ANALYSIS OF BEHAVIOR OF GRAPHITE ON THE BASIS OF NONLINEAR HEREDITY THEORY

N. N. Dergunov, L. Kh. Papernik,
and Yu. N. Rabotnov

The behavior of graphite is described on the basis of the nonlinear heredity theory taking account of the temperature factor in the range 20–3000°C. The necessary characteristics are obtained from the data on creep and from the stress–strain diagrams. A physical interpretation of the obtained results is attempted.

1. The creep deformation of polycrystalline graphite is to a large extent reversible and the relation between the stress and the deformation is appreciably nonlinear even in the range of small stresses. Therefore, for the description of the temporal effects it is meaningful to use the nonlinear heredity theory described by the defining equation [1]

$$\varphi[\varepsilon(t)] = \sigma(t) + \int_0^t K(t-\tau)\sigma(\tau)\,d\tau \tag{1.1}$$

Here $\varphi(\varepsilon)$ is the nominal instantaneous load function. Equation (1.1) shows that the nature of the nonlinear relation between the stress $\sigma(t)$ and the deformation $\varepsilon(t)$ is retained during the entire deformation period. In the case of creep this is responsible for the similarity of the isochronous creep curves.

Equation (1.1) has a close connection with the nonlinear hereditary equation of Volterra-Freshe [2]. Solving Eq. (1.1) for $\varepsilon(t)$ we arrive at the following expression:

$$\varepsilon(t) = \sum_{k=1}^{\infty} a_k\left[\sigma(t) + \int_0^t K(t-\tau)\sigma(\tau)\,d\tau\right]^k \tag{1.2}$$

In describing the behavior of a material with the use of Eq. (1.2) only a finite number of terms need be retained in the expansion depending on the specified accuracy of approximation. An increase in the number of terms of the series does not complicate the determination of the required constants.

As shown in [2], Eq. (1.2) is equivalent to (1.1) in the case where the function $\varepsilon = \varphi^{-1}(\sigma)$ is inverse of the nominal instantaneous load function $\sigma = \varphi(\varepsilon)$ and can be represented in the form of a polynomial in σ:

$$\varepsilon = \varphi^{-1}(\sigma) = \sum_k a_k\sigma^k \tag{1.3}$$

Below we shall use both formulas (1.1) and (1.2) for the description of the behavior of the graphite under investigation assuming that (1.3) is valid.

As the kernel in Eq. (1.1) or (1.2) we shall use the exponential-fractional function with negative parameter:

$$K(t-\tau) = \lambda \mathfrak{I}_\alpha(-\beta, t-\tau), \qquad -1 < \alpha < 0, \quad \beta > 0 \tag{1.4}$$

Moscow. Translated from Zhurnal Prikladnoi Mechaniki i Tekhnicheskoi Fiziki, No. 2, pp. 76–82, March–April, 1971. Original article submitted December 11, 1970.

