GULF GENERAL ATOMIC

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-10433

RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT

FOR THE PERIOD ENDING NOVEMBER 14, 1970

by

G. B. Engle, R. J. Price, and J. C. Bokros

Prepared under
Contract AT(04-3)-167
Project Agreement No. 12
for the
San Francisco Operations Office
U.S. Atomic Energy Commission

November 24, 1970

GULF GENERAL ATOMIC COMPANY, P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

DISCLAIMER

GULF GENERAL ATOMIC

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-10433

RESEARCH ON GRAPHITE

QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING NOVEMBER 14, 1970

by

G. B. Engle, R. J. Price, and J. C. Bokros

Prepared under
Contract AT(04-3)-167
Project Agreement No. 12
for the
San Francisco Operations Office
U.S. Atomic Energy Commission

Gulf General Atomic Project 271

November 24, 1970

GULF GENERAL ATOMIC COMPANY, P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

PREVIOUS REPORTS IN THIS SERIES

GA-4022 - Annual Report, April 1, 1962, through March 31, 1963
GA-5016 - Annual Report, April 1, 1963, through March 31, 1964
GA-5033 - Annaul Report, April 1, 1963, through March 31, 1964 (Task II)
GA-6233 - Annual Report, April 1, 1964, through March 31, 1965
GA-7100 - Annual Report, May 15, 1965, through May 14, 1966
GA-7906 - Annual Report, May 15, 1966, through May 14, 1967
GA-8681 - Annual Report, May 15, 1967, through May 14, 1968
GA-9433 - Annual Report, May 15, 1968, through May 14, 1969
GA-9675 - Quarterly Report for period ending August 14, 1969
GA-9828 - Quarterly Report for period ending November 14, 1969
GA-9968 - Quarterly Report for period ending February 14, 1970
GA-9975 - Three Year Summary Report, May 15, 1967, through May 14, 1970
GA-10268 - Quarterly Report for period ending August 14, 1970

1. INTRODUCTION

The objective of this program is to advance the understanding of relationships between microstructure, properties, and irradiation behavior of carbonaceous materials for advanced high-temperature reactors. The research efforts are directed toward defining the structure of model carbons and porous graphites and evaluating methods for the preparation of new or modified carbon structures with improved irradiation behavior.

The research effort covered by this report (August 15, 1970, through November 14, 1970) consisted of two principal tasks: (1) characterization and irradiation of graphites, and (2) characterization and irradiation of model carbons.

The majority of the experimental efforts during this report period were concerned with the characterization of graphite and carbon specimens being irradiated in capsule GE-H-13-18.* Capsule GE-H-13-18 is operating in the range 550° to 1400°C, and irradiation will continue until fluences of 0.5 to 4.0 x 10^{21} n/cm^2 (E > 0.18 MeV) are reached. Capsule GE-H-13-18 is scheduled for discharge about January or February 1971. About 50 new or previously irradiated specimens are being irradiated concurrently in two other capsules at BNWL, which are operating at 550° and 800°C. These irradiations will continue until a fluence of about 3 x 10^{21} n/cm^2 is reached. Data from these specimens will complement the low-temperature data from the GE-H-13-18 specimens by providing additional data points at higher fluences.

---

*Being irradiated in the Engineering Test Reactor (ETR) by Battelle Northwest Laboratory (BNWL).

2. SUMMARY

CHARACTERIZATION AND IRRADIATION OF GRAPHITES

A series of previously irradiated graphites and a number of new isotropic materials are under study to determine the effect of crystallite size, crystallite orientation, and density on dimensional and property changes. The new series of isotropic graphites had apparent crystallite sizes ranging from 150 to 850 Å. Preirradiation densities and thermal expansivities were also measured. Scanning electron microscope photographs revealed the shape, size, and surface texture of density fractions in a needle-coke graphite.

Experiments to study the temperature-history effects on dimensional changes, the behavior of highly oriented graphites, and the changes in thermal conductivity were continued. Previously irradiated materials are being irradiated to higher fluences, and new materials are also being irradiated.

A series of experiments was initiated to study the effect of coke structure on irradiation behavior. Density and X-ray parameters were measured on fine-structured isotropic cokes, heated to 2600° to 2800°C.

During the past 3 years, specimens have been irradiated in the Dragon reactor to measure irradiation-induced creep in a number of graphites. These specimens are now being measured at RCN, Petten, Holland.

Thermal conductivity specimens are being irradiated.

CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

New data for model carbons with L_c values in the range 50 to 200 Å are reported. Dimensional data are compared for high- and low-density isotropic carbons irradiated at 1250°C to 1.5×10^{22} n/cm^2.

3. CHARACTERIZATION AND IRRADIATION OF GRAPHITES

G. B. Engle, R. J. Price, L. Bailey, and
K. Koyama

EFFECT OF CRYSTALLITE SIZE, CRYSTALLITE ORIENTATION, AND DENSITY ON DIMENSIONAL AND PROPERTY CHANGES OF GRAPHITES

A series of graphites is being irradiated to determine the effect of crystallite size, crystallite orientation, and original density on irradiation behavior. This series includes graphites that range from highly oriented materials with large crystallite sizes to isotropic graphites such as Poco materials. The original specimens (described in Ref. 1) were irradiated in capsule GE-H-13-17 to 1.80 to 3.75 x 10^{21} n/cm^2 at about 1000° to 1280°C. Dimensional and volume changes resulting from the first irradiation were reported last quarter.[2] These specimens are being reirradiated in capsule GE-H-13-18 to a total fluence of about 3 to 8 x 10^{21} n/cm^2. Additional specimens of the graphites from GE-H-13-17 and a number of new materials were added to this series and are being irradiated in capsule GE-H-13-18. A description of the new materials was given in Ref. 2.

Structural characterization was continued on the new materials by measurement of their thermal expansivities and by examination of X-ray diffraction patterns obtained on density fractions. The density fractions were obtained in the usual way by comminution of the bulk sample and separation in the densimeter.[1] The data are given in Table 1. These data are considered routine measurements as part of the characterization work and will be used in conjunction with the values obtained on specimens currently under irradiation. The curves of apparent crystallite size L_c versus apparent density ρ (not given in this report) reveal some differences among the isotropic graphites.

