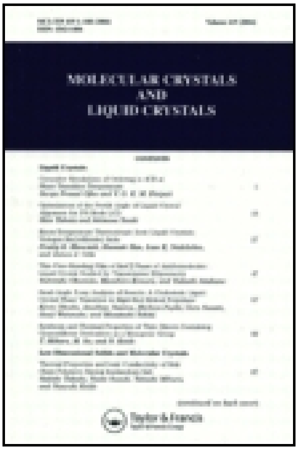

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: P. M. Robinson & H. G. Scott (1970): The Thermodynamics and Mechanical Properties of Anthracene-Carbazole Alloys, Molecular Crystals and Liquid Crystals, 11:3, 239-255

To link to this article: http://dx.doi.org/10.1080/15421407008083517

Molecular Crystals and Liquid Crystals. 1970. Vol. 11, pp. 239–255

The Thermodynamics and Mechanical Properties of Anthracene–Carbazole Alloys

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Received August 19, 1970

Abstract—The heat capacities of seven anthracene–carbazole alloys within the homogeneity range of the ordered α' phase, which extends from 1.5 to 24.5 pct carbazole at room temperature, have been determined over the temperature range 180 to 440 K. At all temperatures, the maximum heat capacity occurred for the 10 pct carbazole alloy. The difference between the enthalpies, and between the entropies, of the alloys and a mixture of the component compounds at 400 K and dilatometry measurements on the 10 pct carbazole alloy indicate that the stability of the α' alloys, with respect to the components, is associated with an increase in vibrational entropy due to a volume change. Heat capacity measurements on quenched and isothermally annealed crystals of a 1.75 pct carbazole alloy give an activation energy of 29.3 kJ mole^{-1} for the transformation of disordered α to ordered α' phase.

Single crystals of the 1.75 pct carbazole alloys were prepared in the α and α' condition. The critical resolved shear stress for slip on both the (001) [010] and (001) [110] systems in the disordered α phase is close to that in zone-refined anthracene. The isothermal transformation of α to α' phase is accompanied by a peak in the curve of critical resolved shear stress against annealing time, which probably corresponds to a critical combination of degree of order and domain size. The overall effect of ordering is to increase the strength of the alloy. The critical resolved shear stress for slip on both basal systems increases as the composition of the α' alloys is increased to the stoichiometric composition of 10 pct carbazole.

1. Introduction

The study of the deformation behavior of zone-refined anthracene and naphthalene$^{(1-3)}$ raised questions about the effect of impurities on the yield and flow stress and the work-hardening characteristics of these compounds. A previous investigation has shown that the presence of impurities in different commercial grades of naphthalene inhibits slip on one of the two basal slip systems.(2) It was considered desirable, therefore, to investigate the effect of alloying on deformation behavior in a binary system. The anthracene-carbazole system was originally chosen because carbazole is a naturally occurring impurity in anthracene and the phase diagrams(4,5) existing at that time showed extensive solid solubility between the components. Preliminary results indicated that the addition of a few per cent of carbazole to anthracene leads to unexpected large increases in the yield and flow stress and to age-hardening phenomena after crystal growth, which were incompatible with complete solid solubility between the components. A re-determination of the phase diagram(6) showed that phase changes occur at low carbazole concentrations and, in particular, that the α terminal solid solution transforms into an ordered α' phase on cooling to ambient temperature.

The present paper is concerned with the kinetics of the transformation from the α to α' phase at low carbazole concentrations and the effect that the transformation has on the deformation behavior of single crystals of the alloys. Heat capacities of alloys across the α' homogeneity range have been measured over a range of temperature to obtain further evidence of their nature. The changes in heat capacity on transformation have then been used to determine the kinetics of the process. On the basis of this information, alloy single crystals were prepared in the α and α' conditions and their deformation behavior studied, although this was limited somewhat by their lack of ductility.

2. Sample Preparation

All samples were prepared from zone-refined anthracene and carbazole purified to a total impurity level of less than 30 p.p.m., as determined by mass spectroscopy. Polycrystalline ingots of alloys containing from 2.0 to 14.3 pct carbazole were prepared by the method described previously(6) and annealed at room temperature for five weeks. Single crystals of some of these alloys were grown from the melt in a Bridgman furnace following closely the procedures described for pure anthracene.(1) The composition of the alloys is quoted in weight per cent carbazole.

3. Heat Capacity of α′ Alloys

The heat capacities of the polycrystalline α′ alloys containing from 2.0 to 14.3 pct carbazole (Fig. 1) were determined over the range 180–440 K by scanning calorimetry using scan speeds of 4 to 32 K per minute.(6) The temperature calibration over this range was carried out using the melting points of high purity mercury, gallium, indium and tin.(7) The heat capacity of zone-refined anthracene(6,8) was used as a standard for the heat capacity measurements. For each alloy, readings were taken at 5 K intervals and a quadratic curve fitted to the experimental results.