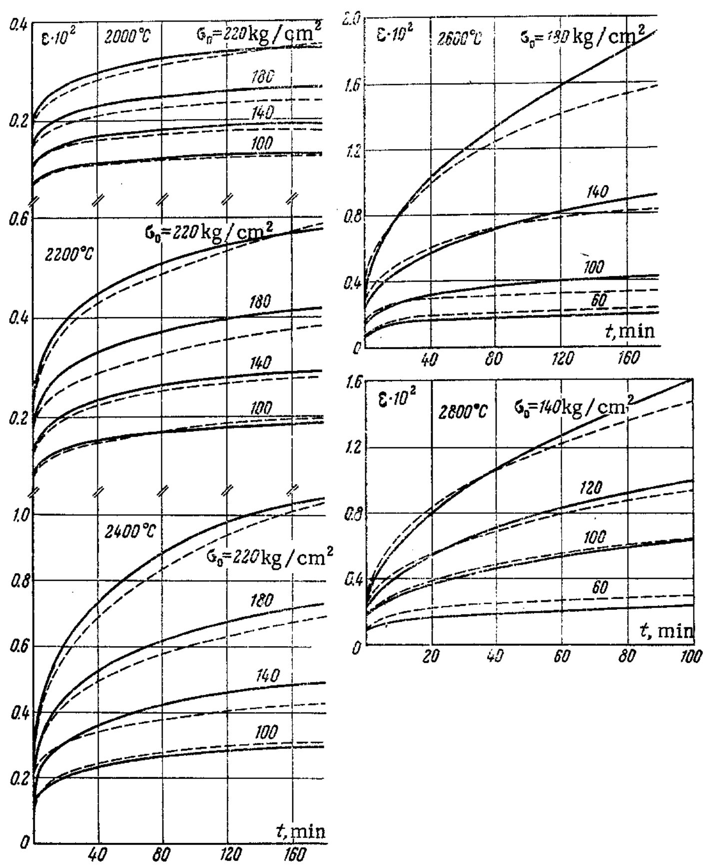

Fig. 1

In the investigation of the behavior of a material in a temperature field all the parameters of the defining equation should be taken to be temperature-dependent. Equations (1.1) and (1.2) with (1.4) taken into consideration can be written in the form

$$\varphi[\varepsilon(t), T] = \sigma(t) + \lambda(T)\int_0^t \text{Э}_{\alpha(T)}(-\beta(T), t-\tau)\,\sigma(\tau)\,d\tau \tag{1.5}$$

$$\varepsilon(t) = \sum_k a_k(T)\left[\sigma(t) + \lambda(T)\int_0^t \text{Э}_{\alpha(T)}(-\beta(T), t-\tau)\,\sigma(\tau)\,d\tau\right]^k \tag{1.6}$$

Here the index k also depends on temperature.

The equations of creep are obtained from (1.5) or (1.6) by putting $\sigma(t) = \sigma_0 = \text{const}$; they have the form

$$\varphi[\varepsilon(t), T] = \sigma_0 f(t, T), \qquad \varepsilon(t) = \sum_k a_k(T)\,\sigma_0^k f^k(t, T)$$

Here we have introduced the notation

$$f(t, T) = 1 + \lambda(T)\int_0^t \text{Э}_{\alpha(T)}(-\beta(T), t-\tau)\,d\tau$$

For $\varepsilon(t) = \varepsilon_0 = \text{const}$ the relaxation of the stresses is described by the equation

$$\sigma(t) = \varphi(\varepsilon_0, T)\left[1 - \lambda(T)\int_0^t \text{Э}_{\alpha(T)}(-\beta(T) - \lambda(T), t-\tau)\,d\tau\right]$$

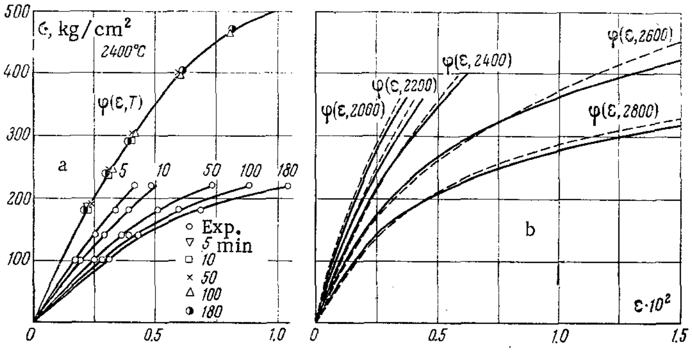

Fig. 2

In order to be able to use this model for polycrystalline graphite it is necessary to determine the characteristics of the material as functions of the temperature.

We shall determine the necessary parameters from the data on creep at constant stresses and fixed temperatures by the method described in [2]. As before, the similarity of the isochronous creep curves of the material at various constant temperatures should be checked. Furthermore, the question of the feasibility of the use of stress-strain diagrams obtained for very rapid loading at the corresponding temperatures as the instantaneous loading curves should be cleared up.

2. Graphite of mark VPP with medium grain structure was used for the investigation. The material had the following characteristics: limiting tensile strength 130 kg/cm^2, specific weight 1.85 g/cm^3, and graphitation temperature ~ 3000°C. The samples were cut parallel to the axis of pressing from blanks with dimensions $\phi = 220$ and $l = 300$ mm. Detailed information on the technology of production of graphite is given in [4].

The samples for creep tests and for tests under rapid loading had identical operating part with $\phi = 10$ and $l = 50$ mm. The tests under rapid loading were conducted with tenfold repeatability at each temperature, while the creep tests were carried out with twofold repeatability at each stress level. The selection of identical samples at each temperature was done from the measurement of electrical resistance. The investigations were carried out on DST-5000 equipment reequiped for graphite tests. The samples were heated in an electrical resistance furnace with a tubular heater in argon flow. The displacements of the sample heads were transmitted by extensometric rods made of graphite, quartz, and Invar directly from the sample to the indicator head, where the displacement was converted into an electrical signal which was automatically recorded by a potentiometer; in the case of rapid loading it was recorded on a two-coordinate potentiometer PDS-021 in the coordinates $p \sim \Delta l$, while in the creep tests it was recorded on ÉPP-09 in $\Delta l \sim t$ coordinates. A tensometric dynamometer served as the load sensor. The deformation of the sample fillets was taken into consideration in the analysis of the experimental data. During the tests the temperature was maintained constant automatically with an accuracy of ± 25°C with the use of a dilatometric sensor. The temperature was changed by an optical pyrometer of Pyronet type with an accuracy of 1%.