TABLE 1
DENSITY, X-RAY PARAMETERS, AND THERMAL EXPANSIVITY
OF GRAPHITES UNDER IRRADIATION IN GE-H-13-18

Material Type	Density (g/cm^3)			X-Ray Parameters, Å		Thermal Expansivity (Mean CTE x 10^6, $°C^{-1}$)			
		Immersion in Liquid				Parallel		Perpendicular	
	Bulk	Bulk	Powder	C_o	L_c[a]	22°-500°C	22°-1000°C	22°-500°C	22°-1000°C
H-327[b] Anisotropic (edge)	1.745	2.080	2.225	6.716	1122	1.45 1.33	- -	3.05 3.06	- -
H-327[b] Anisotropic (center)	1.745	2.060	2.220	6.716	1065	1.44 1.54	- -	2.94 2.67	- -
AXF-8QGB Isotropic	1.902	2.066	2.150	-	-	7.10 6.90	7.59 -	6.68 7.18	7.22 -
H-419 Isotropic	1.789	2.143	2.220	6.740	328				
H-421 Isotropic	1.774	2.045	2.155	6.745	280	6.07 6.30	6.66 -	6.04 6.29 6.31 6.18	6.54 - 6.80 -
H-337 Isotropic	2.016	2.140	2.190	6.721	740	5.24 5.26	5.89 -	4.94 5.10	5.60 -
HL-18 Isotropic	1.860	2.100	-	-	-	5.15 5.35	5.57 -	4.94 5.44	5.50 -
L-31 Isotropic	1.625	2.095	2.110	-	186	5.81 5.75	6.44 -	5.77 6.00	6.40 -

[a] L_c is mean value (see Ref. 1 for details of calculation).

[b] Specimens taken from the edge or center of an 18-in-diameter log.

Graphite H-337, which appears to be nearly isotropic from the thermal expansivity values (isotropy ratio 1.01), had a relatively high $\overline{L}_c$ of 740 Å, which approaches that of a needle coke. This material also had a rather wide distribution of L_c values from 385 to 950 Å. Graphite L-31 had unusually low L_c values and a rather limited range (150-190 Å). This material approaches the pyrocarbons in its apparent crystallite size. The densities of the bulk and powder when measured by immersion in the liquids of the densimeter column were nearly the same and low. Thus, very few closed pores were destroyed during the comminution process. This behavior has also been observed for pyrocarbons. About 88 vol % of the material was in the range 2.09 to 2.14 g/cm^3, 10 vol % was below 2.09 g/cm^3, and 2 vol % was in the range 2.14 to 2.26 g/cm^3.

Density fractions of a needle-coke graphite (CHN) on which a considerable amount of high-temperature irradiation data are available were prepared and examined with a scanning electron microscope (SEM). The characteristics of the particle shape, size, and surface texture were clearly visible. There was an apparent split in the general characteristics of the particles at $\rho \gtrless 2.20$ g/cm^3; those above appeared "needle like" and those below "chunky". This split represents 85 vol % > 2.20 g/cm^3 and 15 vol % < 2.20 g/cm^3 and approximates the volume of filler and binder-impregnant carbon believed to be used in the original mix. The density fractions will be reseparated in an effort to improve the separation and thus improve the sensitivity of the analysis with the SEM.

EFFECT OF TEMPERATURE HISTORY ON DIMENSIONAL CHANGES

There are regions in HTGR cores where the graphite temperatures are initially high but during the lifetime of the graphite drop to lower temperatures. Therefore, the effect of the temperature history on the dimensional changes of the graphite is of interest.

In previous work a number of graphites were irradiated to intermediate fluences at ∿ 1000° and 1450°C, and the irradiation was continued to higher fluences at lower temperatures.[3] These experiments showed an apparent temperature history effect similar to that observed in model carbons[4] but were not conclusive because of the small number of experimental data points. These studies are being continued to higher fluences, and additional specimens have been included to provide data at other temperatures. The materials included in this study along with temperature and fluence values were reported last quarter.[2]

IRRADIATION EFFECTS IN HIGHLY ORIENTED CARBONS AND GRAPHITES

Data obtained from irradiation experiments on highly oriented carbons and graphites with various crystallite sizes are useful for developing an understanding of irradiation effects in polycrystalline graphites. In the present series of experiments, samples of hot-worked graphite, as-deposited massive pyrolytic carbon, and massive pyrolytic carbon annealed at 2900°, 3000°, 3100°, and 3300°C before irradiation are being irradiated at 750° to 800°C and at 1225° to 1300°C. Results obtained to date were summarized in Ref. 4. The samples are being reirradiated in capsule GE-H-13-18. The additional neutron fluences anticipated are 0.6×10^{21} n/cm^2 at 800°C and 4×10^{21} n/cm^2 at 1275°C.

COKE STUDIES

Calcined petroleum coke particles constitute a major portion of binder-filler graphites. Therefore, the behavior of the filler particles is an important factor in the determination of the irradiation behavior of the binder-filler artifacts.

A description of the cokes selected from various sources for characterization and irradiation were reported previously.[2] The raw cokes were heated to 2800°C in helium prior to preparation for irradiation. The cokes are being irradiated to 3.0 x 4.0 x 10^{21} n/cm^2 at 1000° and 1275°C in GE-H-13-18.

Three of the fine-grained isotropic petroleum cokes were comminuted and separated into density fractions. The density and X-ray data are given in Table 2.

THERMAL CONDUCTIVITY CHANGES

Irradiation-induced thermal conductivity changes are important in the design of high-temperature reactors when the graphite is utilized to transfer heat from the fuel to the coolant.

A series of specimens is being irradiated in capsule GE-H-13-18. The preirradiation thermal conductivity data were given in Ref. 4. About 130 specimens are being irradiated initially to about 0.3 to 4 x 10^{21} n/cm^2 at 550°, 800°, 1000°, and 1275°C.

CREEP STUDIES

The Dragon Project has made space available to Gulf General Atomic in the Dragon reactor, on a cooperative basis, for the purpose of irradiating restrained shrinkage specimens. The specimens were prepared at Gulf General Atomic, and the irradiation and postirradiation measurements are being done at Dragon, or RCN, Petten, Holland. The graphites varied widely in apparent crystallite sizes (L_c 500 to 1600 Å), and the effect of L_c on creep constants is being sought.

Measurements of the restrained specimens are now underway at Petten after a considerable delay due to the heavy work load in the Petten Laboratory. Further results from this experiment are expected within the next few months.

TABLE 2
DENSITY AND X-RAY PARAMETERS OF COKES

Source Material	Specimen Number	Estimated Heat-Treatment Temperature (°C)	Graphitized Density (g/cm^3)[a]	X-Ray Parameters, Å	
				$\overline{L}_c$	C_o
Vacuum-reduced petroleum crude	223B1	2680	2.140	382	6.740
Vacuum-reduced petroleum crude	223C2	2805	2.150	300	6.745
Gilsonite coke	223C3	2815	2.165	395	6.745

[a] Measured by immersion in liquid.