The heat capacities at 50 K intervals of seven alloys within the α′ homogeneity range are given in Table 1; the reproducibility of the measurements was ± 1.2 J $\text{mole}^{-1}\ \text{k}^{-1}$. At all temperatures, the maximum heat capacity within the homogeneity range occurred for the 10.0 pct carbazole alloy. The heat capacity of each alloy showed an increasingly positive deviation from the heat capacities of the component compounds as the temperature was increased (Fig. 2).

The difference between the enthalpies, and between the entropies, of the alloys and a mixture of the component compounds at 400 K was calculated from the heat capacities of the alloys and the components,(6,8) taking 200 K as a standard state (Table 2). The enthalpy of each alloy was larger than that of the components but the free energy change was negative, and therefore the alloys were stable with respect to their component compounds because the difference between the entropy of the alloys and their components was sufficiently large and positive (Table 2). The maximum free energy change for the α′ alloys at 400 K, and at other temperatures between 200 and 400 K, occurred for the 10 pct carbazole alloy, indicating that this is the most stable alloy across the homogeneity range. This behavior is typical of ordered alloys centered about a stoichiometric composition and with a defect structure on either side of stoichiometry.(7,9) The heat capacity measurements, therefore, support the conclusion reached previously(6) that the α′ alloys are ordered and are centered about a stoichiometric composition of 10 pct carbazole. Preliminary neutron diffraction experiments also indicate that the 10 pct carbazole alloy is ordered.(10)

If the alloys are ordered, the larger entropy of the alloys compared

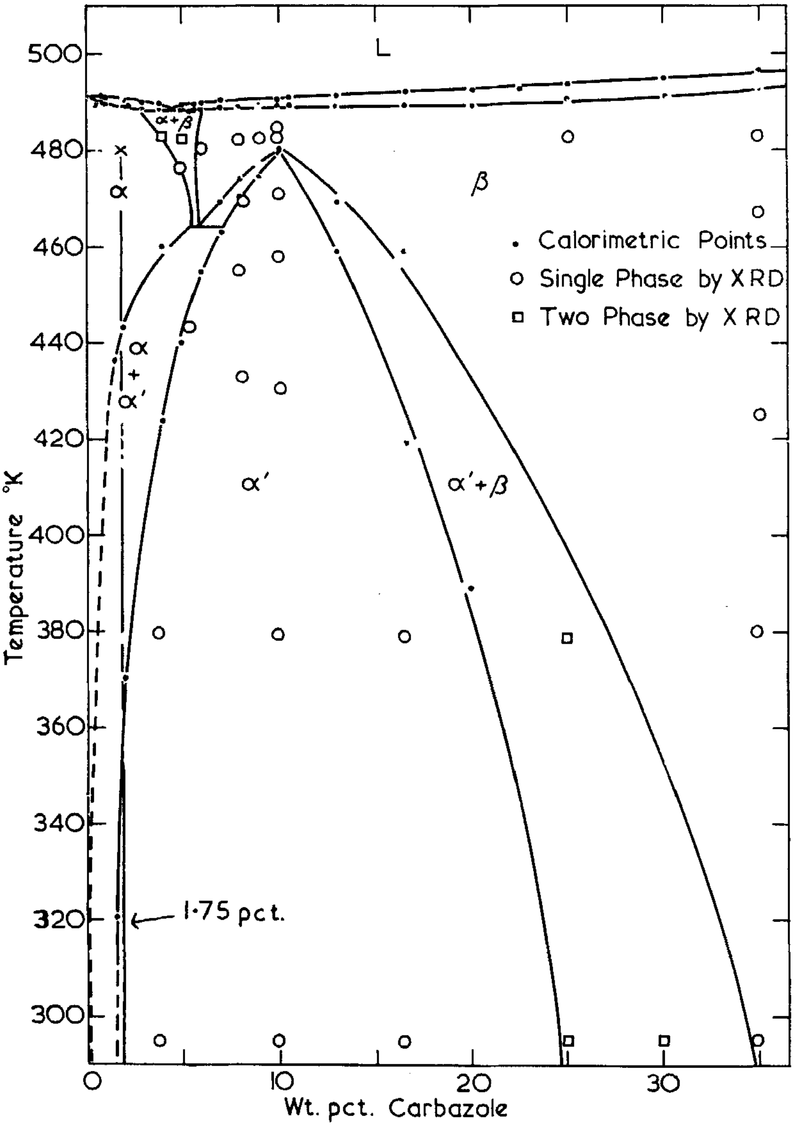

Figure 1. The anthracene-carbazole phase diagram in the region 0 to 30 pct carbazole (after ref. 6).

