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STRAIN-INDUCED PRECIPITATION OF THE Ni_3 (Al, Ti) PHASE IN A NICKEL-BASE SUPERALLOY

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SUMMARY

An investigation was conducted to determine the effect of strain on the $Ni_3(Al, Ti)$, γ', precipitation reaction in nickel-base superalloys. Specimens of a representative alloy of this type, Waspaloy, were exposed for 29 hours at 1400°F. At different points in the exposure cycle specimens were strained 2 percent in tension. Thin films for transmission electron microscopy were prepared from these samples. The particle sizes of the γ' phase present in each of the thin films were measured and distribution curves fitted to the data. Comparison of the γ' particle size distributions developed in the specimens as a function of the time at which they were strained relative to the distributions developed in unstrained specimens exposed for the same length of time showed conclusively that strain-induced precipitation of the γ' phase occurred at 1400°F.

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INTRODUCTION

The elevated temperature strength of nickel-base heat-resistant alloys is primarily governed by the amount and dispersion of the precipitate phase, $Ni_3(Al, Ti)$. This phase, γ', is usually present in the alloys in the form of small randomly dispersed spherical particles. The number of these particles, their size and spacing, are usually considered to be the principal factors controlling the high temperature properties of nickel-base alloys.

This study was undertaken to determine whether the γ' phase is subject to strain-induced precipitation. Such precipitation, if it occurs, could cause a significant variation in the properties of the alloys in the vicinity of stress concentrations. Nickel-base alloys in sheet form are known to be quite sensitive to the presence of notches and stress concentrations when exposed under creep conditions. It is possible that strain-induced γ' precipitation might be a contributing cause of the observed notch sensitivity. Before any detailed study of the relations between strain-induced precipitation and notch sensitivity can be conducted it is necessary to establish as fact that strain-induced γ' precipitation occurs in Ti + Al hardened nickel-base alloys. The present study was carried out for that purpose.

EXPERIMENTAL MATERIAL AND PROCEDURES

Specimens of a nickel-base alloy were exposed at 1400°F for a constant time period. At different times during exposure the specimens were strained in tension. Thin films were prepared from these specimens as well as from specimens which were not strained during exposure. Comparisons were then made of the γ' particle size distributions present in the films as a function of the exposure cycle the specimen had received. These comparisons allowed determination of whether or not strain-induced precipitation of γ' had occurred during exposure.

Material

The commercial alloy used in this study, Waspaloy, had the following reported chemical composition (weight percent):

C	Si	Mn	Cr	Co	Mo	Ti
0.08	0.07	0.04	19.63	3.49	4.26	2.99

Al	Fe	S	B	Zr	Ni
1.40	2.3	0.07	0.0048	0.03	Balance

The Waspaloy was received in the form of 0.030-inch thick cold reduced sheet. Specimen blanks cut from the sheet were solution treated for 0.5-hour at 2050°F then air cooled. These blanks were aged for 20 hours at 1400°F and air cooled; they were then machined into finished tensile specimens (Fig. 1). All subsequent temperature and strain cycles were applied to the finished machined specimens.

Heat Treatments

As previously stated, the sheet material used in this study was aged for 20 hours at 1400°F. The specimens made from this sheet material were exposed for an additional 29 hours at 1400°F in order to develop the proper distribution of γ' particle sizes. During the latter portion of the exposure, the specimens were subjected to different conditions of stress and/or strain. These were as follows:

Sample A. Exposed 20 hours at 1400°F, A.C., strained 2 percent in 1 hour at 1400°F, A.C., exposed an additional 8 hours at 1400°F.
Sample B. Exposed 26.5 hours at 1400°F, A.C., strained 2 percent in 1 hour at 1400°F, A.C., exposed 1.5 hours at 1400°F.
Sample C. Exposed 29 hours at 1400°F.
Sample D. Exposed 29 hours at 1400°F under a stress of 40,000 psi.

Because Samples A and B were air cooled after each portion of the cycle and hence were not truly comparable with Sample C, which had been subjected to uninterrupted ageing, one additional sample was studied:

Sample E. Exposed 26.5 hours at 1400°F, strained 2 percent in 1 hour at 1400°F, exposed an additional 1.5 hours at 1400°F.