4. CHARACTERIZATION AND IRRADIATION OF MODEL CARBONS

J. C. Bokros, J. L. Kaae, W. Ellis, and F. Gagnon

A considerable amount of new data for model carbons with L_c values in the range 50-200 Å have been obtained from the GE-H-13-17 capsule. These data together with previously unreported data are summarized in Fig. 1 (density changes), Fig. 2 (shape change data for anisotropic specimens at constant high density), and Fig. 3 (dimensional change data for isotropic carbons). The plot in Fig. 4 compares the dimensional behavior of high-and low-density isotropic carbons at 1250°C irradiated to a total fluence of 1.5×10^{22} n/cm^2.

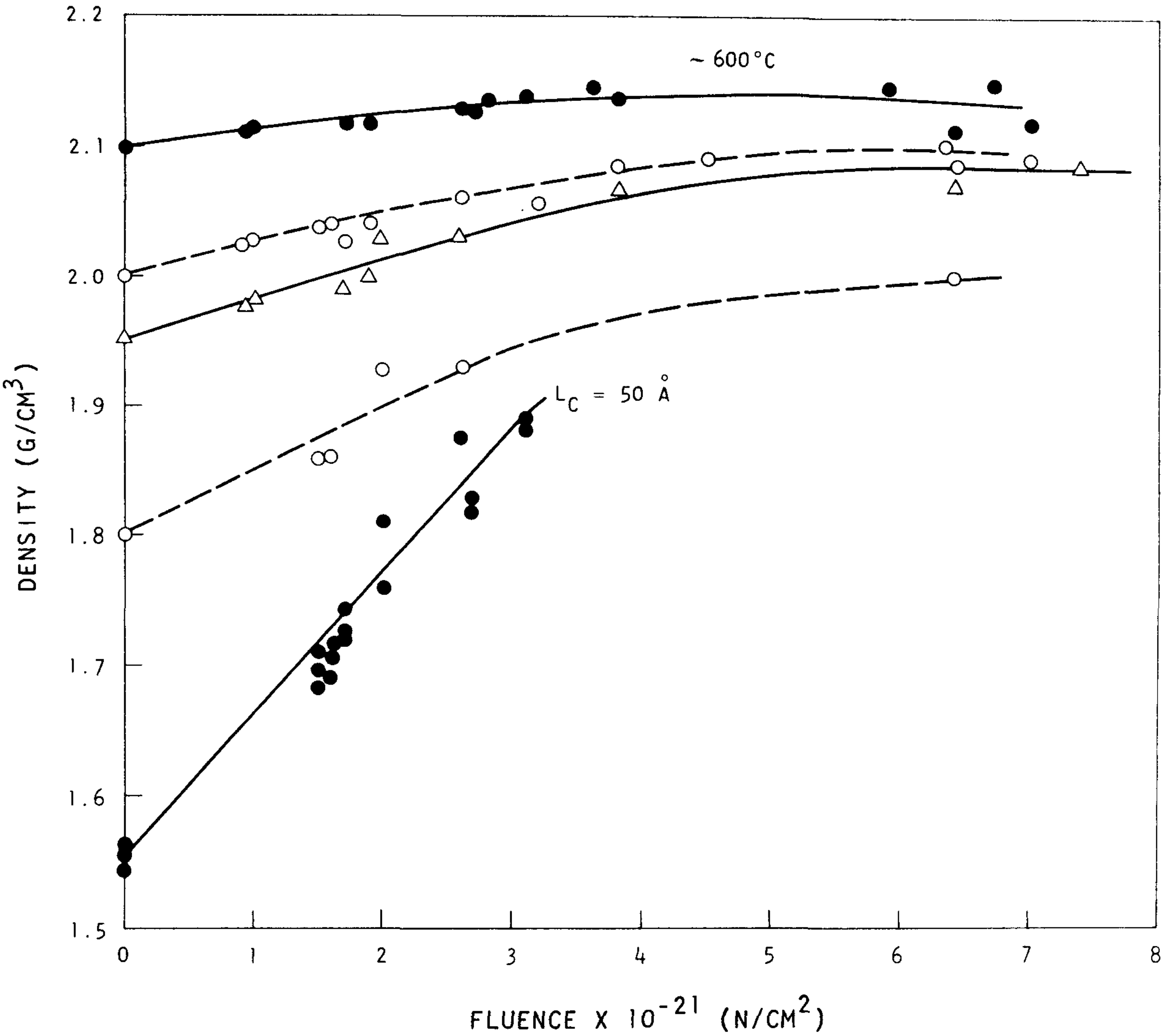

Fig. 1. Density changes of LTI carbons versus fluence.
(a) ∿600°C

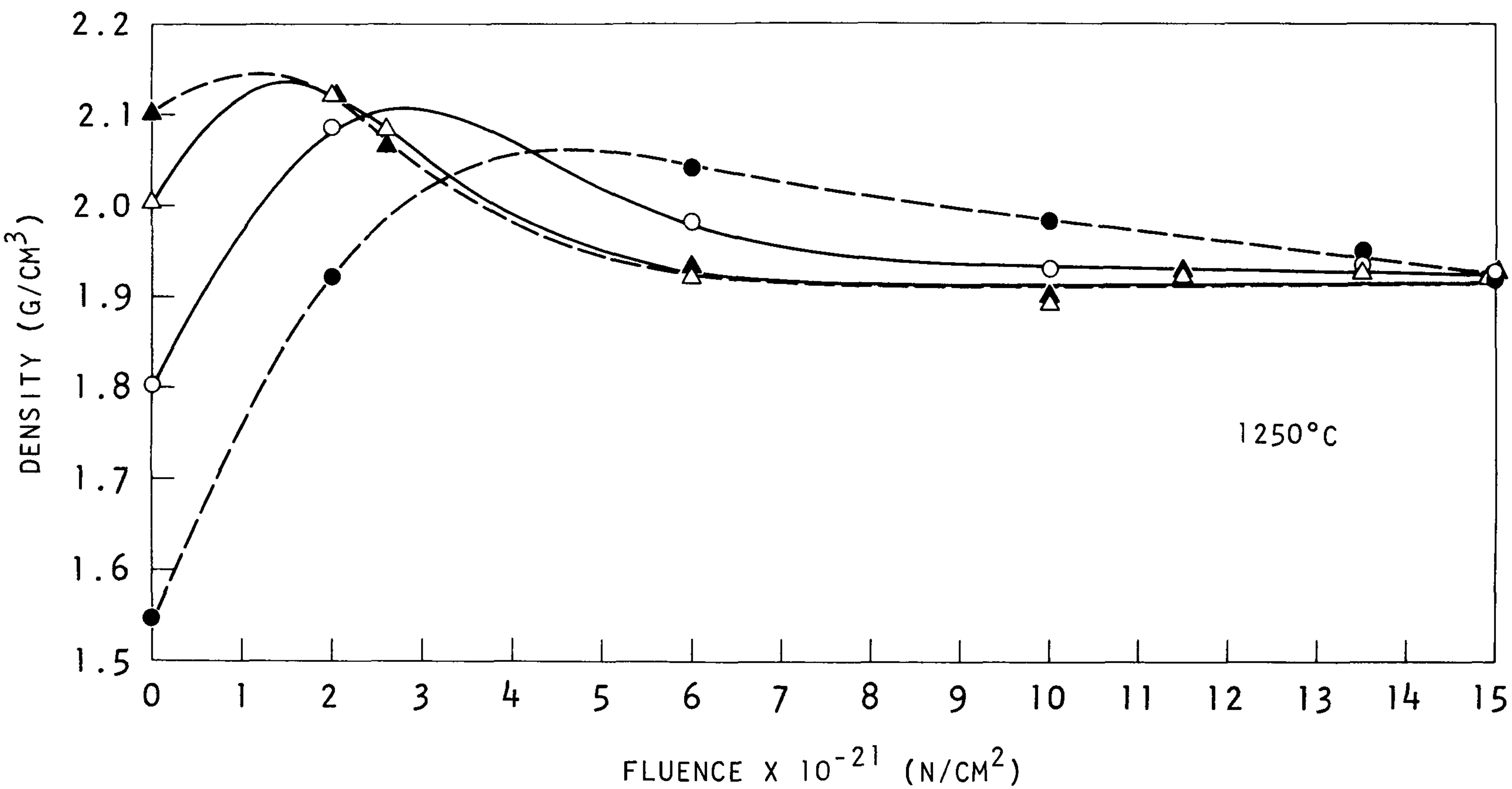

Fig. 1. Density changes of LTI carbons versus fluence.
(c) 1250°C

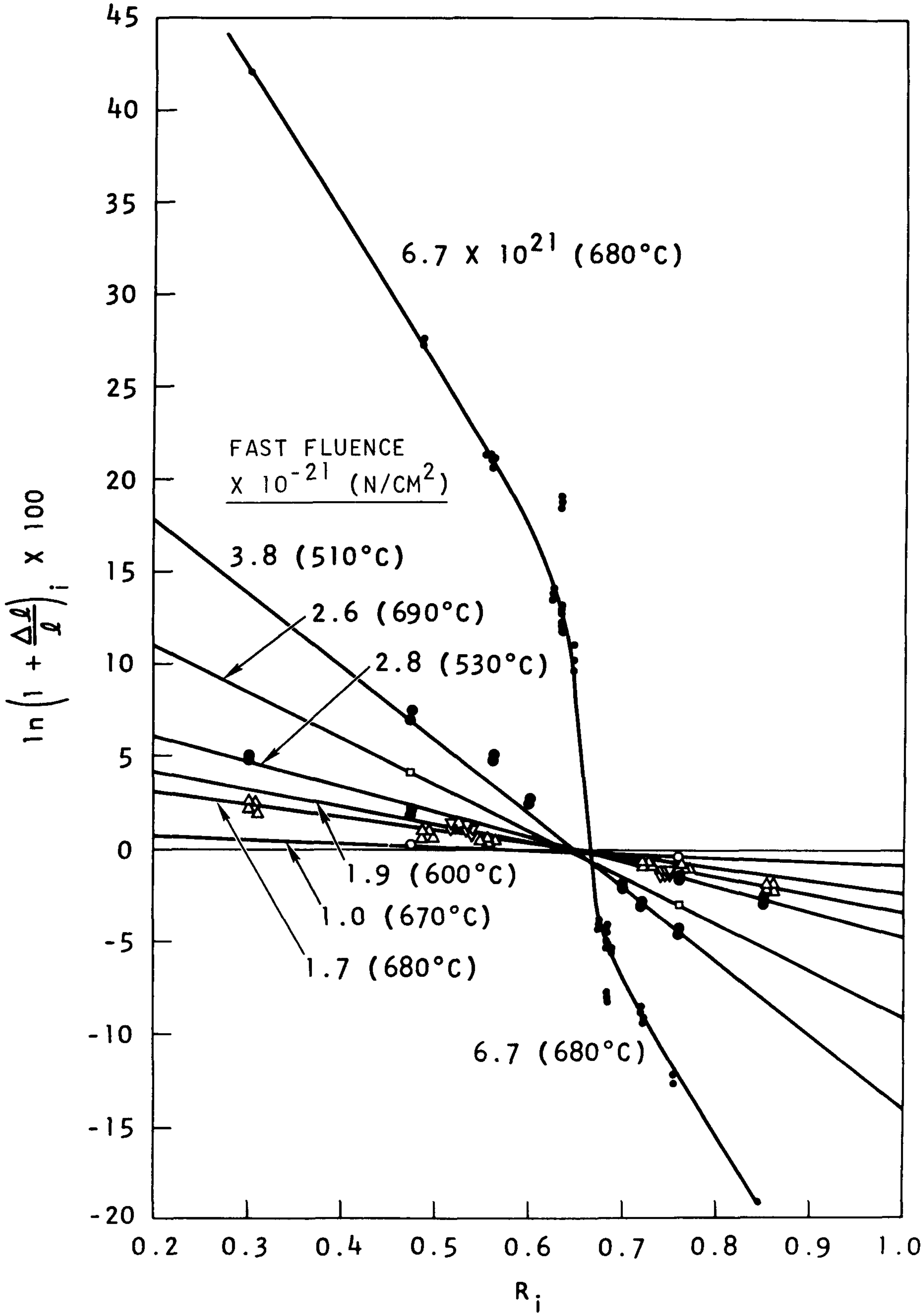

Fig. 2. Shape change data for anisotropic specimens at constant high density. (a) 510° to 680°C