TABLE 1 The Heat Capacities of α' Alloys in the Anthracene-Carbazole System

Composition (pct carbazole)	Cp, J mole^{-1} k^{-1} 200 K	250 K	300 K	350 K	400 K
2.0	130.1	157.0	190.0	229.0	—
4.0	130.5	160.0	193.5	230.0	276.0
6.0	132.1	162.5	196.0	234.0	279.0
8.0	133.0	165.5	200.5	240.0	283.0
10.0	134.9	168.5	202.0	244.0	286.0
11.8	134.0	166.1	199.0	236.5	280.0
14.3	132.0	161.1	192.5	234.5	278.5

with the compounds will be associated with vibrational rather than configurational effects. As the crystal structure of the α' phase is the same as that of anthracene,(6) the increased vibrational entropy in the alloys may be associated with an increased volume compared with the components, rather than with a change in structure or bond strength. To check this hypothesis, a series of dilatometry experiments was carried out.

4. Variation of Volume with Temperature

The change in volume of the compounds and the 10 pct carbazole alloy with temperature from 298 K to about 5 K below the melting point was measured with a simple dilatometer. The bulb which contained the sample was of pyrex tube with a bore selected to match the sample diameter, and was joined to a length of precision bore capillary tubing of 0.050 cm nominal bore: mercury was used as the liquid in the dilatometer. The weighed sample, in the form of a cylinder about 0.3 cm diameter and 6 cm long, was placed in the dilatometer bulb, together with a short pyrex rod of similar diameter, to avoid excessive dead space, and the bulb was then sealed. The dilatometer was evacuated for several hours to a nominal 10^{-4} torr and the mercury was introduced before removing the dilatometer from the pumping line, thus avoiding trapped air in the dilatometer bulb.

The volume changes were determined by measuring the height of the mercury column in the capillary with a cathetometer while

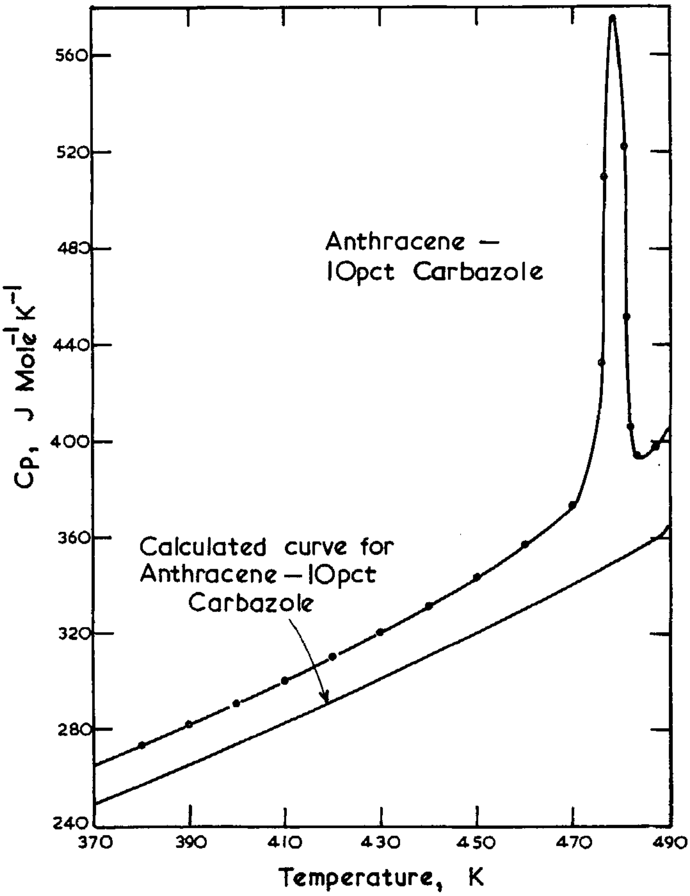

Figure 2. The heat capacity of α' phase alloy containing 10 pct carbazole compared with that calculated from the heat capacities of the component compounds.

heating the bulb in an oil bath at about 1 K/min. Measurements made on heating and again on cooling showed no significant hysteresis. At the conclusion of each run the mercury was removed from the dilatometer and weighed to determine its volume: typically this was 0.2 cm^3, compared with 0.5 cm^3 for the sample (also determined from mass and density). The total volume change at each temperature was corrected for that of the mercury and of the pyrex bulb to give that of the sample alone.

TABLE 2 The Difference between the Enthalpies, Entropies and Free Energies of α′ Alloys and a Mixture of the Component Compounds† at 400 K, taking 200 K as a Standard State

Composition (pct carbazole)	ΔH (kJ mole^{-1})	ΔS (J mole^{-1} k^{-1})	ΔF (kJ mole^{-1})
4.0	0.113	0.335	−0.021
6.0	0.379	1.280	−0.133
8.0	1.244	4.400	−0.516
10.0	1.820	6.090	−0.616
11.8	1.042	3.640	−0.414
14.3	0.406	1.380	−0.146

† Throughout the text the phrase "mixture of component compounds" refers to a mechanical, rather than a chemical, mixture of the compounds of the same overall composition as the alloy in question.

