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Authors

Hoyt, J.J.
Bragg, R.H.

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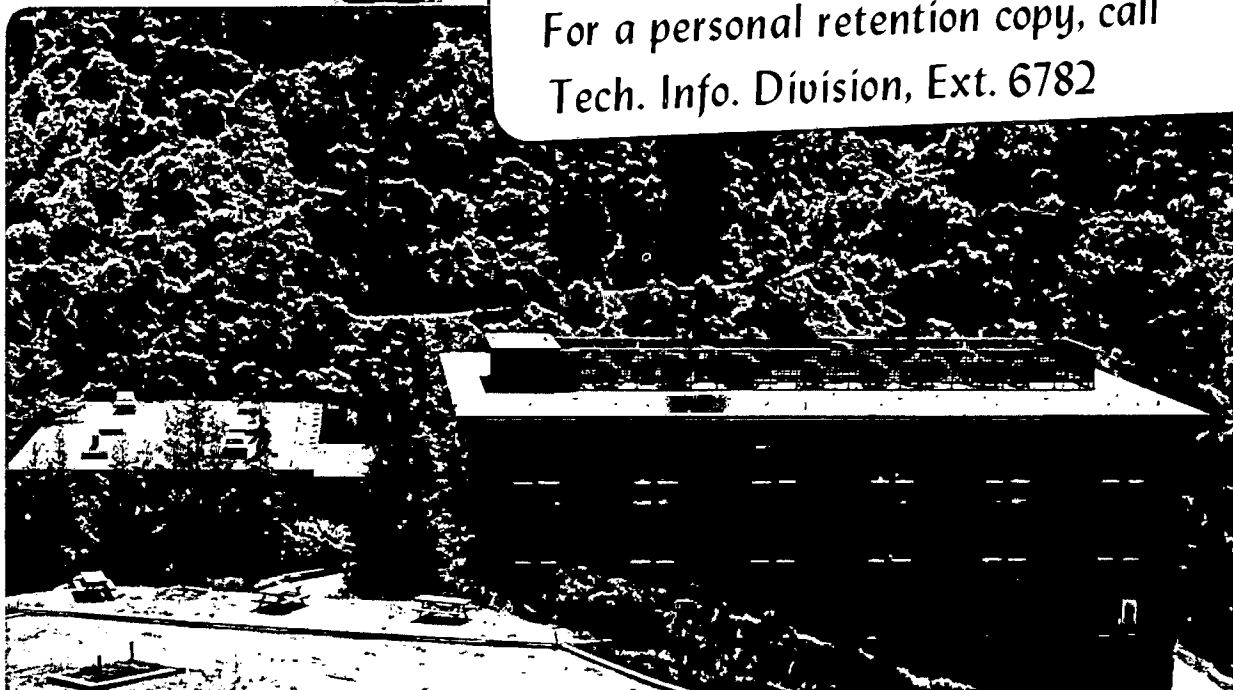
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PORE SIZE AND GROWTH KINETICS IN GLASSY
CARBON USING SMALL ANGLE X-RAY SCATTERING

J. J. Hoyt and R. H. Bragg

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, CA 94720

ABSTRACT

Small angle X-ray scattering was used to determine the average radius of gyration of pores in glassy carbon as a function of heat treatment time (HTt) and heat treatment temperature (HTT). The voids were found to coarsen such that \bar{R}_g^3 is proportional to HTt. The results agree with the theory of diffusion controlled precipitate growth in alloy systems.

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1. Introduction

It has been shown¹ that the total pore volume of glassy carbon depends only on heat treatment temperature (HTT) and not heat treatment time (HTt). This indicates that pore coarsening is occurring. Lifshitz and Slyozov² showed that the bulk diffusion controlled growth of precipitates in alloy systems can be described by:

$$\bar{r}^3 - \bar{r}_i^3 = \frac{9 \gamma D C_0 \Omega^2}{8 RT} t$$

where \bar{r} is the average particle radius, \bar{r}_i the initial average radius, γ is the interfacial energy between matrix and solute, C_0 is the equilibrium solubility of precipitates, D is the diffusion coefficient, Ω is the molar volume of solute, and RT has the usual meaning. Assuming pore growth in glassy carbon occurs by the migration of vacancies and that the void shape is not spherical but remains constant during heat treatment, it is reasonable to assume that the average radius of gyration of the pores raised to the third power is proportional to the heat treatment time.