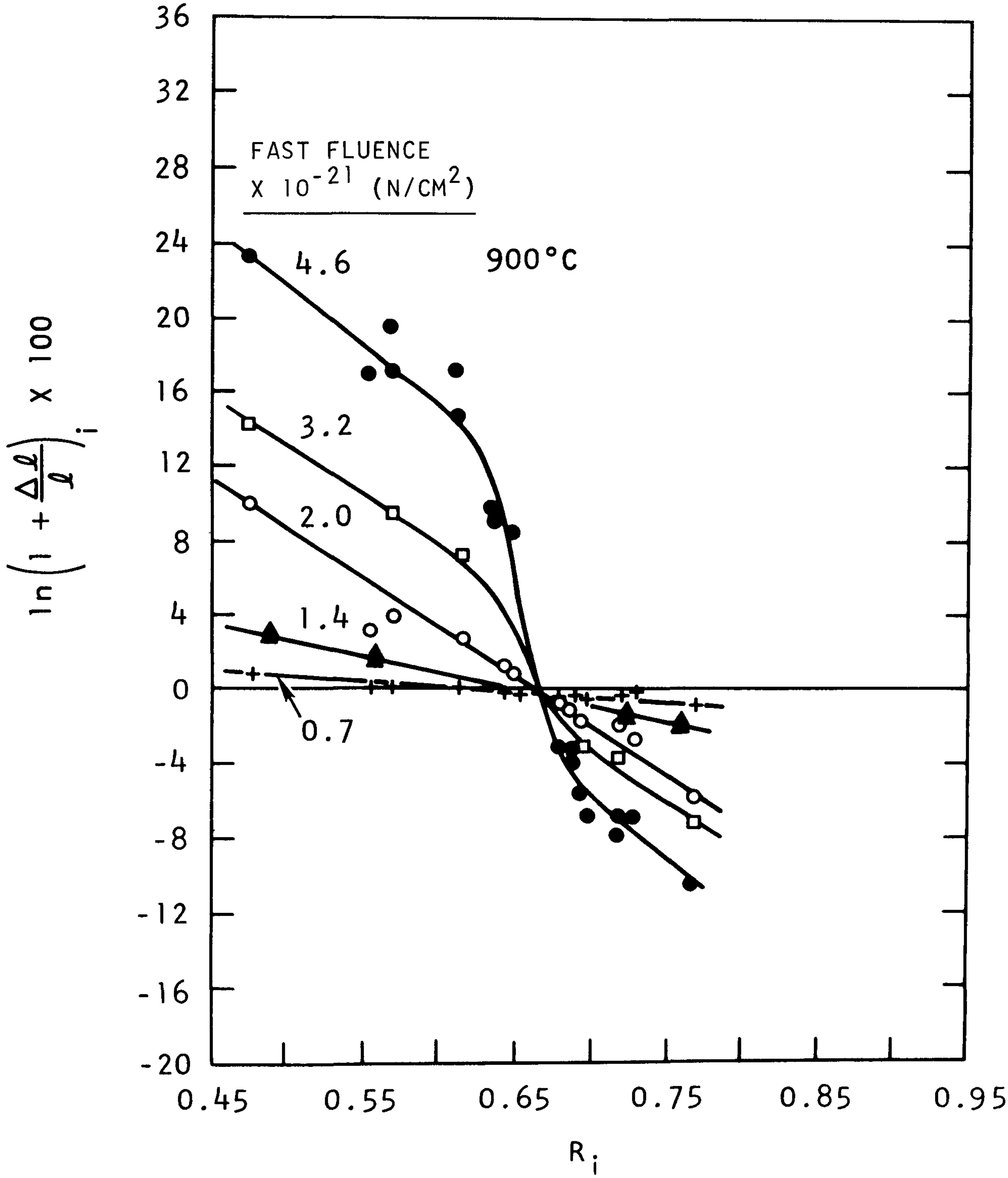

Fig. 2. Shape change data for anisotropic specimens at constant high density. (b) 900°C