The ratio of the volume change, V, to the room temperature volume, V^0, for the alloy and for anthracene and carbazole were approximately the same at temperatures below 340 K. At higher temperatures the fractional volume change, V/V^0, for the alloy became progressively larger than that for the component compounds (Fig. 3). Similar deviations of the heat capacity of the alloy from that of its components (Fig. 2) showed that the entropy of the alloy became progressively greater than that of a mixture of the compounds as the temperature was increased. The concurrent changes in volume and heat capacity suggest that the large entropy of the alloy, which appears to be the main stabilizing factor, may be associated with an increase in the vibrational entropy, because of geometrical considerations, compared with that in the compounds.

5. Kinetics of Transformation of 1.75 pct Carbazole Alloy

The transformation of α′ alloys close to the stoichiometric composition has been described previously$^{(6)}$ but the present interest is in the comparatively sluggish transformation of the low carbazole alloys. Under equilibrium conditions, a 1.75 pct carbazole alloy will be α phase above 445 K and α′ phase below 360 K (Fig. 1). Cleaved wafers from single crystals of this alloy were heated to 480 K in the scanning calorimeter, held at temperature for 30 minutes and then cooled to temperatures between 300 and 360 K in 80 to 90 seconds.

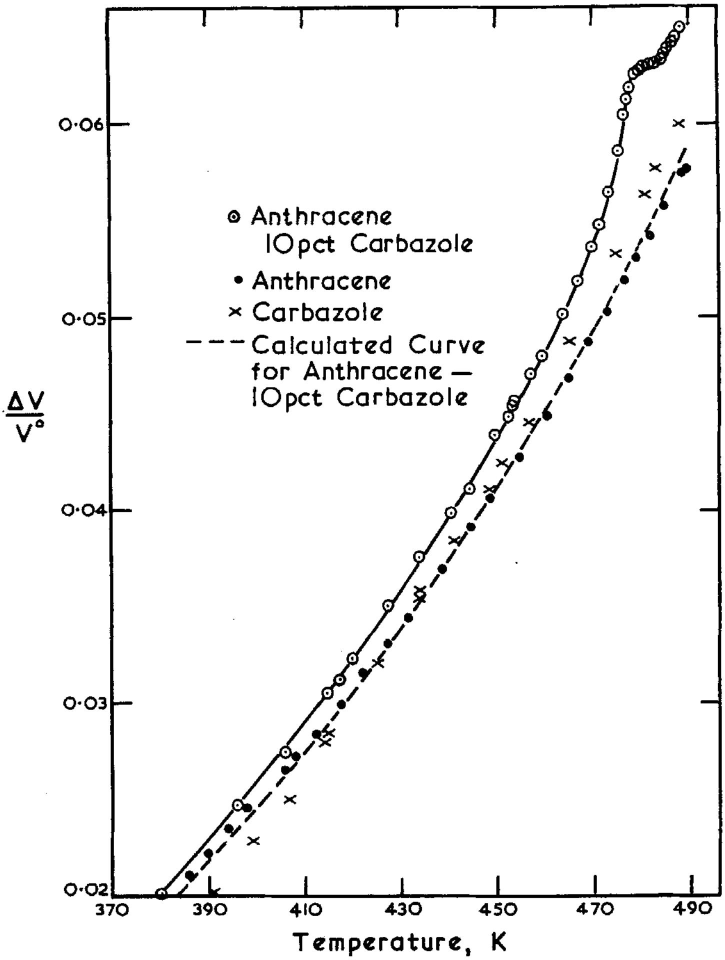

Figure 3. The ratio of the volume change, V, to the room temperature volume, V^0, for anthracene, carbazole and the 10 pct carbazole alloy as a function of temperature.

The specimens were then held at constant temperature in the calorimeter.

The heat capacity measurements were made by heating at 64 K per minute from the isothermal annealing temperature until a steady state, with respect to the differential power input, was established. The difference between this and the isothermal base line is a measure of the heat capacity of the sample. After the steady state had been established the specimen was cooled as rapidly as possible to the original annealing temperature. Each test took approximately 30 seconds and involved heating to 14 K above the isothermal annealing temperature. It was considered that the time at the higher temperature was insufficient to significantly affect the isothermal ageing.

Isothermal annealing curves for three temperatures are shown in Fig. 4. After a short incubation period, the heat capacity of the alloy increased with the time at constant temperature until an equilibrium value was reached, the change in heat capacity amounting to 7–9 pct. The heat capacities of quenched and of quenched and annealed alloys for a number of annealing temperatures are shown in Fig. 5. The heat capacities of the quenched alloys lie on the linear extrapolation to the annealing temperature of the heat capacity–temperature curve for the α phase at the α – (α + α') phase boundary (Fig. 5). At the annealing temperatures, the heat capacities of the quenched metastable α phase are lower than the heat capacity of the