The choice of temperature and time of exposure was dependent upon the following factors:

1. For accuracy in particle size measurements, the γ' particles should be relatively large.
2. In order to distinguish between thermally- and strain-induced precipitation it is necessary to expose the specimens at a temperature which causes relatively rapid growth of the γ' phase.
3. Under conditions which cause rapid growth of the γ' phase, the distribution of particle sizes produced by strain will rapidly approach and merge with the distribution of γ' particles present prior to straining. It was therefore considered desirable to determine the distribution of γ' particle sizes shortly after straining of the specimens.
4. The γ' particle sizes have to be small relative to the thickness of the film in order to minimize the influence of the polishing characteristics of the film on the γ' distribution.

Experiments conducted with the alloy showed that ageing for 20 hours at 1400°F plus exposure for 29 hours at this temperature yielded the best combination of exposure conditions relative to the aforementioned limiting factors.

Thin Film Preparation

Samples for thinning were cut from standard strip tensile specimens (Fig. 1). The samples measured approximately 0.5-inch square by 0.025-inch thick. These specimens were mounted in wax and reduced in thickness to approximately 0.005-inch by grinding on wet silicon carbide papers down to 600 grit.

Further reduction in thickness was achieved by electropolishing using the Bollman technique (Ref. 3). The electrolyte was composed of 60 percent phosphoric acid and 40 percent sulphuric acid. Satisfactory polishing action resulted when an applied potential of 7.5 volts was used. An insulating lacquer (Microstop) was applied to the edges of the sample to prevent preferential dissolution in these areas during electropolishing. The electropolishing apparatus is shown in Figure 2. By varying the relative positions of the specimens and the pointed electrodes it was possible to control the amount of metal removed from various sections of the specimen. This technique was particularly useful in eliminating the slightly rounded surface produced by mechanical polishing. Electropolishing was continued until a hole developed in the specimen, at which stage the lacquer was dissolved in acetone. The specimen edges, including the hole, were then relacquered and the process continued until the film thickness was less than 0.001-inch.

Final thinning before microscopic examination was accomplished by the Dupres method (Ref. 4). This technique involved welding a small section (approximately 0.2 square inches) of the thinned metal between stainless steel washers; these washers not only supported the film but also produced a uniform current density during the final electropolishing. Polishing was discontinued as soon as a hole developed in the film. The film was then stored under toluene until it was examined in the electron microscope.

Metallography

The thin films were studied by transmission electron microscopy using a JEM microscope operated at 100KV.

Particle size distributions were determined from 8-inch by 10-inch enlargements (total magnification of approximately 2.5×10^5) of electron micrographs obtained from several areas of each film. Between 3 and 5 individual determinations of γ' particle size distributions were made from each film. In each case the diameters of about 250 particles were measured to the nearest 0.5 mm. The individual enlargements used for the size determinations were not all at identical magnifications. Consequently the actual γ' particle sizes which fell into any given 0.5 mm. subdivision varied with magnification. Since the frequency of occurrence of any particular size particle was affected by the size interval used to establish the distribution, the results were normalized by the inclusion of a magnification factor. This permitted direct comparison of the various distributions.

Curves representing the distribution of particle sizes as a function of frequency of occurrence were fitted through the data points. As verification for the profiles obtained in this manner a computer was used to derive the distribution curves obtained from specimens C and E. Polynomials of the type

$$a + bx + cx^2 + dx^3 + \ . \ . \ . \ . \ .$$

up to degree ten were fitted to the data. The selection of the most appropriate curve was made by the determination of the polynomial which minimized the residual sum of squares.

RESULTS

The γ' particle size distributions obtained from the exposed specimens are presented in Figures 3 to 7. These graphs show a wide variation in the profile of the distributions as a function of:

1. Whether or not the specimens were strained during the exposure for 29 hours

and

2. The time at which the specimens were strained during the exposure cycle.

The γ' particle size distribution obtained from Sample A (strained 2 percent 8 hours prior to completion of the 29 hour exposure at 1400°F) is shown in Figure 3. As is evident from examination of this graph, the major peak in the distribution profile occurred at a particle size of about 320A. A second peak occurred at a γ' particle size of approximately 250A. From the massed results it is questionable whether, in fact, the second peak actually exists. The individual determinations do, however, indicate its existence.

The results obtained from Sample B (strained 2 percent 1.5 hours before the end of the exposure cycle) distinctly show the presence of two different major peaks in the distribution curve (Fig. 4). Again the more pronounced peak in the distribution profile occurred at a γ' particle size of approximately 320A. In this specimen, however, the position of the secondary peak was shifted to a smaller particle size, about 150A.

Figure 5 shows the γ' particle size distribution measured in Sample C which was not strained at any time during the 29 hour exposure at 1400°F. This curve shows only one peak, unlike the curves for Samples A and B. The position of this peak, approximately 320A, corresponded very closely to that of the major peaks found in both Samples A and B.