In previous work Bose and Bragg¹ used small angle X-ray scattering to study the growth of voids in glassy carbon by determining the radius of gyration from a method first proposed by Guinier³ (i.e., from the slope of $\ln I$ vs. h^2 plot). A kinetic analysis was not possible because the radius of gyration calculated by the Guinier technique is not representative of the average pore size but rather, is heavily weighted towards the larger pores in the system.

Hosemann⁴ outlined a method of determining the average radius of gyration from small angle X-ray data by assuming a Maxwellian distribution

of particle sizes and a Guinier scattering function of the form $\exp(-h^2 R_g^2/3)$. In this technique, the data plotted as $h^2 I(h)$ vs. h gives the parameters, h_m which represents the scattering vector at the maximum of the curve, and h_T which is defined by the intersection with the h -axis of the tangent of the curve at the inflection point on the high angle side of the curve. Then, the average radius of gyration is given by:

$$\bar{R}_g = \frac{1}{h_m} \sqrt{\frac{6}{n+2}} \frac{\Gamma\left(\frac{n+2}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)}$$

where the parameter n is found from the relation:

$$\frac{h_T}{2h_m} - 1 \cong \frac{1}{\sqrt{2(n+1)}}$$

The present work suggests that large pores in glassy carbon grow at the expense of smaller pores by the diffusion of vacancies. Small angle X-ray scattering is employed to determine the average pore size as a function of HTT and HTt and the results are compared to the theory of precipitate growth in alloy systems.

2. Experimental

Glassy carbon, GC-1000 samples 5.1 cm x 1.8 cm (2" x 11/16") were ground to a thickness of .13 cm (.05") using a diamond wheel. The samples were heat treated in a graphite Astro Furnace at 2100°C and 2500°C for times ranging from one to 24 hours. An inert atmosphere of helium was employed during all the heat treatments.

The small angle scattering apparatus used is shown schematically in Figure 1. The system is equipped with an argon/methane filled linear position sensitive detector (sample to detector distance = 161 cm). A monochromatic, point collimated beam of Cu K_α X-ray radiation was used throughout the investigation. A more detailed description of the small angle scattering system can be found elsewhere.⁵

3. Results and Discussion

Figure 2 shows typical h^2I vs. h data (HTt = 15 hrs, HTT = 2100°C). It can be seen that the shape of the curve agrees quite well with that predicted by Hosemann's theory. From the values $h_M = .095 \text{ \AA}^{-1}$ and $h_T = .368 \text{ \AA}^{-1}$ the average radius of gyration was found to be $\approx 7.9 \text{ \AA}$. It should be noted that effects due to interparticle interference can be neglected if the quantity g defined as:

$$g = \frac{h_T}{2h_M} - 1$$

is greater than or equal to the packing density of the particles in the specimen. This was found to be the case for all the samples studied.

Figures 3 and 4 show the growth of voids with time at 2100°C and 2500°C. The observed linearity between the average radius of gyration to the third power (\bar{R}_g^3) and HTt suggests that the mechanisms for pore growth in glassy carbon is one of vacancy diffusion from smaller to larger pores.

Despite the fact that the same as-received material was used for each sample, the initial pore size predicted from the intercept of the line in Figure 3 (2100°C) is found to be much lower than that predicted

from Figure 4 (2500°C). This apparent discrepancy can be explained in terms of an irreversible volume expansion which occurs in heat treated glassy carbon. The density of a heat treated glassy carbon sample shows an initial decrease but quickly reaches a constant value at constant HTT. This permanent dimensional change depends on heating rate, temperature, and sample thickness.

Presently, there exists two explanations of the density loss phenomenon. Mehrotra et al.⁶ hypothesize the density decrease is due to the large difference in thermal expansion coefficients in the c and a directions of the glassy carbon matrix. This anisotropy leads to microcracking which irreversibly increases the internal pore size. Fischbach and Rorabaugh⁷ have proposed that the volume expansion occurs by the internal pressure exerted from the evolution of pyrolysis gases within the pores.

4. Conclusion

The average radius of gyration of the pores in glassy carbon raised to the third power was found to be linearly related to the heat treatment time. The proposed mechanism is vacancy diffusion, such that large pores grow at the expense of smaller pores.

ACKNOWLEDGMENT

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Figure Captions

Fig. 1. Schematic of small angle X-ray scattering apparatus.

Fig. 2. Typical $h^2 I(h)$ vs. h plot showing parameters h_M and h_T .

Fig. 3. Pore coarsening at 2100°C.

Fig. 4. Pore coarsening at 2500°C.