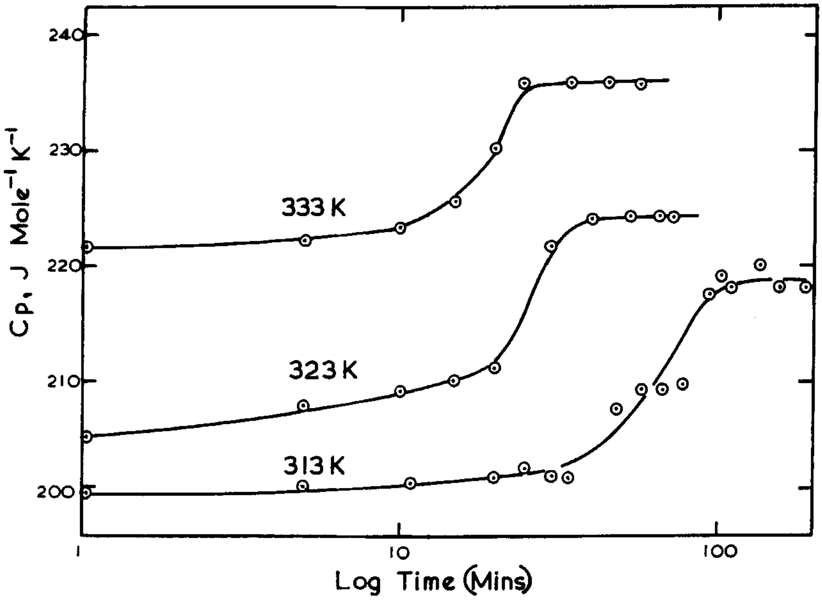

Figure 4. The changes in heat capacity of a 1.75 pct carbazole alloy on isothermal annealing after quenching from 480 K.

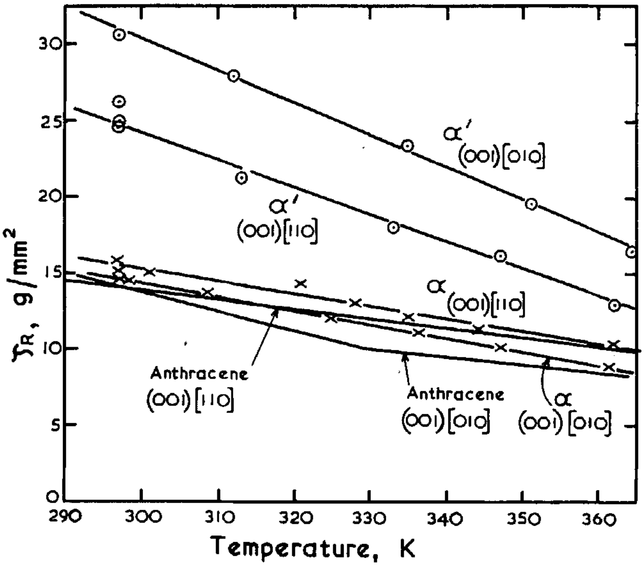

Figure 5. The heat capacity of a 1.75 pct carbazole alloy after quenching and after isothermal annealing at various temperatures to the plateau level.

equilibrium α' phase even though the α phase is disordered and the α' phase ordered.

The plot of the time taken to reach the equilibrium level of the heat capacity against temperature gives an activation energy for the transformation of the α to α' phase of 29.3 kJ mole^{-1} (Fig. 6).

6. The Influence of Heat Treatment on Mechanical Properties

In view of the variability of the tensile properties of " as grown " crystals of low carbazole alloys, crystals were subjected to annealing treatments based on the kinetics of the $\alpha \rightarrow \alpha'$ transformation as determined by the heat capacity measurements. Single crystals of the 1.75 pct carbazole alloy, 25 mm long and 3.2 mm diameter, were sealed in thin-walled glass capsules under an atmosphere of nitrogen, annealed at 470 K for 30 minutes and then quenched into an ice-water mixture, the capsules being broken under water. Heat capacity measurements indicate that this treatment retained the high-temperature α phase.

The quenched crystals were tested in tension in an Instron tensile

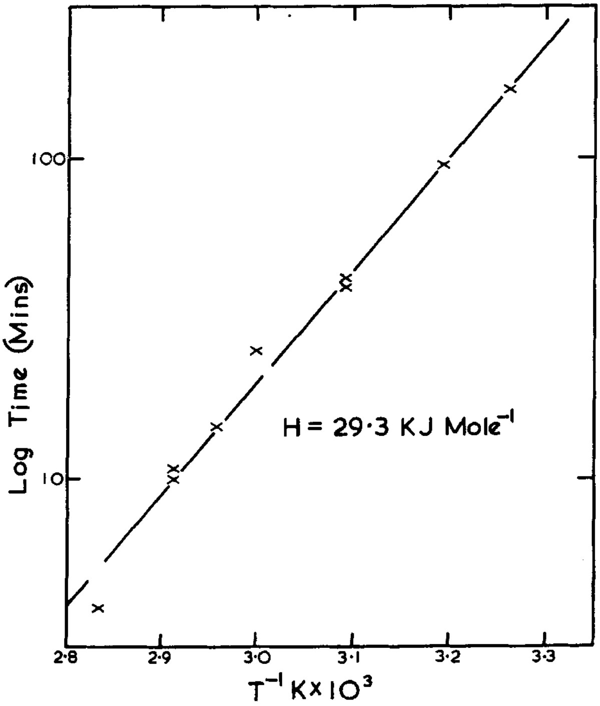

Figure 6. The time to reach the plateau level of the heat capacity after quenching from 480 K, as a function of annealing temperature.