Considerable scatter existed in the results from Sample D. This sample was subjected to a stress of 40,000 psi during the exposure cycle. The distribution profile of γ' particle sizes (Fig. 6) tended to be somewhat narrower and flatter than that exhibited by Sample C, which was exposed unstressed for the same time period. The data indicate that this specimen had a higher fraction of small particles than did Sample C.

Figure 7 shows the distribution curve measured from Sample E. The exposure cycle to which this sample was subjected differed only slightly from that of Sample B. Sample B was air cooled just prior to and just after straining while Sample E was held at 1400°F throughout the exposure. The time at which both specimens were strained 2 percent was the same, however. The distribution curve from Sample E was very similar to that of Sample B, in both cases major peaks at smaller particle sizes; 150A for Sample B and 175A for Sample E.

The computer-fitted distribution curves for Samples C and E are shown in Figure 8. The polynomial equations which best fitted the data were of the eighth degree. These curves, like those previously presented in Figures 5 and 7, show a distinct difference in the γ' particle size distribution between the two specimens. The distribution profile from Sample C (unstressed exposure) showed only one peak while that from Sample E (strained 2 percent 1.5 hours before the end of the exposure cycle) showed two distinct peaks.

DISCUSSION

Thermal ageing would be expected to produce a unimodal distribution of γ' particle sizes. Furthermore if strain causes an additional precipitation of γ' over and above that occurring during thermal ageing, it would be expected that a bimodal distribution of particle sizes would be developed in specimens strained at a proper time during the ageing cycle. The distribution peak which occurred at the smaller particle sizes would be the result of strain-induced precipitation while the second peak would be due to thermally-induced precipitation.

The above reasoning has been employed in the evaluation of whether or not strain-induced precipitation of γ' occurs in nickel-base alloys. Waspaloy specimens were subjected to slightly different thermal and/or strain cycles and the resultant γ' particle size distributions compared. These specimens were treated so that two (A and B) were strained at fixed points in the ageing sequence while a third (C) was not strained during a similar ageing cycle. As a consequence, any differences in the profiles of the γ' particle size distributions in these specimens should be due to strain. Comparison of the distribution curves (Figs. 3, 4 and 5) does in fact indicate a "strain" effect, since the distributions differed quite considerably. The strained specimens exhibited a bimodal distribution of particle sizes while the unstrained specimen showed a unimodal distribution.

The exposure conditions of Samples A and B were not truly identical to that of Sample C, however. This raised a question as to the validity of the interpretation of the results. Sample C was subjected to uninterrupted ageing at 1400°F while Samples A and B were air cooled to room temperature prior to and subsequent to the straining operation. Therefore it was possible that the second distribution peak evident at the smaller particle sizes in Figures 3 and 4 may have been due to cooling from the exposure temperature and not due to strain. Particle size data from a fourth specimen, E, confirmed that the second peak evident in Figures 3 and 4 was due to strain and not due to precipitation on cooling from the ageing temperature. This sample was processed in the same manner as Sample B except that it was held at 1400°F throughout the exposure cycle. The γ' particle size distribution curve obtained from the specimen (Fig. 7) contained the second peak associated with strain-induced precipitation of the γ' phase.

The similarity of the particle size distributions from Samples B and E (Figs. 4 and 7) might lead to the conclusion that cooling from the exposure temperature does not influence the state of the γ' phase. This would probably be incorrect. Other work conducted at the University of Michigan had indicated that the state of the γ' phase is very sensitive to cooling rate (Ref. 5) as shown by differential density measurements. It is true, however, that the techniques employed in the present study are probably not sufficiently sensitive to detect minor changes in γ' state such as might result between specimens subjected to slight differences in exposure cycles. There is no doubt, though, that the procedures used in this study were sufficiently sensitive to detect the presence of strain-induced γ' precipitation.

The conclusions drawn by visual comparison of the particle size distributions obtained from Samples C and E (Figs. 5 and 7) were checked by a curve-fitting method utilizing a computer to minimize bias. The distribu-

tions obtained (Fig. 8) were similar to those shown in Figures 5 and 7. This should be taken as further verification of the occurrence of strain-induced γ' precipitation.

The results obtained from Sample D (Fig. 6) which was exposed under a stress of 40,000 psi also confirm the existence of strain-induced precipitation of the γ' phase. The larger number of small particles and the smaller number of large particles in the stressed specimen as compared to the unstressed specimen (Sample C) indicates that strain-induced γ' precipitation occurred during stressed exposure.