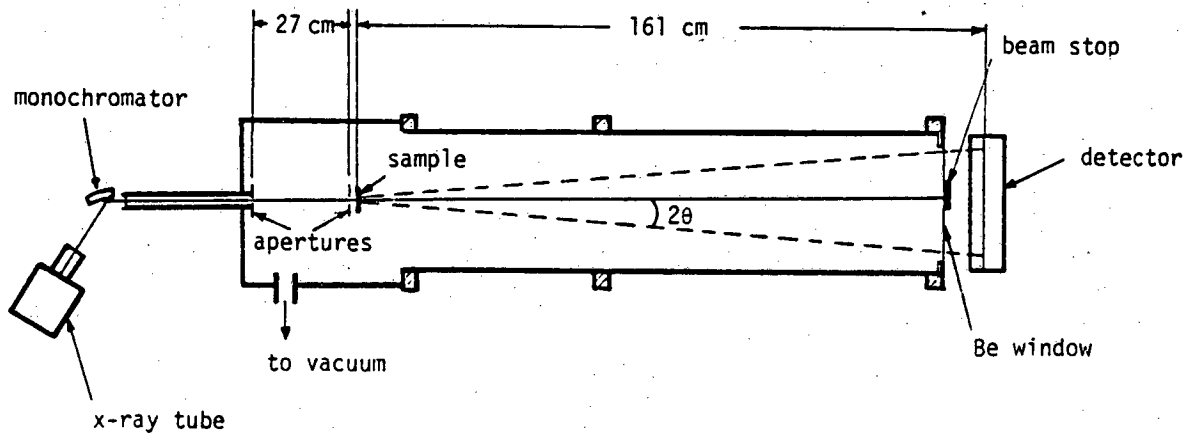


Fig. 1. Schematic diagram of the small-angle x-ray scattering system.

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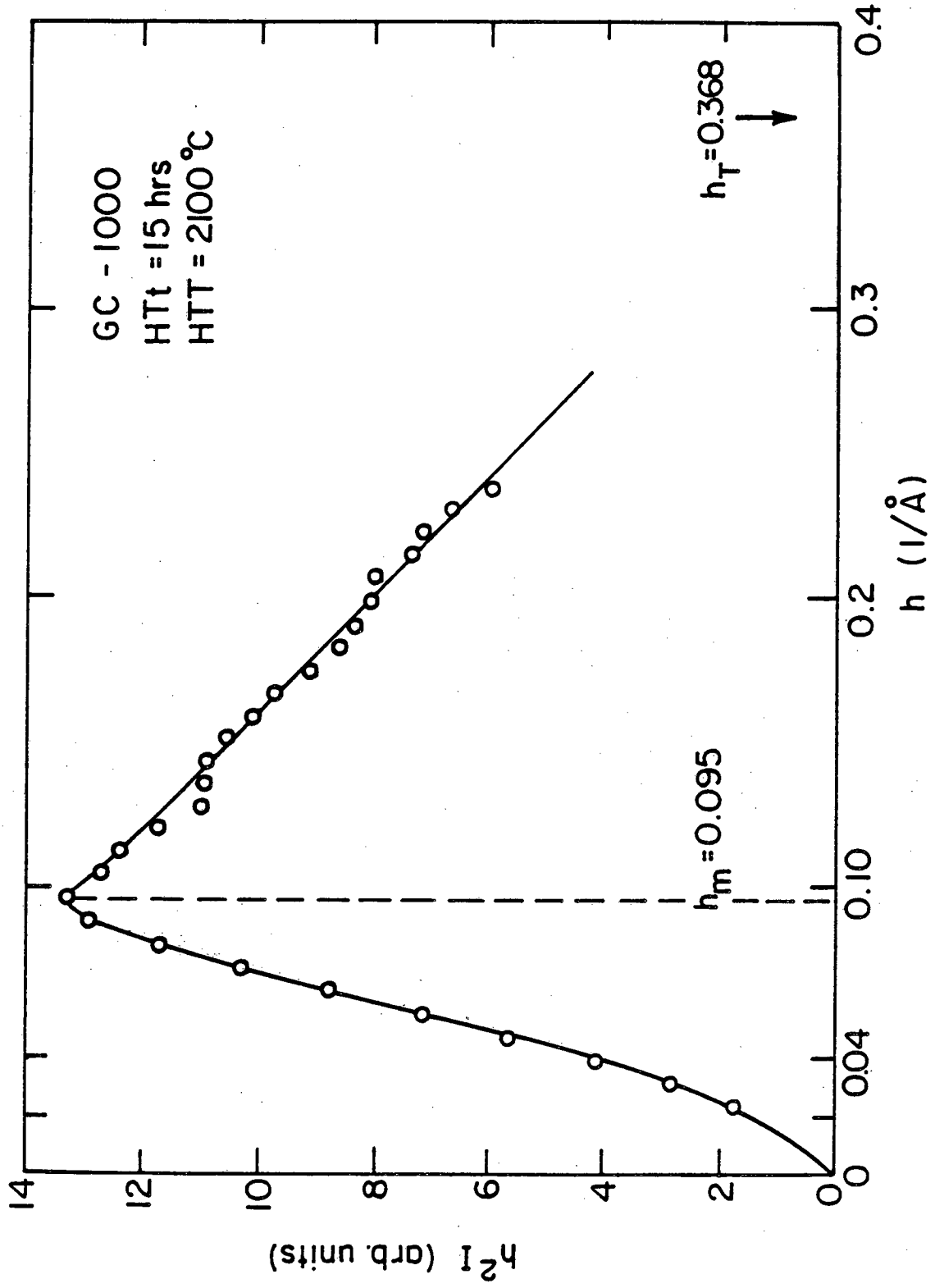