testing machine; the form of the stress-strain curves was similar to that of pure anthracene(1) although the amount of plastic deformation was small. The critical resolved shear stress for slip on the active slip system was calculated from the stress for the onset of plastic deformation, measured as the stress at which the stress-strain curve deviated from linearity. The active slip system was taken as the basal slip system with the highest Schmid factor,(11) after initial examination of slip traces on heavily deformed crystals indicated that, as in zone-refined anthracene,(1) only the (001) [010] and (001) [110] slip systems were active in unconstrained deformation in tension. The quenched crystals were isothermally annealed at temperatures from room temperature to 343 K and the critical resolved shear stress then determined at room temperature. Some crystals were used for successive ageing treatments at one temperature; the crystals being strained to just past the yield point in each case. No difference was noted between the results for these crystals and ones which were given single ageing treatments. Typical isothermal ageing curves for quenched crystals which deformed on either the (001) [010] or (001) [110] systems are shown in Fig. 7. The critical resolved shear stress for quenched crystals which deformed on either system was 15–18 g/mm². On isothermal annealing this increased to a peak value, in times which corresponded with those needed for completion of the α to α' transformation as determined by the heat capacity measurements, and then decreased to a plateau level (Fig. 7). The plateau level was greater than the quenched value for all annealing temperatures and increased as the annealing temperature was decreased.

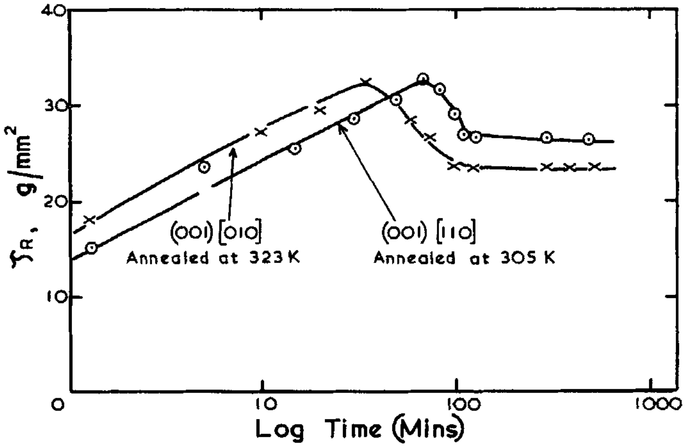

Figure 7. The change in critical resolved shear stress, τ_R, for slip on the (001) [010] and (001) [110] systems on isothermal annealing after quenching from 480 K.

The critical resolved shear stress of the quenched alloys and those which had been aged to the plateau level were determined at constant strain rate over the temperature range 293 to 360 K (Fig. 8). At temperatures above 330 K some ageing of the quenched alloys undoubtedly took place during the test, leading to higher values than would be obtained from completely untransformed alloys. The temperature dependence of the critical resolved shear stress of the quenched alloy for slip on both the (001) [010] and (001) [110]

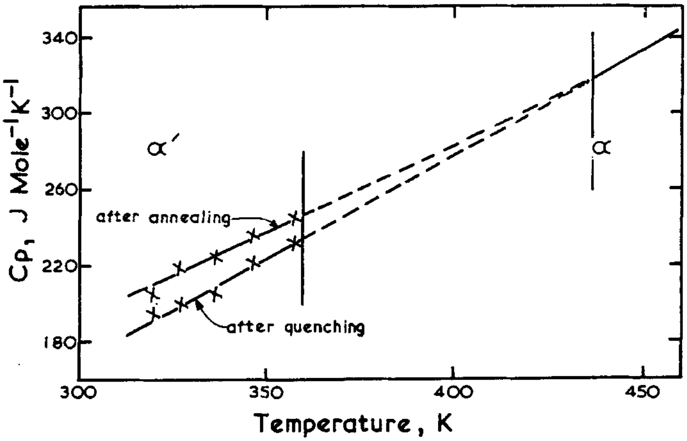

Figure 8. The critical resolved shear stress, τ_R, for slip on both basal systems in an ordered and in a disordered 1.75 pct carbazole alloy as a function of composition.

systems was slightly greater than that of zone-refined anthracene(1) (Fig. 8). On ageing to the fully transformed α′ phase, the critical resolved shear stress at any temperature increased, as did the temperature dependence. The effect of ordering on the critical resolved shear stress appears to be more marked for (001) [010] slip than for (001) [110] slip (Fig. 8).