The relation between the particle size distributions obtained from the thin sections and the true distribution will be dependent on the nature of the polishing action and the thickness of the film. From replicas of the electrolytically polished surface it was evident that fairly uniform dissolution of the γ' phase and the matrix had occurred. The appearance of the thin films did, however, indicate that the γ' was removed at a slightly higher rate than the matrix. The distributions can therefore be expected to be shifted only slightly by this effect; the greatest influence occurring at the larger particle sizes. Since in each case the distribution of larger particles was approximately the same, any slight error introduced by the polishing characteristics of the film should not affect conclusions derived from comparison of the distribution curves.

Decreasing the film thickness will shift the distributions towards finer particles sizes. Since, however, the γ' particle sizes were small compared with the film thickness very little influence of this effect was observed, as is evident by the near constancy of the major peak (Fig. 9). Mathematically it can be shown not only that this effect is small within the range of film thicknesses used but also that it is not possible to produce a second peak in the distribution curve by variation in film thickness.

Since small particles could have been hidden under large particles it is probable that fewer of the small particles were counted in the electron micrographs than were actually present in the films. If this is correct then not only would the number of small particles be increased in each case but also the absolute difference in the particle size distributions between the strained and unstrained samples would be magnified. With the exception of Sample D, relatively few particles had diameters near the lower limits of the size range. As a consequence a variation of a few particles counted in this region could have an appreciable effect on the results. If small-sized particles were hidden in the micrographs, the result would be to reduce the magnitude of the distribution peak caused by strain-induced precipitation.

In some cases the apparent scatter of the massed results from a single specimen made it difficult to decide whether a true second peak existed in the particle size distribution curve. The individual determinations of particle size profile, however, strongly indicated the occurrence of a second peak and for this reason the curves through the massed data were drawn to show the existence of the strain-induced precipitate. Independent of the shape of the curves, the distinct increase in the number of small particles in the strained material is sufficient proof of the occurrence of strain-induced γ' precipitation.

CONCLUSION

Strain has been shown to affect the γ' reaction at 1400°F in Waspaloy, a nickel-base precipitation hardened alloy. The γ' particle size distribution profile was dependent on both the thermal and strain history. Comparison of γ' particle size distributions in samples subjected to similar thermal cycles with and without stress has shown that strain-induced precipitation of γ' occurred in this alloy.

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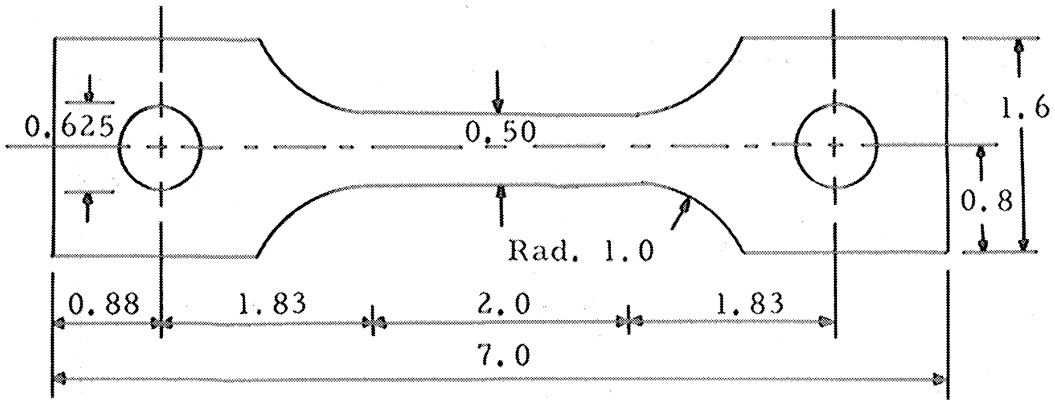

Figure 1. Smooth Tensile Specimen (dimensions in inches).

