THE TEMPERATURE DEPENDENCE OF ELASTIC CONSTANTS
OF POLYCRYSTALLINE GRAPHITE

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Introduction

The graphite crystal structure exhibits extremely high anisotropy in bonding, as evidenced in the thermal conductivity, thermal expansion, and elastic constants. The anisotropy of these bulk properties appears well correlated to the preferred orientation of the crystalline phases. The elastic constants of bulk graphite exhibit a temperature dependence which is not representative of direct crystalline properties (i.e., a maximum near the final fabrication temperature). This behavior is not typical of the behavior of polycrystalline forms of less anisotropic elements.

The anisotropy of the crystalline elastic constants is related to the first derivative of the interatomic force versus distance relationship; i.e., the harmonic bonding approximation. The anisotropy of the thermal expansion coefficients depends upon the second derivative of the interatomic force relationships; i.e., the anharmonic aspects of the various bonds. The temperature dependence of the elastic constants in the classical regime is rooted, in part, in the anharmonic aspects of the various bonds.

The purpose of this note is to explore the relationships between free thermal strains, restrained cooldown strains in bulk graphites, and their interaction through the anharmonic aspects of the bonding between basal planes.

Theoretical Aspects

The simplifying notion that the final graphitization temperature, T_g, approximates a stress free state will be used. During cool-down, the "c" directions of the crystal will undergo very large free contractions, while the "a" directions will contract considerably less. If there is good particle to particle bonding, this will give rise to constraint of the "c" direction contraction and the development of tensile strains and stresses in the "c" directions. Compressive strains and stresses will also be developed in the "a" directions.

Because of the large differences in stiffness between the "a" and "c" directions, most of the differential contraction will be taken up by developing large "c" direction strains. The magnitude of these strains, ϵ_{33}^* will be a function of the microstructure, including factors such as the relative particle to particle orientations, the general degree of preferred orientation, the location of pores and cracks, and the convolution of basal planes within the coke particle. For the present purposes, their magnitude at temperature, T, will be estimated as

$$\epsilon_{33}^* \simeq 1/3(\alpha_c - \alpha_a)(T_g - T) \tag{1}$$

where α_c and α_a are the crystalline thermal expansion coefficients.

Mrozowski (Ref. 1) has argued that these strains give rise to microcracks and a resulting decrease of elastic modulus. The microcrack closing and unspecified "healing" which occurs upon reheating is taken to be the physical basis of the modulus dependence. While microcrack formation associated with this mechanism does occur, not all of the differential microstrains are relieved and it is difficult to accept chemical or other means of restoring the stress carrying ability of basal plane cracks at relatively low temperatures.

Seldin (Ref. 2) and others, have observed that the only crystal elastic constants which are of the same order of magnitude as bulk elastic constants are those of basal plane extension and shear (C_{33} and C_{44}). Based upon this, the bulk elastic behavior appears to be dominated by crystalline shear. Therefore, factors which reduce the basal plane elastic constants will result in reduction of bulk elastic stiffnesses.

Green and Spain (Ref. 3) have recently reported experimental determinations of the anharmonic elastic constants of the basal plane

$$\frac{1}{C_{33}}\frac{\partial C_{33}}{\partial \epsilon_{33}} = -15 \quad \text{and} \quad \frac{1}{C_{44}}\frac{\partial C_{44}}{\partial \epsilon_{33}} \simeq -10 \tag{2}$$

These are in good agreement with values deduced by Kelley (Ref. 4) from theoretical studies of the thermal expansion coefficients and elastic moduli. Very strong sensitivity of elastic constants to layer spacing is implied. The tie between anharmonic basal plane bonding, thermal expansion, and bulk elastic response is through Eqs. (1) and (2) and an appropriate particulate composite relationship; e.g., Price (Ref. 4) or Smith (Ref. 5).

Results

Combinations of Eqs. (1) and (2) provides the following approximations for the effective in situ elastic crystal constants.

$$C_{44}^* = C_{44} \{1 - 1/3(10)(\alpha_c - \alpha_a)(T_g - T)\} \tag{3}$$

$$C_{33}^* = C_{33} \{1 - 1/3(15)(\alpha_c - \alpha_a)(T_g - T)\} \tag{4}$$

Specifically, for $T_g - T = 2400°C$, and $\alpha_c - \alpha_a = 35 \times 10^{-6}/C°$ the approximate in situ elastic constants are

$$C_{44}^* = 0.72\, C_{44} \quad \text{and} \quad C_{33}^* = 0.58\, C_{33} \; . \qquad (5)$$

These imply a 28 to 42 percent decrease in room temperature bulk stiffness as a result of cooldown from graphitization.

Discussion

The present rationalization of temperature dependence of elastic properties is unique to highly anisotropic crystal structures, and would not occur in highly symmetric crystal structures. The rationalization of the influences of differential thermal contraction, bond anharmonicity, and bulk properties is schematically summarized in Fig. 1, where the departure from behavior of ordinary solids is emphasized.