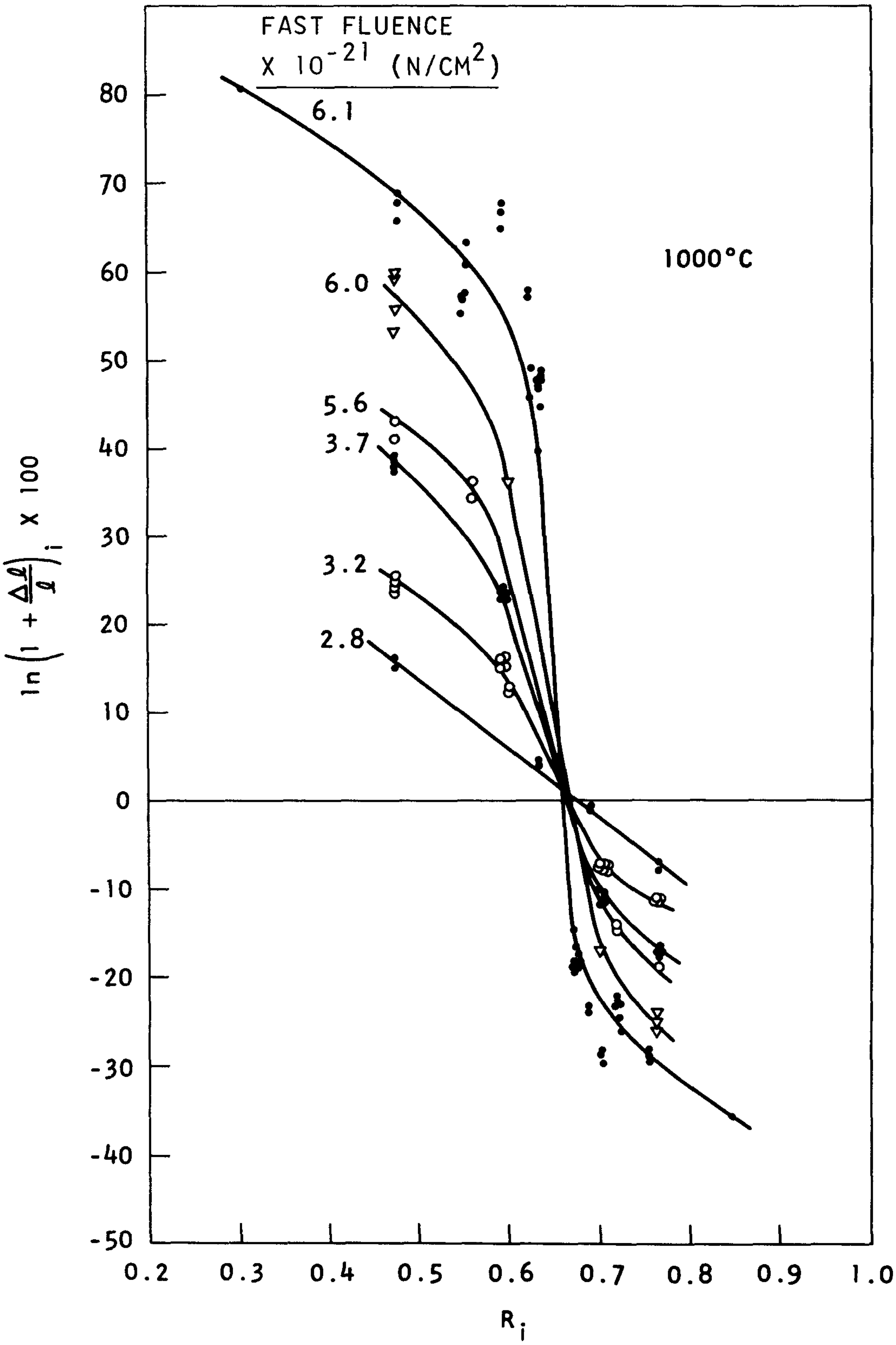

Fig. 2. Shape change data for anisotropic specimens at constant high density. (c) 1000°C

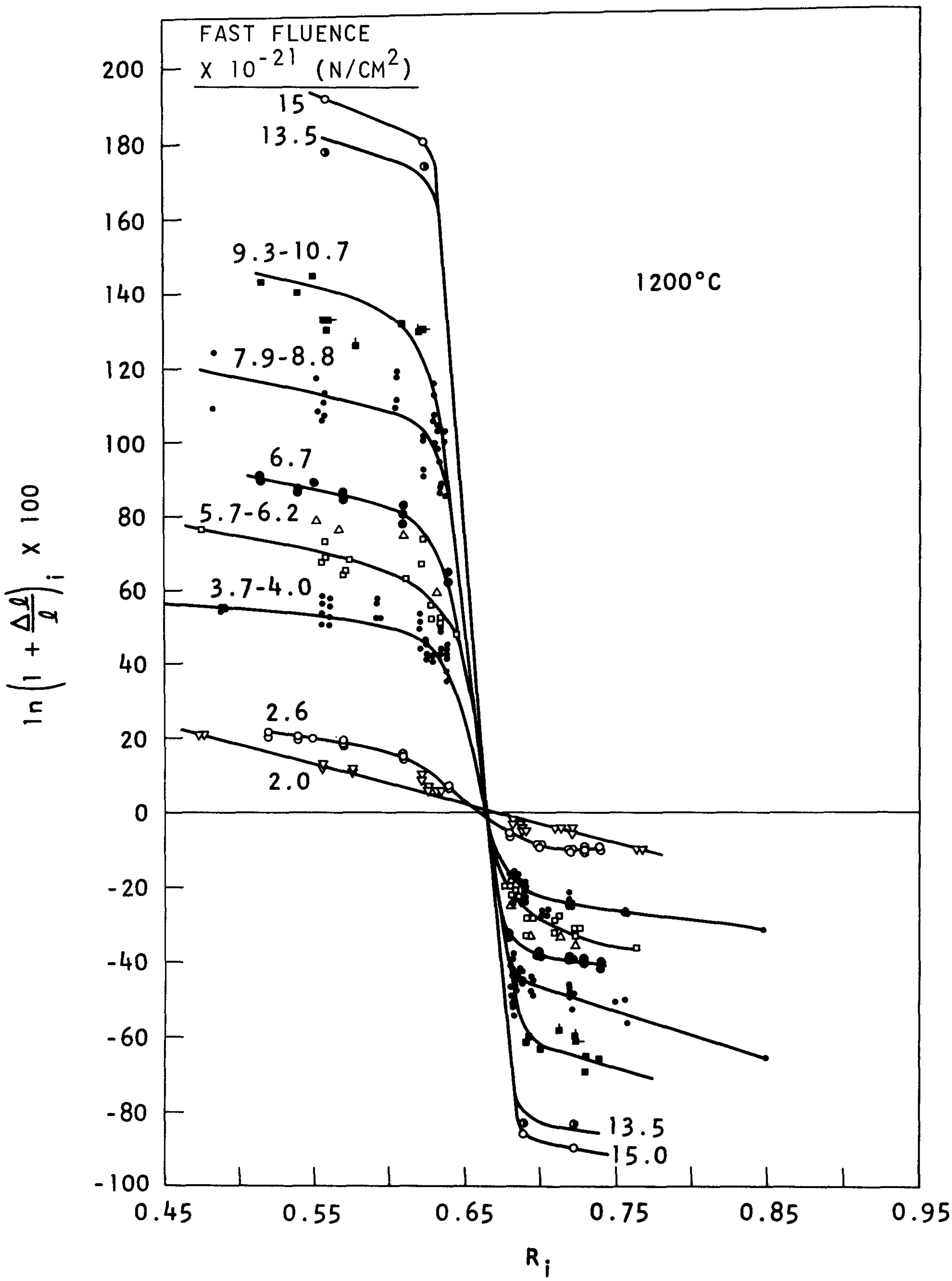

Fig. 2. Shape change data for anisotropic specimens at constant high density. (d) 1200°C