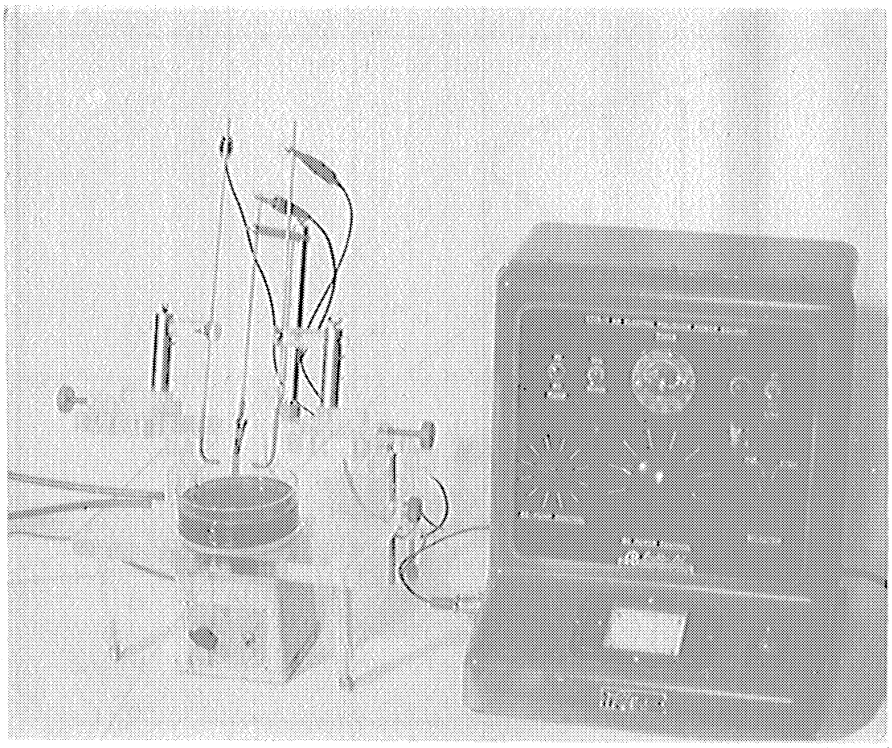

Figure 2. Fisher Apparatus and Power Source Used for Electropolishing.