Actual mesophase coke microstructures need explicit attention. High degrees of preferred orientation as occur in some pyrolytic graphites and fibers would result in far less average differential contraction and, by implication, less peaking of modulus versus temperature. Modulus versus temperature trends for pyrolytic graphite, T50 fiber and ATJS bulk graphite in Fig. 2 support this hypothesis. More normal modulus behavior occurs in the absence of large differential cooldown strains (Fig. 3).

The concept of altered in situ crystalline elastic coefficients (and possibly thermal expansion coefficients by a similar approach) as a function of layer plane spacing could provide an important step in developing quantitative structure-property relationships for various carbon forms. An important contribution to neutron irradiation induced increases in elastic constants of reactor graphites may be through the relief of cooldown micro stresses accompanying point defect formation and/or migration. Also, the role of the anharmonic bonding terms would imply that for bulk graphites, elastic linearity is only an approximation at any strain level and therefore unequal mechanical stiffnesses in tension and compression could logically follow. The differential crystalline stresses are also often considered the source of the observed strength increases with temperature.

Conclusion

The rational use of in situ crystal constants differing from the free crystal constants has potential for contributing to the understanding of the complex structure properties relations known to exist in carbon forms.

References

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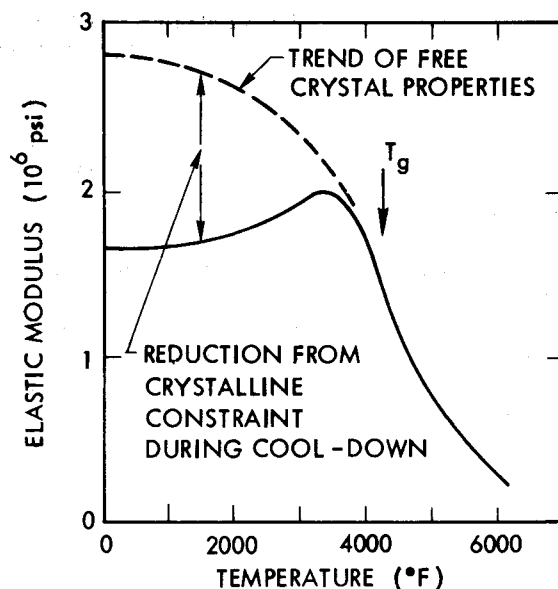6. Smith, R. E., et al., Carbon, 14, 185 (1976).

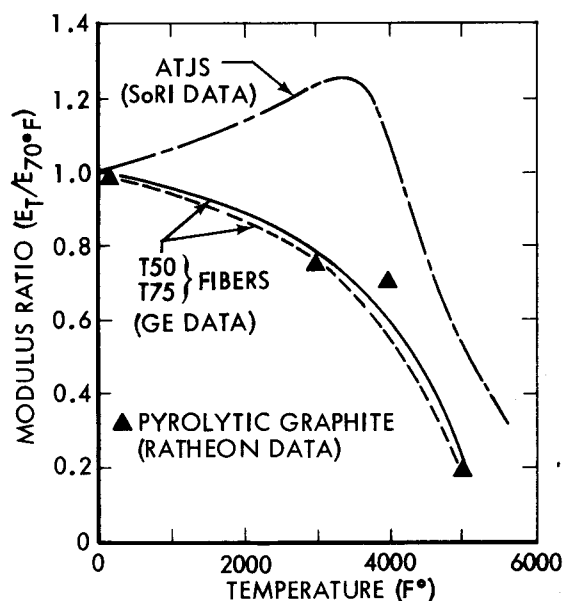Fig. 1. Crystalline and Bulk Modulus Vs. Temperature
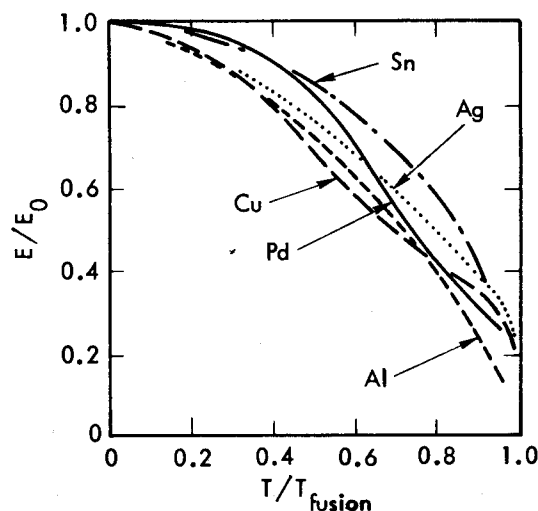

Fig. 2. Modulus Vs. Temperature for Carbon Forms

Fig. 3. Modulus Vs. Temperature Trends for Metals