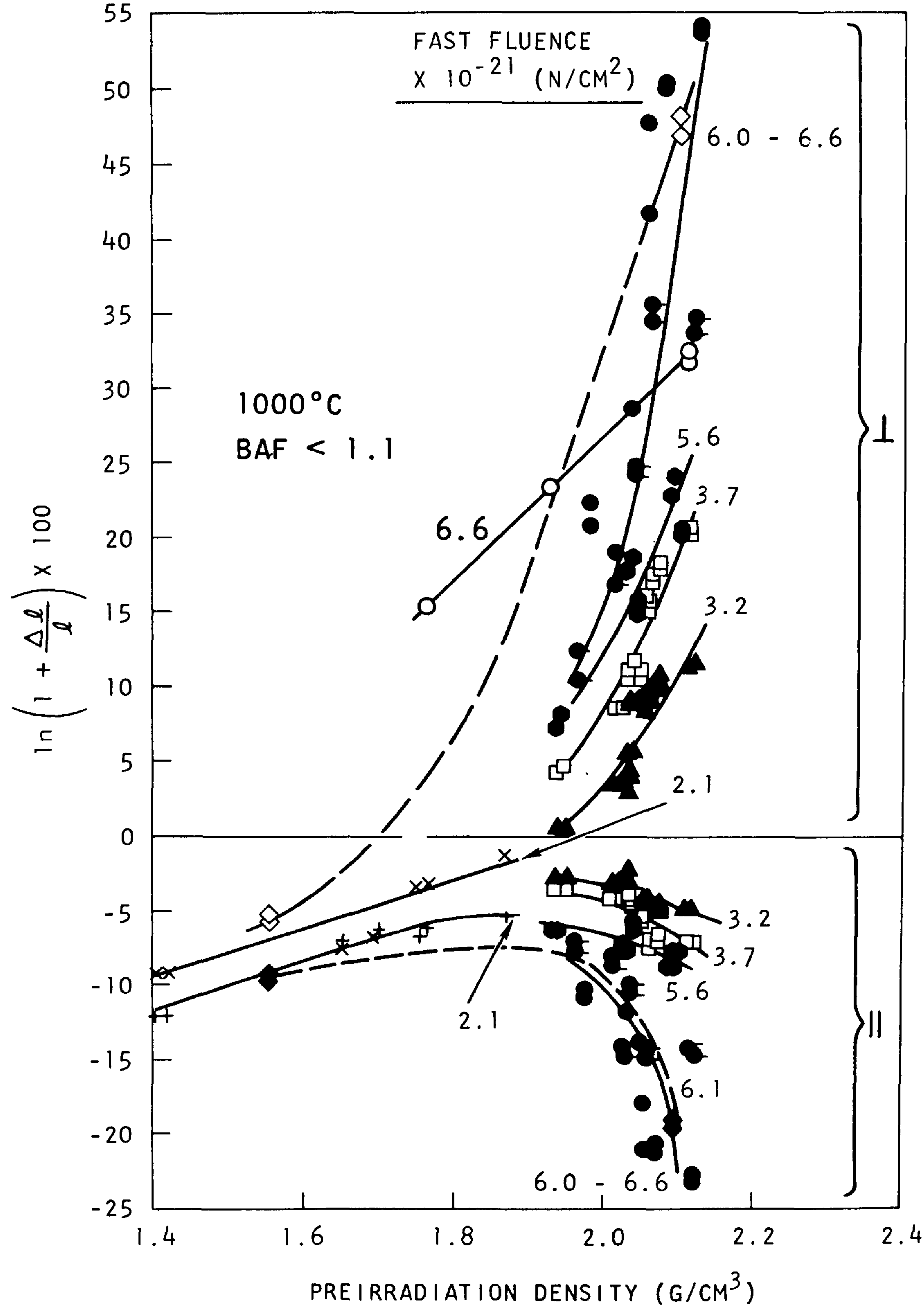

Fig. 3. Dimensional change data for isotropic carbons.
(a) 1000°C

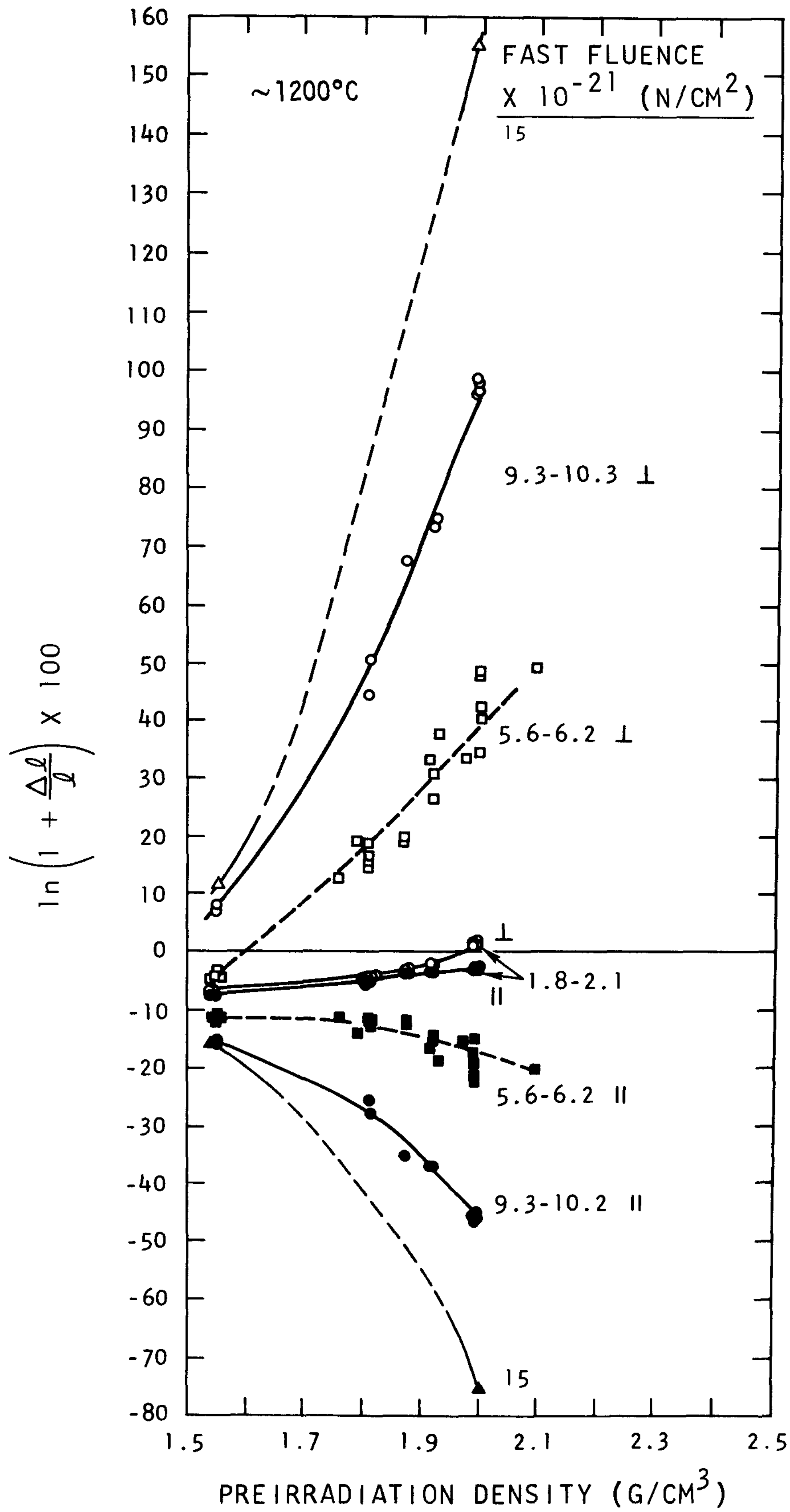

Fig. 3. Dimensional change data for isotropic carbons.
(b) ~1200°C

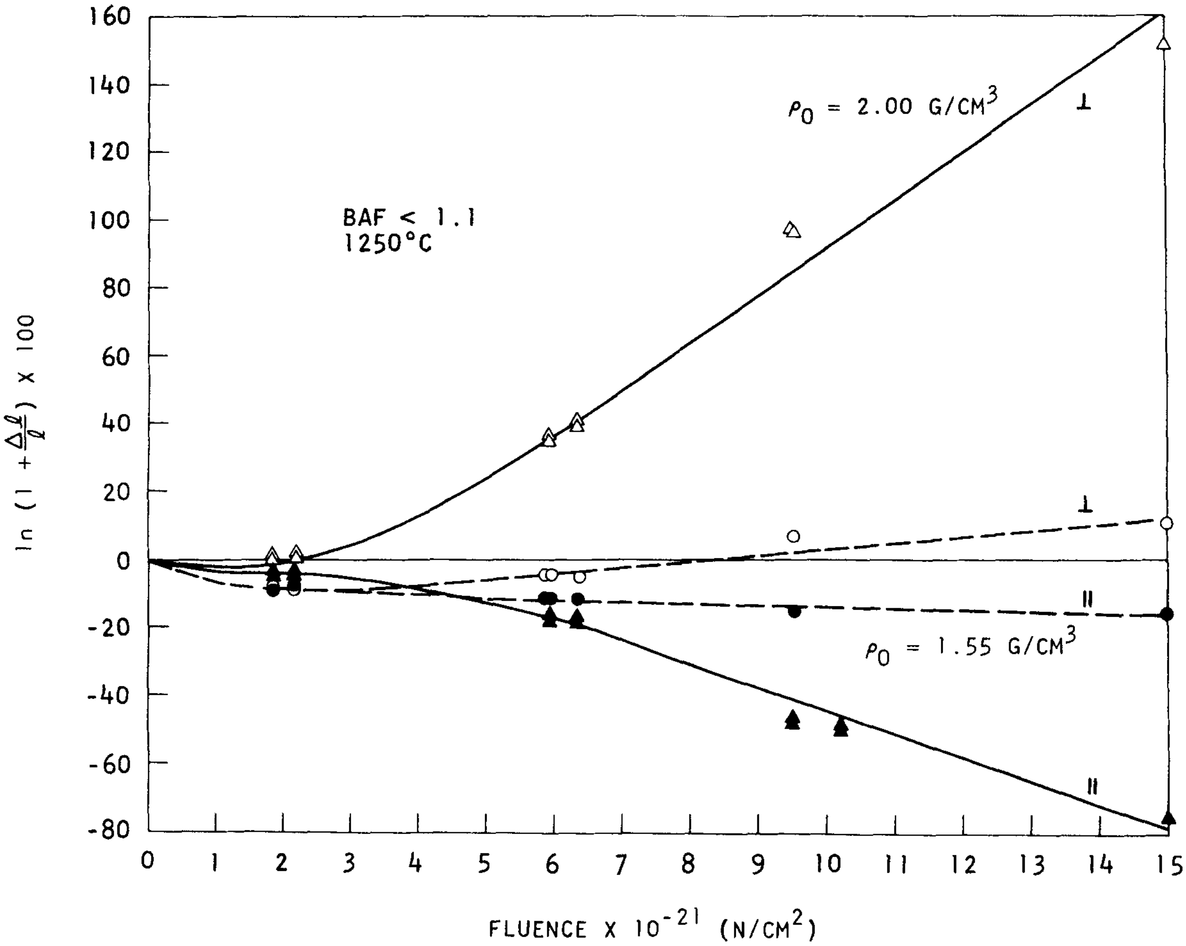

Fig. 4. Comparison of the dimensional behavior of high- and low-density isotropic carbons at 1250°C irradiated to a total fluence of 1.5 x 10^{22} n/cm^2

TOPICAL REPORTS AND PUBLICATIONS

The current status of topical reports and publications resulting from investigations performed under this program is as follows:

GA-9421 "Apparatus and Procedure to Determine Density and Structural Distributions in Carbons and Graphites," G. B. Engle, W. H. Morris, and L. Bailey, Carbon 8, 393 (1970).

GA-9617 "Density and Structural Distributions in Artificial Graphites," G. B. Engle, Carbon 8, 485 (1970)

GA-9900 "Irradiation Behavior of Isotropic Carbons," J. C. Bokros and D. W. Stevens, February 24, 1970 (accepted for publication in Carbon).

GA-9972 "Irradiation Behavior of Nuclear Graphites at Elevated Temperatures," G. B. Engle, March 4, 1970 (submitted for publication in Carbon).

GA-9919 "Irradiation-Induced Dimensional Changes and Creep of Isotropic Carbon," J. L. Kaae and J. C. Bokros, March 11, 1970 (accepted for publication in Carbon).

GA-9971 "The Influence of Pitch-Binder Coke Content on the Properties and Irradiation Behavior of Molded Graphite," G. B. Engle, March 12, 1970 (accepted for publication in Carbon).