Fig. 2

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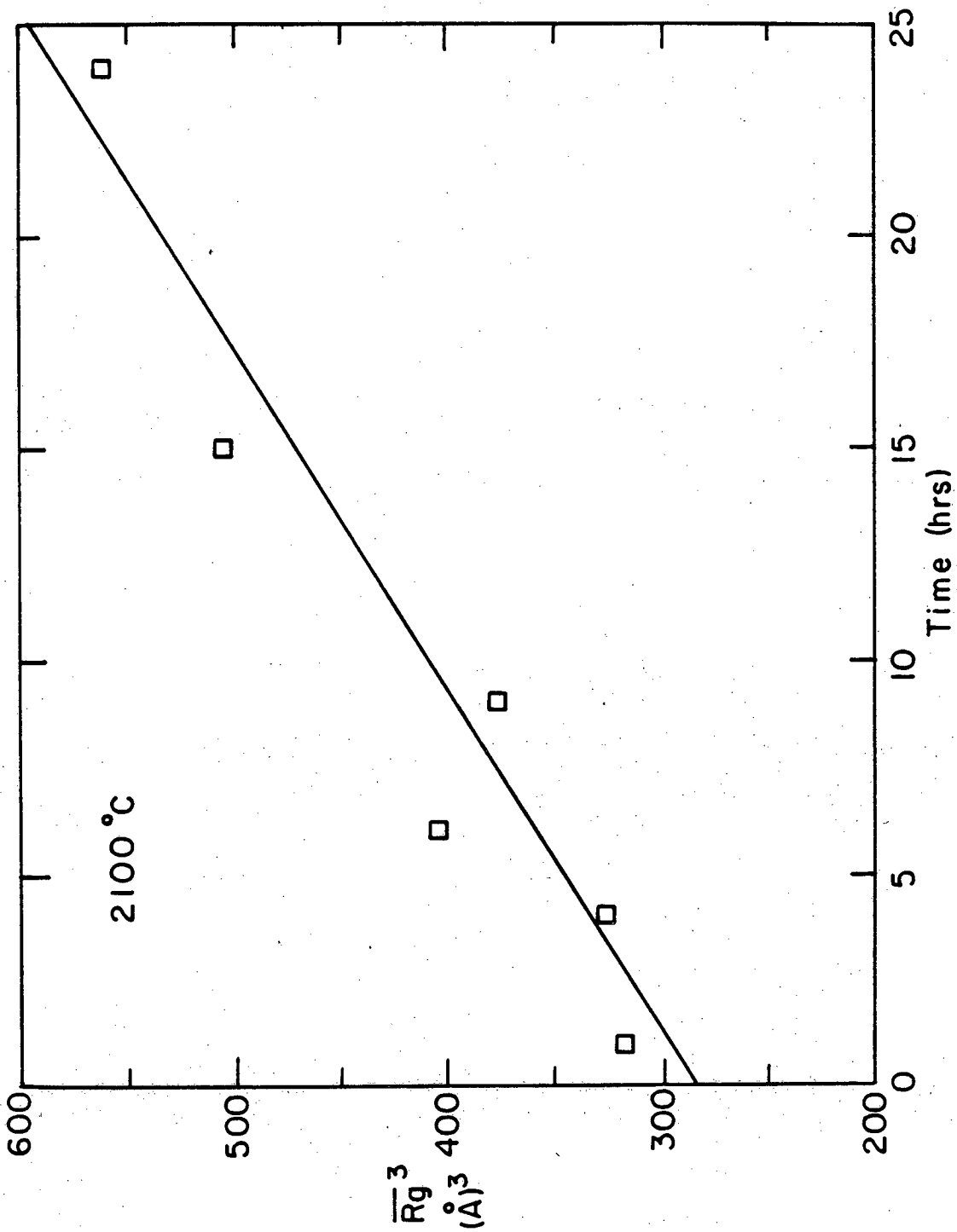