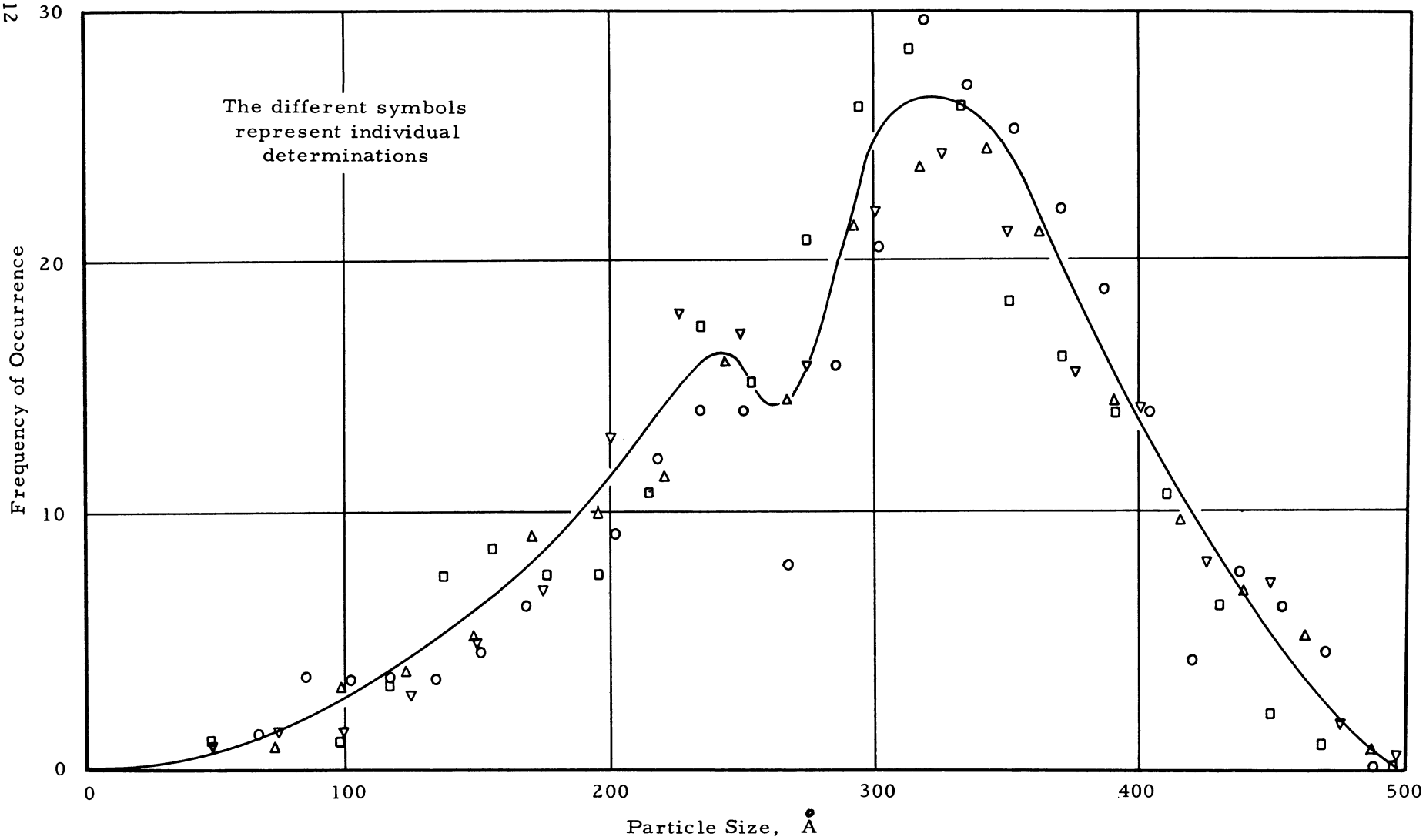

Figure 3. Distribution of γ' Particle Sizes of Sample A. Exposed 20 hours at 1400°F, A.C., strained 2 percent in 1 hour at 1400°F, A.C., exposed an additional 8 hours at 1400°F.