GA-9974 "Isochronal Annealing Kinetics and Neutron-Induced Dimensional Changes of Titanium-Doped Pyrolytic Carbon," R. J. Price and J. C. Bokros, May 11, 1970 (accepted for publication in Carbon).

GA-10162 "Annealing of Neutron-Irradiated Pyrocarbons," R. J. Price and J. C. Bokros, June 8, 1970 (submitted for publication in Carbon).

GA-9970 "Low-Temperature Graphitization of Cokes and Binder-Filler Artifacts," G. B. Engle, July 17, 1970 (submitted for publication in Carbon).

GA-10101 "Irradiation-Induced Dimensional Changes in Imperfect Graphite Crystals," J. C. Bokros, G. L. Guthrie, and D. W. Stevens, June 29, 1970 (submitted for publication in Carbon).

REFERENCES

1. Engle, G. B., "Density and Structural Distributions in Artificial Graphites," Carbon 8, 485 (1970).

2. Engle, G. B., R. J. Price, and J. C. Bokros, "Research on Graphite, Quarterly Progress Report for the Period Ending November 14, 1970," USAEC Report GA-10268, Gulf General Atomic, August 13, 1970.

3. Engle, G. B., "Effect of Temperature History on the Dimensional Changes of Nuclear Graphites," USAEC Report GA-10001, Gulf General Atomic, March 23, 1970.

4. Engle, G. B., R. J. Price, J. C. Bokros, and J. L. White, "Research on Graphite, Three Year Summary Report, May 15, 1967, through May 14, 1970," USAEC Report GA-9975, Gulf General Atomic, June 1, 1970.