilatometer chamber. Under these conditions, the temperature gradient along the sample was <1 K. For high-temperature measurements, data points collected at 5 K temperature intervals during cooling and heating were averaged, giving a unique set of thermal expansion data per sample.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The averaged data from the five/six sets of low/high-temperature thermal expansion measurements obtained on Pyros are shown as a function of temperature in Table I along with expansivity values. The expansivity was obtained by taking the derivative of a cubic-spline polynomial fitting performed to the averaged $\Delta L/L$ experimental data. Table I also shows a comparison between expansivity values obtained in the

Table I. Thermal Expansion and Expansivity of Pyros Between 20 and 1273 K[a]

Temperature (K)	(a) $\frac{L_T - L_{293}}{L_{293}}$	(a) $\alpha = \frac{1}{L_{293}} \frac{dL}{dT}$ (K^{-1})	(b) $\alpha = \frac{1}{L_{293}} \frac{dL}{dT}$ (K^{-1})
20	-2282×10^{-6}	0.14×10^{-6}	
30	−2279	0.50	
40	−2272	0.85	
50	−2259	1.81	
60	−2236	2.85	
70	−2204	3.85	
80	−2161	4.79	
90	−2108	5.56	
100	−2048	6.40	
110	−1980	7.19	
120	−1904	7.93	
123	−1880	8.01	8.92×10^{-6}
130	−1823	8.40	9.24
140	−1736	8.90	9.65
150	−1645	9.40	10.02
160	−1548	9.93	10.34
170	−1448	10.20	10.63
180	−1344	10.45	10.89
190	−1237	10.76	11.13
200	−1127	11.23	11.35
210	−1014	11.40	11.55
220	−899	11.59	11.74
230	−782	11.68	11.92
240	−664	12.16	12.08
250	−542	12.18	12.24
260	−419	12.57	12.39
270	−294	12.60	12.53
290	−39	12.97	12.79
293	0	13.05	12.83
303	131	13.22	12.95
353	799	13.44	13.52
403	1479	13.70	14.03
453	2172	14.07	14.50
503	2883	14.40	14.96
553	3612	14.72	15.39
603	4363	15.25	15.82
653	5138	15.75	16.24
703	5938	16.31	16.66
753	6766	16.85	17.07
803	7622	17.40	17.48
853	8507	18.00	17.88
903	9422	18.58	18.28
953	10369	19.25	18.69
1003	11346	19.83	19.09
1053	12355	20.50	19.49
1103	13394	21.12	19.89
1153	14464	21.70	20.29
1203	15564	22.22	20.68
1253	16692	22.85	21.08
1273	17152	23.15	21.24

[a] (a) Present investigation; (b) values from Ref. 4.

present investigation (a) and those calculated using Eq. (2) (b). The difference observed between a and b in Table I is due to the accuracy of expansion and temperature measurements and, eventually, to a slight variation in the composition of the Pyros used by Chevenard (82% Ni, 7% Cr, 5% W, 3% Mn, and 3% Fe [4]).

The maximum variation in expansivity results obtained for different samples was $<0.5\%/<1\%$ for samples used for low/high-temperature measurements. Since this is the accuracy of expansivity measurements, we conclude that the stock is of consistent quality.

Figure 1 is a plot of the thermal expansion of Pyros. Some experimen-

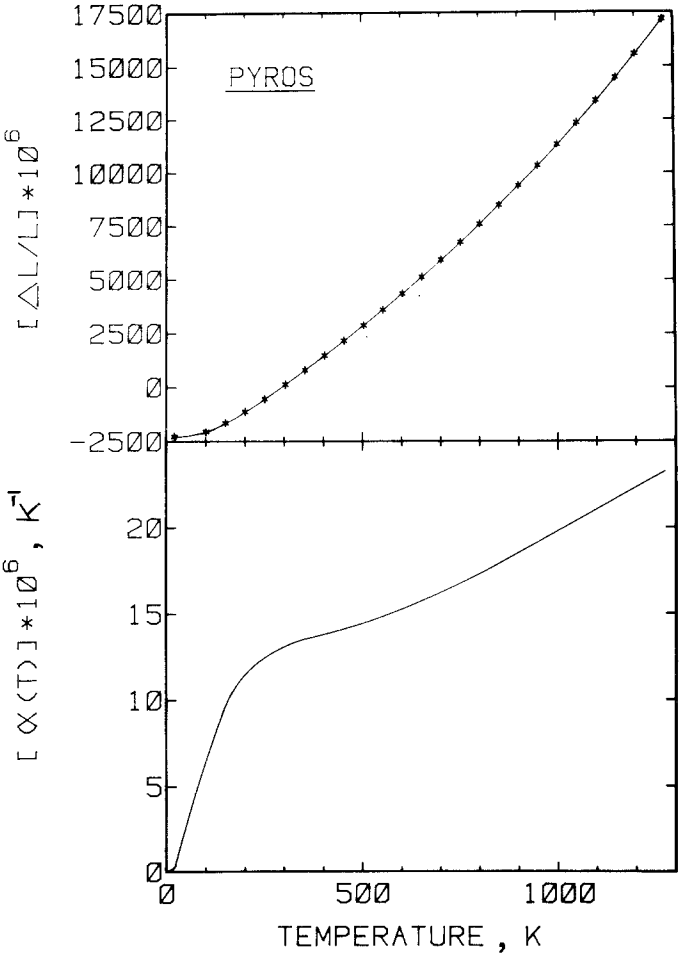

Fig. 1. Thermal expansion and expansivity of Pyros.

tal points are reported to indicate the data spread, and the smooth curve was obtained with the cubic-spline polynomial fitting. A plot of the expansivity is also reported in Fig. 1.

Results obtained on Pyros show that it is a stable material between 20 and 1273 K and that expansivity values fall within those of the α and γ phases in steels.

Many thermal expansion measurements are made using relative techniques. This produces a need for available stable materials of known expansion (standard reference materials). These materials are extremely useful in the testing and calibration of thermal expansion apparatuses, allowing for correction of their systematic errors and for evaluation of the accuracy of their thermal expansion measurements. The National Bureau of Standards, in a program to establish a series of standard reference materials (SRM's) for thermal expansion, has certified the following materials using an interferometer technique to an accuracy of about 10 ppm [13]:

SRM 736—copper, certified from 20 to 800 K [10];
SRM 739—fused silica, certified from 80 to 1000 K [12];
SRM 731—borosilicate glass, certified from 80 to 680 K [13];
SRM 737—tungsten, certified from 80 to 1800 K [15]; and
SRM 732—sapphire single crystal, certified from 293 to 2000 K [16].

Since it is beneficial to use a SRM with characteristics similar to those of the material that will be measured, Pyros should be of special interest to laboratories that are concerned with expansion measurements on steels. Therefore, we strongly suggest that Pyros be considered as a suitable reference material for thermal expansion measurements on steels, and until more accurate results are obtained, we propose our results on Pyros as reference data between 20 and 1273 K.

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