The " as-grown " single crystals of 8.0 and 10.0 pct carbazole alloys, which are α′ phase after growth, deformed on the same basal slip system as the low carbazole alloys although the ductility was severely limited and in some crystals it was difficult to obtain evidence of plastic deformation. Increasing the carbazole content of the alloys increased the critical resolved shear stress at 298 K from 25–30 g/mm^2 for the 1.75 pct alloy to 130–140 g/mm^2 for the 8.0 pct alloy and to a maximum of 180–190 g/mm^2 for the 10 pct alloy.

7. Discussion

The present experimental results, and those reported previously,(6) indicate that the α′ phase in the anthracene-carbazole system is an ordered structure based on the α terminal solid solution. It is envisaged that the ordered structure, which is being determined by neutron diffraction measurements,(10) has eight molecules per unit cell with *a* and *b* lattice parameters twice those in anthracene(12) and the *c* parameter remaining the same. This gives a stoichiometric composition of 12.5 mole pct carbazole, rather than the experimentally observed 10 pct (10.6 mole pct), with carbazole molecules at 0, 0, 0 and anthracene molecules at $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, 0$; $\frac{1}{2}, 0, 0$; $\frac{1}{4}, \frac{1}{4}, 0$; $\frac{1}{4}, \frac{3}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, 0$; and $\frac{3}{4}, \frac{3}{4}, 0$. The non-stoichiometric alloys may contain defects in the form of vacancies, substitutional atoms destroying the ordered arrangement or complexes consisting of combinations of these defects. The heat capacity measurements suggest that the stability of the α' phase, compared with the component compounds, depends on a positive entropy change on formation associated with an increase in volume, rather than on a decrease in enthalpy.

The activation energy for the isothermal transformation of α to α' phase in a 1.75 pct carbazole alloy as determined by heat capacity measurements, is 29.3 kJ mole^{-1}. This is well below the activation energy for self-diffusion in anthracene,(13–15), even allowing for the large spread in the latter values, which range from 83.7(15) to 175.5(13) kJ mole^{-1} for lattice diffusion and 54.4(15) kJ mole^{-1} for diffusion along sub-boundaries. Self-diffusion in anthracene occurs by a vacancy mechanism(13) and the activation energy determined from diffusion measurements is that for vacancy formation and movement. The rate of ordering in anthracene-carbazole alloys, as in intermetallic compounds,(16) is probably proportional to the vacancy concentration and the rate of isothermal transformation after quenching from a high temperature will give an activation energy for vacancy movement. The present results, together with those from diffusion measurements, suggest that in these alloys the activation energy for vacancy movement is 0.2 to 0.5 that for vacancy formation.

Tensile tests carried out on quenched single crystals of a 1.75 pct carbazole alloy showed that significant changes in the critical resolved shear stress occur as the alloy transforms isothermally from the disordered α to the ordered α' phase. Changes in strength with changes in the state of order have been recognized for some time in intermetallic compounds(17–18) and several theories(19–22) have been advanced to explain the effect on mechanical properties of unit dislocations in an ordered, as opposed to a disordered, structure. An additional strengthening mechanism in ordered alloys is provided by the existence of domain boundaries between one ordered region and another which offer resistance to slip because the passage of dislocations creates additional anti-phase boundaries.(18). Ardley's results on Cu_3Au(23) showed that the strength at low-temperature is dependent on both the degree of long-range order and on the size of the domains. Lawley *et al.*(24) observed that the strength of Fe_3Al passes through a maximum as the change from disordered to ordered bcc occurs during isothermal annealing after quenching from a high temperature. They showed that the maximum was associated with a critical combination of domain size and transient order.(24)

The heat capacity measurements on anthracene-carbazole alloys indicate that on isothermal annealing after quenching the maximum critical resolved shear stress occurs when the alloy approaches the fully ordered state. Unfortunately with these alloys no estimate of the concurrent domain size can be made by electron microscopy because of excessive radiation damage. The decrease in critical resolved shear stress from the maximum to plateau level is presumably associated with an increase in domain size, which will tend to soften the alloy. The combination of degree of order and domain size in the fully annealed alloys is such that the critical resolved shear stress is always larger than that of the quenched disordered alloys.

The critical resolved shear stress for the quenched 1.75 pct carbazole alloy and its temperature dependence are only slightly higher than for anthracene for slip on both the (001) [010] and (001) [110] systems. This is in contrast to naphthalene in which the presence of impurities in commercial samples has a marked effect on both the magnitude and temperature dependence of the critical resolved shear stress, eventually inhibiting slip on the (001) [110] system.(2). The small effect of carbazole additions on the tensile properties of anthracene when the alloys are disordered is probably associated with the similarity in the size and shape of the two molecules.(25) On ordering, however, there is a sharp increase in the critical resolved shear stress at any temperature (Fig. 8); the change being largest at low temperatures where the domain size may be expected to remain small. In the restricted temperature range in which these alloys could be tested, the lower limit being imposed by a lack of ductility and the higher by the transformation temperature, there was no indication of an increase in strength of the ordered alloy with increasing temperature as observed for Cu_3Au(23) and CuZn(26) tested below the transformation temperature.