A detailed description of the equipment is given in [5].

3. The experiments yielded data on creep at temperatures of 2000, 2200, 2400, 2600, and 2800°C in a wide range of constant stresses (Fig. 1, dashed lines).

Families of isochrones were constructed from the creep curves for each temperature; the isochrones showed quite good similarity for all temperatures. Therefore the families of the isochrones were approximated by expression (1.5) and the values of the parameters $\alpha(T)$, $\beta(T)$, and $\lambda(T)$ of the kernel were determined. The curves of $\sigma = \varphi(\varepsilon, T)$ were constructed from formula (1.5) by extrapolation from each isochronous curve for the obtained values of the parameters of the kernel. A family of creep isochrones for T = 2400°C is shown in Fig. 2a as an example; the averaged curve obtained from the set of extrapolated points is also shown in the same figure; open circles denote the experimental data.

Computations carried out for each temperature showed that the parameters $\alpha(T)$ and $\beta(T)$ are practically independent of temperature and have values close to −0.5 and 0.1 respectively. The parameter $\lambda(T)$ showed a weak dependence on temperature. Therefore the values of $\lambda(T)$ were refined keeping the values $\alpha = -0.5$ and $\beta = 0.1\ (\text{min})^{-0.5}$ fixed for all temperatures. The values thus obtained are:

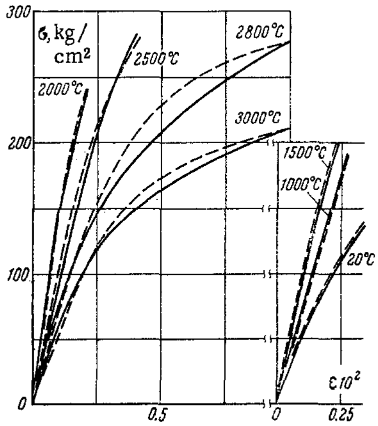

Fig. 3

$T =$	2000	2200	2400	2600	2800	°C
$\lambda(T) =$	0.1	0.14	0.21	0.23	0.23	$(\min)^{-0.5}$

Extrapolated instantaneous load curves $\sigma = \varphi(\varepsilon, T)$ are shown in Fig. 2b (dashes).

Thus it is established that the parameters of ϑ-function remain constant in a wide range of temperatures. This considerably simplifies further use of the investigated model. The effect of the temperature is taken into consideration only by the instantaneous load function $\sigma = \varphi(\varepsilon, T)$ and the parameter $\lambda(T)$ in the case of relation (1.5) or by the set of coefficients $a_k(T)$ and $\lambda(T)$ in the case of the equivalent relation (1.6).

For elucidating the applicability of stress-strain diagrams as the instantaneous load curves, data on rapid loading at 20, 1000, 1500, 2000, 2500, 2800, and 3000°C were obtained (dashed lines in Fig. 3). The obtained diagrams were approximated by (1.3) where the first four terms are retained.

As a result the following values of the coefficients are obtained:

$T =$	20	1000	1500	2000	2500	2800	3000	°C
$a_1 =$	1.55	1.45	1.05	0.6	0.98	1.3	$1.6 \cdot 10^{-3}$	cm^2/kg
$a_2 =$	6.4	0	0.5	1.05	0.7	0.25	$0.1 \cdot 10^{-6}$	$(cm^2/kg)^2$
$a_3 =$	0	0	0	0	0.28	0.53	$0.78 \cdot 10^{-8}$	$(cm^2/kg)^3$
$a_4 =$	0	0	0	0	0	0.85	$2.8 \cdot 10^{-10}$	$(cm^2/kg)^4$

The curves computed from formula (1.3) with the above values of the coefficients are shown in Fig. 3 by continuous lines.

