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Pressure Dependence of Creep in White Phosphorus*

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Bending creep in white phosphorus is reported at 27° and 41°C at pressures to 6 kbar. The activation volume for creep is approximately 50.3×10^{-24} cm³/atom, which is about the same as that determined by Nachtrieb and Lawson for self-diffusion.

INTRODUCTION

THE activation volumes for creep in an alkali halide (AgBr)[1] and in a number of metals (Pb,[2,3] Sn,[4] Zn,[5] Cd,[5] and Na[6]) have previously been reported. This paper reports similar studies on white phosphorus.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Samples were prepared from white phosphorus purchased from General Chemical Division of Allied Chemical and Dye Corporation of New York (their grade H036 Code 2056). An ingot of the material approximately $1\times1\times1$ cm was compressed under water (38°C) to approximately 0.30 cm thickness. Samples were then cut under water to finished size, approximately $0.25\times0.25\times2.5$ cm. The "useable" finished samples were transparent and visually free from cracks or fissures. Where internal cracks or fissures were present the sample would inevitably break immediately upon loading. The pressure equipment, three-point-loading device and deflection measuring equipment were previously described.[3–5] The differential transformer used to measure beam deflection had a linear region of approximately 1 cm length and an output of 5 V/cm. The applied load was approximately 0.2 kg applied at the center of the beam. Deflection rates between approximately 10^{-6} to 10^{-4} cm/sec were observed depending on pressure and sample size.

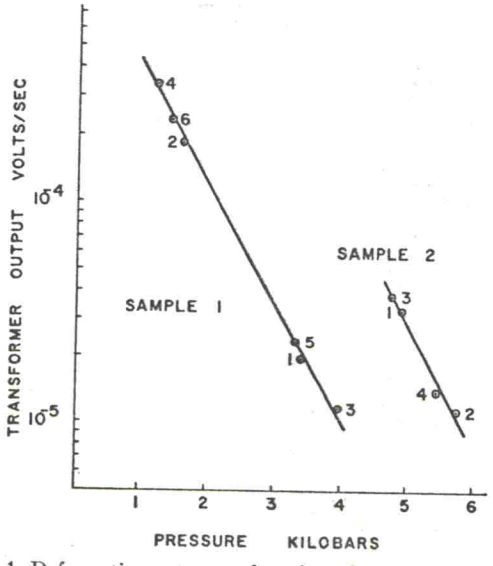

FIG. 1. Deformation rate as a function of pressure. The difference in deflection rate between samples 1 and 2 is due to sample size.

Dow Corning 200 fluid (100 cs) was used as the pressure medium because of the extreme inflammability of phosphorus upon removal from hydrocarbons such as kerosene or pentane. The Dow Corning fluid became very viscous at high pressures and it was necessary to limit the pressures to 6 kbars. The white phosphorus was loaded into the stressing device and pressure vessel in an atmosphere of argon or nitrogen.

EXPERIMENTAL RESULTS

Figure 1 shows the effect of pressure on creep rate for two typical samples. The activation volume was determined from

$$\Delta V^{\ddagger}=[KT/(P_2-P_1)]\ln(\dot{\epsilon}_1/\dot{\epsilon}_2), \qquad (1)$$

where K is Boltzman's constant, T the absolute temperature, and $\dot{\epsilon}_1$ the deformation rate at pressure P_1. The average activation volume at 27°C on 12 samples was 50.3×10^{-24} cm³/atom; the average deviation was 3.7×10^{-24}. All the experimental data could be satisfied by $\Delta V^{\ddagger}=(50.3\pm\frac{8}{6})\times10^{-24}$ cm³/atom. For three samples deformed at 41°C, the activation volume appeared to be pressure dependent. The results are shown in Table 1.

TABLE I. Activation volume for creep in white phosphorus at 41°C.

Pressure range	Apparent activation volume determined from Eq. (1)
0.7 to 3 kbar	$(54\pm4)\times10^{-24}$ cm³/atom
2.5 to 4.5 kbar	$(50\pm2)\times10^{-24}$ cm³/atom
4.0 to 6.0 kbar	$(47\pm1)\times10^{-24}$ cm³/atom

Nachtrieb and Lawson[7] report the activation volume for self-diffusion in white phosphorus at 27°C to be 30 cm³/mole (49.7×10^{-24} cm³/atom). These studies would therefore lend support to a mechanism in which creep is diffusion-controlled.

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