Fig. 3

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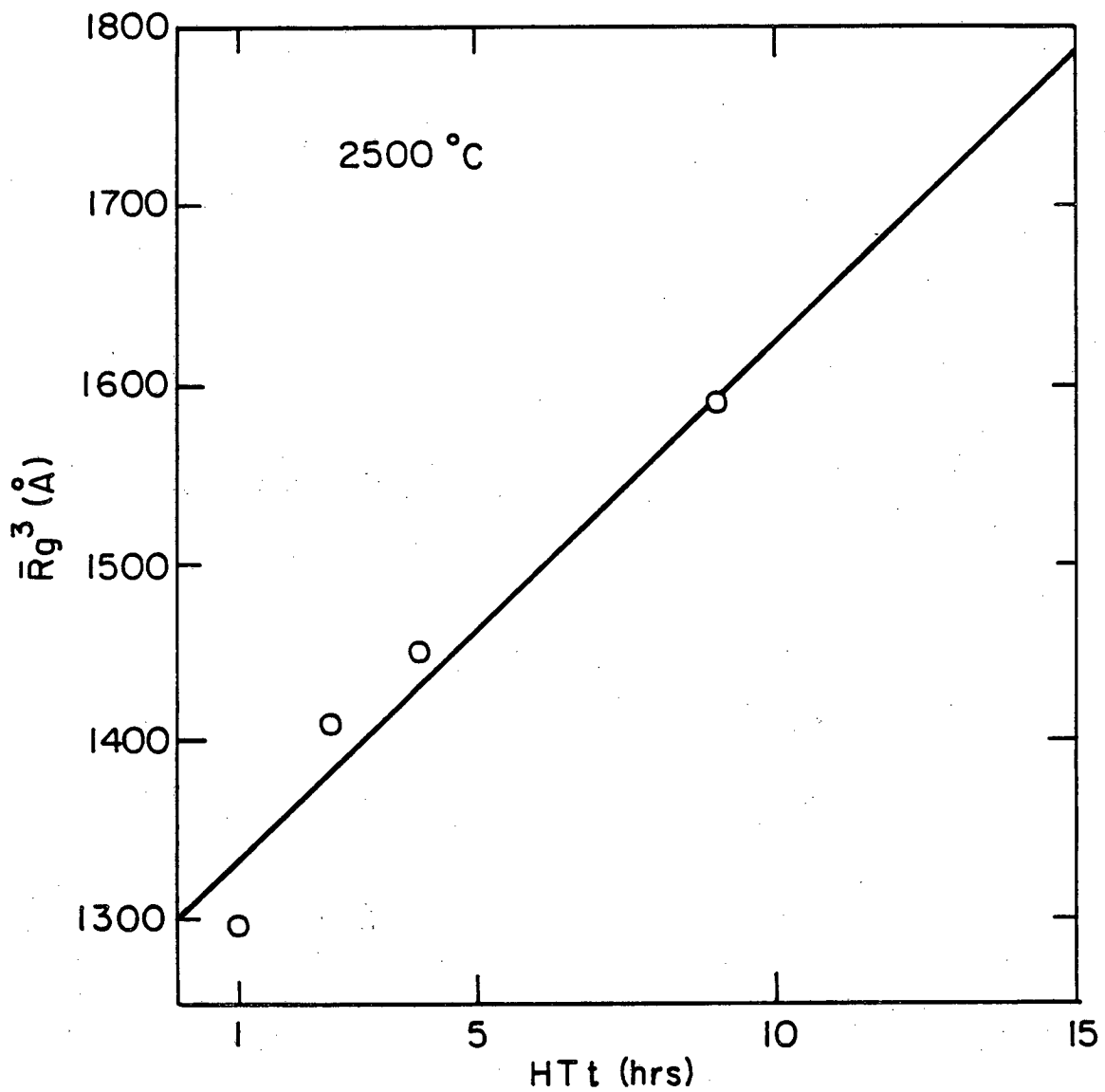


Fig. 4

XBL 82I-5010

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