For extending the obtained results to the intermediate temperatures in the range 20-3000°C we shall take the parameter of ϑ-function constant in Eq. (1.6): $\alpha = -0.5$ and $\beta = 0.1$. We shall also assume that the temperature dependence of the coefficients $a_k(T)$ and $\lambda(T)$ is of Arrhenius type and is of the form

$$a_k(T) = a_k^\circ \exp\left(-\frac{U_k}{RT}\right) \qquad (k = 1, 2, 3, 4) \tag{3.1}$$

$$\lambda(T) = a_\lambda^\circ \exp\left(-\frac{U_\lambda}{RT}\right) \tag{3.2}$$

Here T is the absolute temperature, U_k and U_λ are constants having the sense of activation energies of some mechanism, R is the gas constant, and a_k° and a_λ° are constants.

In order to obtain the values of the parameters occurring in (3.1) and (3.2) we approximate the obtained experimental dependences $a_k(T)$ and $\lambda(T)$ by piecewise linear functions in the coordinates $\log a_k, \lambda \sim 1/T$. The result of this approximation is shown in Fig. 4. As seen from this figure, three segments in the high-temperature range can be separated out: 1500-2000°C, 2000-2500°C, 2500-3000°C; in each segment the parameters in formulas (3.1) and (3.2) are constant:

$T =$	1500—2000	2000—2500	2500—3000	°C
$U_1 =$	—8.9	13.7	13.7	kcal/g-atom
$U_2 =$	11.8	—1.1	—69.5	kcal/g-atom
$U_3 =$	0	36.6	36.6	kcal/g-atom
$U_4 =$	0	0	119.0	kcal/g-atom
$U_\lambda =$	0	22.8	0	kcal/g-atom
$a_1^\circ =$	$0.85 \cdot 10^{-4}$	$28.5 \cdot 10^{-4}$	$28.5 \cdot 10^{-4}$	cm^2/kg
$a_2^\circ =$	$13.8 \cdot 10^{-6}$	$0.81 \cdot 10^{-6}$	$16.9 \cdot 10^{-10}$	$(cm^2/kg)^2$
$a_3^\circ =$	0	$20.7 \cdot 10^{-7}$	$20.7 \cdot 10^{-7}$	$(cm^2/kg)^3$
$a_4^\circ =$	0	0	$2.8 \cdot 10^{-6}$	$(cm^2/kg)^4$
$a_\lambda^\circ =$	0	14.9	0.23	$(\min)^{-0.5}$

At temperatures below 1500°C the coefficient $a_1(T)$ changes little; the coefficient $a_2(T)$ has a minimum in the range 300-500°C. Additional experiments are necessary in order to explain this minimum.

However, graphite is used mainly in the range of high temperatures; therefore the investigation of the temperature range below 1500°C is not of much interest.

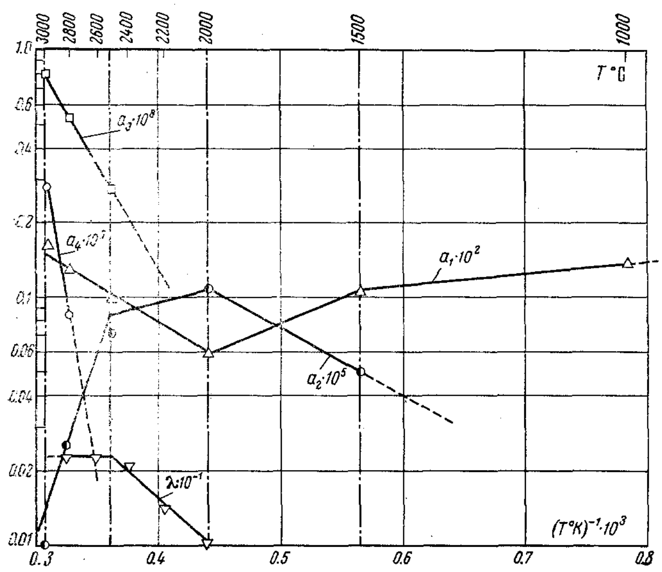

Fig. 4

The curves computed from formula (1.3) with the coefficients $a_k(T)$ obtained from formula (3.1) at the corresponding temperature are shown in Fig. 2b for comparison with the instantaneous load curves $\sigma = \varphi(\varepsilon, T)$.

Considering the intrinsic scatter of the properties of the material and also the fact that the stress-strain diagrams are obtained during a small but nonzero time interval, the agreement should be considered completely satisfactory. Hence, at sufficiently rapid loading rates the stress-strain diagrams can be used as the instantaneous load curves.