The critical resolved shear stress of the α' alloys at room temperature (0.6 T_M) increases with increasing carbazole concentration to a maximum value of 180–190 g/mm^2 for the stoichiometric 10 pct alloy. This is analogous to the behavior in intermetallic compounds which exist over a homogeneity range.(18,27) The structural defects present in the non-stoichiometric intermetallic alloys increase their strength with respect to the stoichiometric alloy at low temperatures but decrease their strength at higher temperatures (generally $> 0.6\, T_M$) because of enhanced diffusion rates in a region where deformation is largely diffusion controlled.

The disorder to order changes and their effect on the critical resolved shear stress provide an explanation for the variability of the tensile results for " as-grown " single crystals of low carbazole alloys. The kinetics of transformation indicate that equilibrium will be maintained during the cool from the growth temperature of 480 K to 320–330 K over four days but that non-equilibrium conditions may pertain during the subsequent rapid cool to room temperature, leading to varying degrees of order, and different yield strength, in different crystals. Subsequent changes in the degree of order on standing at room temperature may account for the observed " age-hardening " of " as-grown " crystals. The time scale associated with the latter changes would be expected to be longer than that for the isothermal transformation of disordered α phase quenched from a higher temperature.

REFERENCES

1. Robinson, P. M. and Scott, H. G., *Acta Met.* **15**, 1581 (1967).
2. Robinson, P. M. and Scott, H. G., *Acta Met.* **15**, 1230 (1967).
3. Robinson, P. M. and Scott, H. G., *Mol. Cryst.* **11**, 13 (1970).
4. Kravchenko, M. and Eremenko, A. P., *Zhur Priklad. Khim.* **25**, 662 (1952); *Chem. Abst.* **47**, 9742 (1953).
5. Brandstatter-Kuhnert, M. and Weil, H., *Monatsh. Chem.* **88**, 1007 (1957).
6. Robinson, P. M. and Scott, H. G., *Mol. Cryst.* **5**, 387 (1969).
7. Hultgren, R., Orr, R. L., Anderson, P. D. and Kelley, K. K., " Selected

values of thermodynamic properties of metals and alloys," John Wiley and Sons Inc., New York (1963).
8. Goursot, P., Girdhar, H. L. and Westrum, E. F., *C.R. Acad. Sc. Paris* **226,** 949 (1968).
9. Robinson, P. M. and Bever, M. B., Chapter 3 " Intermetallic compounds," Westbrook, J. H. ed., John Wiley and Sons Inc., New York (1967).
10. Sabine, T. M., A.A.E.C. Lucas Heights, private communication.
11. Schmid, E. and Boas, W., " Plasticity of crystals," F. A. Hughes, London (1950).
12. Sinclair, V. C., Robertson, J. M. and Mathieson, A. McL., *Acta Cryst.* **3,** 251 (1950).
13. Sherwood, J. N. and Thomson, S. J., *Trans. Faraday Soc.* **56,** 1443 (1960).
14. Lee, C. H., Kevorkian, H. K., Reucroft, P. J. and Labes, M. M., *J. Chem. Phys.* **42,** 1406 (1965).
15. Reucroft, P. J., Kevorkian, H. K. and Labes, M. M., *J. Chem. Phys.* **44,** 4416 (1966).
16. Vineyard, G., *Phys. Rev.* **102,** 981 (1956).
17. Stoloff, N. S. and Davies, R. G., *Prog. Mater. Sci.* **13** *(1966).*
18. Beeler, J. R., Brown, N., Lawley, A., Chapters 14, 15 and 24, " Intermetallic compounds," Westbrook, J. N. ed., John Wiley and Sons Inc., New York (1967).
19. Cottrell, A. H., " Properties and microstructure," A.S.M., Cleveland (1954).
20. Sumino, K., *Sci. Rept. Res. Inst. Tohoku Univ.*, Ser. A. **10,** 283 (1958).
21. Flinn, P. A., *Trans. AIME* **218,** 145 (1960).
22. Brown, N., *Phil. Mag.* **4,** 693 (1959).
23. Ardley, G. W., *Acta Met.* **3,** 525 (1955).
24. Lawley, A., Vidoz, E. A. and Cahn, R. W., *Acta Met.* **9,** 287 (1961).
25. Robinson, P. M. and Scott, H. G., *Mol. Cryst.* to be published.
26. Barrett, C. S., *Trans. AIME* **200,** 1003 (1954).
27. Wood, D. L. and Westbrook, J. H., *Trans. AIME* **227,** 771 (1963).