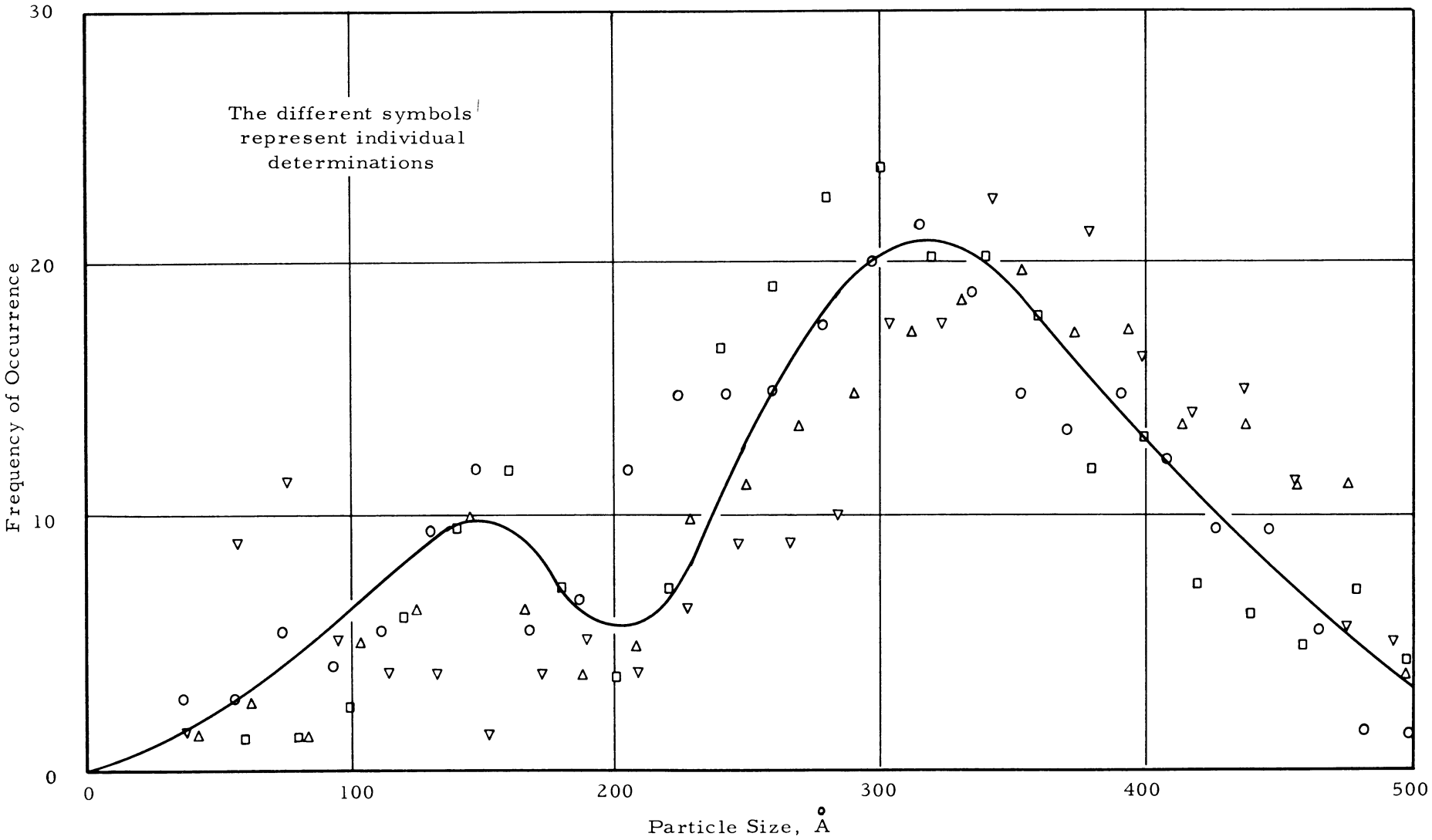

Figure 4. Distribution of γ' Particle Sizes of Sample B. Exposed 26.5 hours at 1400°F, A.C., strained 2 percent in 1 hour at 1400°F, A.C., exposed an additional 1.5 hours at 1400°F.

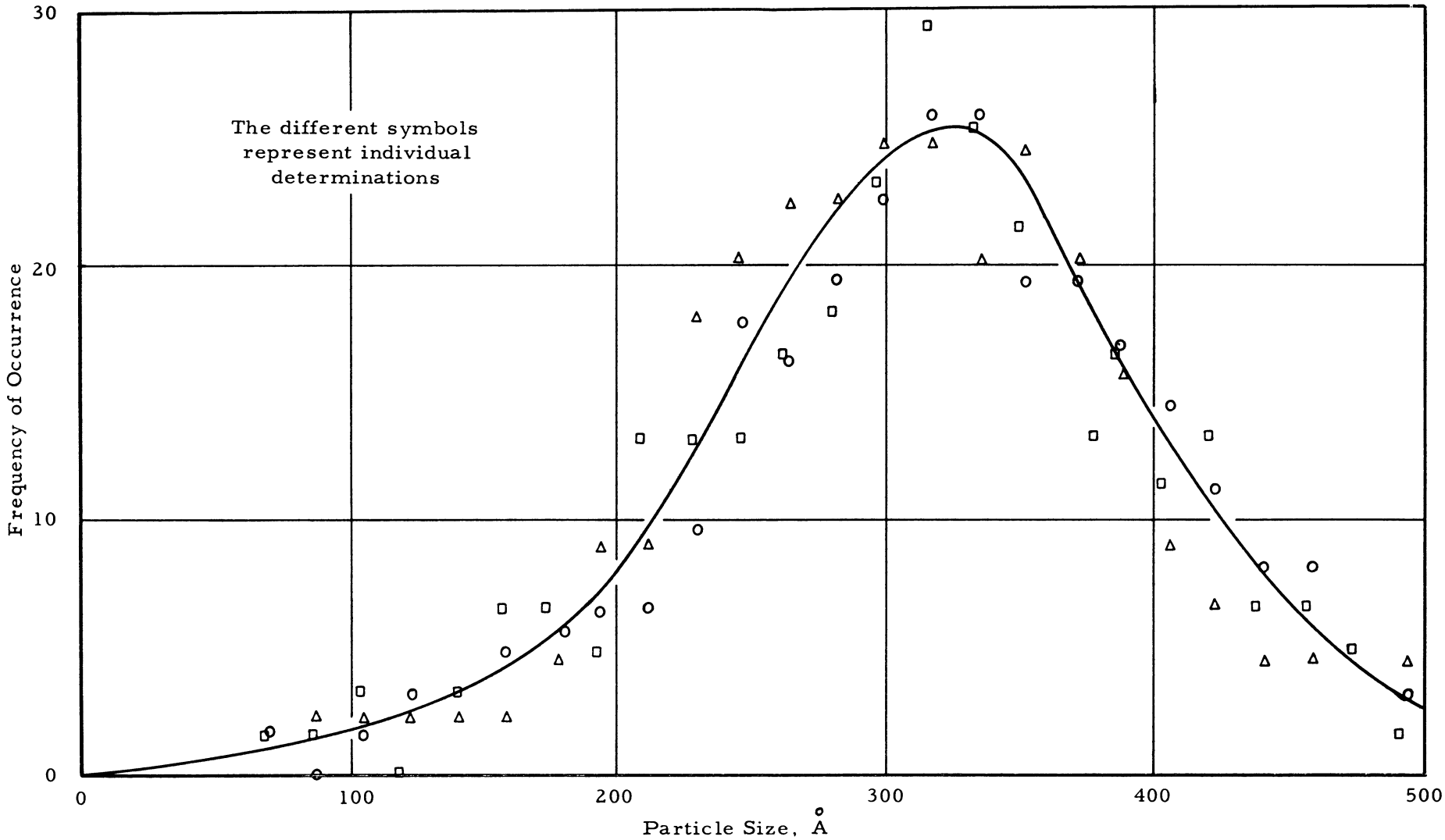

Figure 5. Distribution of γ' Particle Sizes of Sample C. Exposed 29 hours at 1400°F.