As shown in [2], the case of determination of the deformation characteristics within the framework of the investigated model can be considerably simplified, appreciably reducing the volume of required long experiments on creep.

The creep curves were computed from (1.6) for constant stresses and temperatures corresponding to the experimental values. The computed curves are shown for comparison in Fig. 1 by the continuous lines. The agreement with the experiment is satisfactory.

4. The proposed phenomenological model describes the relation between the stress and the deformation by a fourth degree polynomial.

The authors did not aim at an exact description of the deformation and creep curves, since a large inhomogeneity and, hence, instability in the behavior under deformation is characteristic of graphite. Besides, the determination of the values of the entire set of parameters of the defining equation is not unique.

The self-similar behavior of the variation of the temperature-dependent coefficients, shown in Fig. 4, can be explained in the following way.

The nature of variation of the coefficient $a_1 = 1/E$ reflects the temperature behavior of the instantaneous modulus of elasticity E.

The curve of variation of the coefficient a_2, responsible for the base slip, has a minimum in the range 300-500°C. This fact is apparently related to the anisotropic compression of the crystals along the axis perpendicular to the base plane and to the blocking of the systems of base slip. Anisotropic compression is a consequence of the anisotropy in the thermal expansion coefficient. For a monocrystal this coefficient has a negative value along the base plane up to 500°C and is equal to $\sim -1.5 \cdot 10^{-6}$ deg^{-1}, while along the axis perpendicular to the base plane it has a positive value $\sim 28 \cdot 10^{-6}$ deg^{-1} [6]. The coefficient increases as it goes over into the range of positive values. The monotonic increase of strength and the low strength in the range 1500-2500°C indicates the predominance of the mechanisms of base slip.

An intense increase of the strength accompanied by an increase of plasticity in the temperature range 2500-2800°C indicates a change of the mechanism responsible for plastic deformation. A similar phenomenon (intense deformation reinforcement) is observed in some metals with hexagonal structure and is explained by activation of nonbase slip systems caused by the temperature increase [7]. Probably this occurs in graphite at temperatures of the order of 2500°C and is reflected in the change of the deformation curve and, hence, in the appearance of the term $a_3\sigma^3$.

As the temperature increases (in the range 2800-3000°C) the concentration and the mobility of point defects increases: the vacancies in the base plane and the interphase atoms injected between the planes [8]; on one hand this leads to a distortion of the planes and a decrease of the base slip, and on the other hand to an increase of the role of the mechanisms controlling diffusion.

A confirmation of the above statement apparently lies in the appreciable plasticity 10-20% and in the more mildly sloping deformation curves in the range 2800-3000°C. Due to this the coefficient a_4 becomes nonzero.

The values of the activation energy must be regarded as "apparent" [9], since they are a result of the action of several mechanisms.

The above explanation of the phenomenological model represents only a scheme which can be made more detailed later on.

LITERATURE CITED

1. Yu. N. Rabotnov, Creep of Construction Elements [in Russian], Nauka, Moscow (1966).
2. Yu. N. Rabotnov, L. Kh. Papernik, and E. I. Stepanychev, "Application of nonlinear heredity theory to the description of temporal effects in polymer materials," Mekhanika Polimerov, No. 1 (1971).
3. Yu. N. Rabotnov, L. Kh. Papernik, and E. N. Zvonov, Tables of Exponential-Fractional Functions of Negative Parameters and Its Integrals [in Russian], Nauka, Moscow (1969).
4. A. M. Sigarev, Toward the Problem of Improvement of Properties of Graphite for Anodes of Mercury Rectifiers, in: Constructional Materials Based on Graphite [in Russian], Metallurgiya, No. 4 (1969).
5. N. N. Dergunov and V. N. Barabanov, "Tests on short-period strength in stretching and compression of carbon-graphite materials in the range 20-3000°C," in: Construction Materials Based on Graphite [in Russian], Metallurgiya, No. 4 (1969).
6. W. G. O'Driscoll and J. C. Bell, "Graphite, its properties and behavior," Nucl. Engng., 3, No. 32 (1958).
7. R. Cahn, "Recovery and recrystallization," in: Physical Metallurgy [Russian translation], Vol. 3, Mir (1968).
8. F. Walker, Chemical and Physical Properties of Carbon [Russian translation], Mir, Moscow (1969).
9. F. Garofalo, Laws of Creep and Lasting Strength of Metals and Alloys [in Russian], Metallurgiya, Moscow (1968).