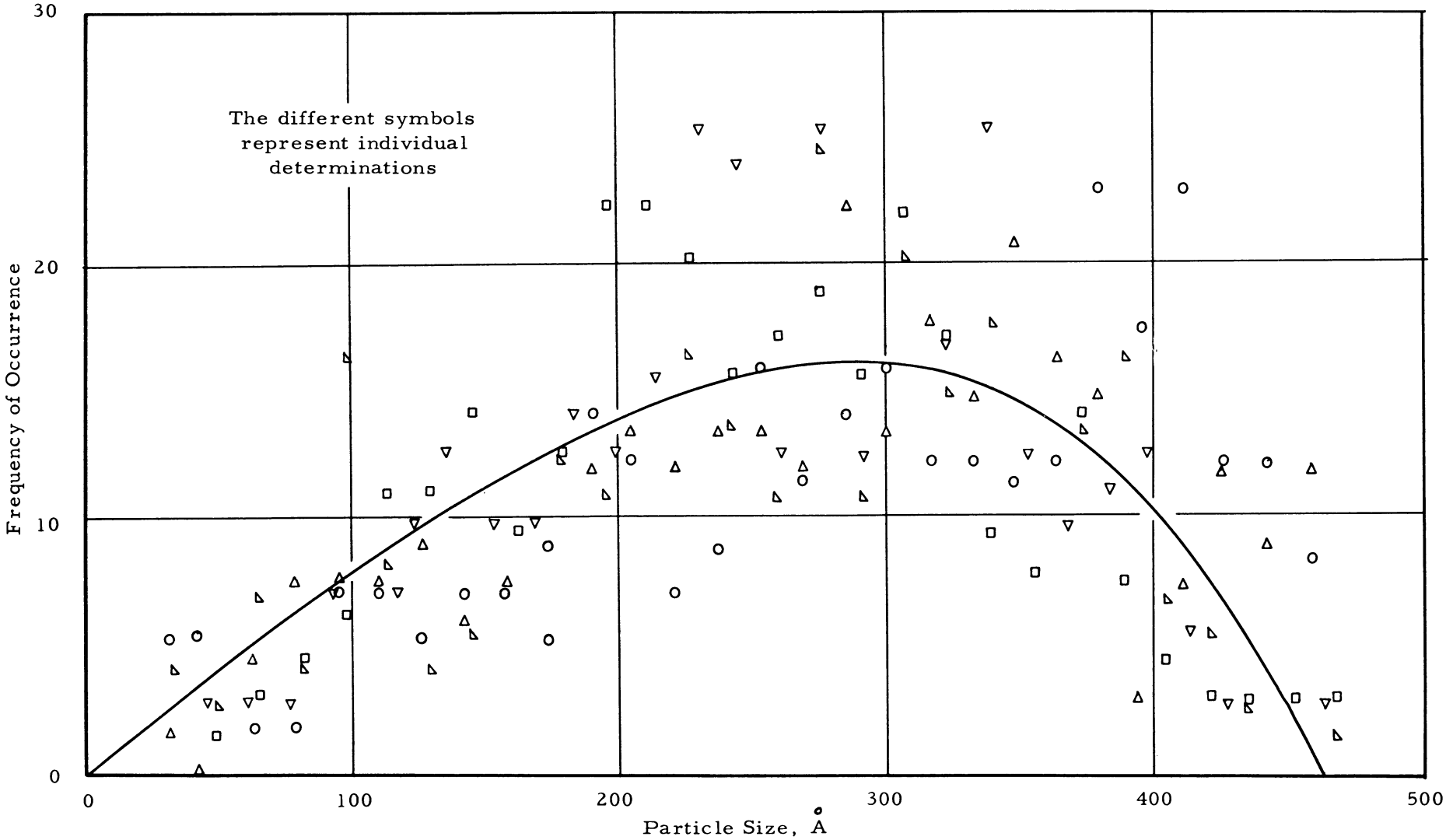

Figure 6. Distribution of γ' Particle Sizes of Sample D. Exposed 29 hours at 1400°F under stress of 40,000 psi.

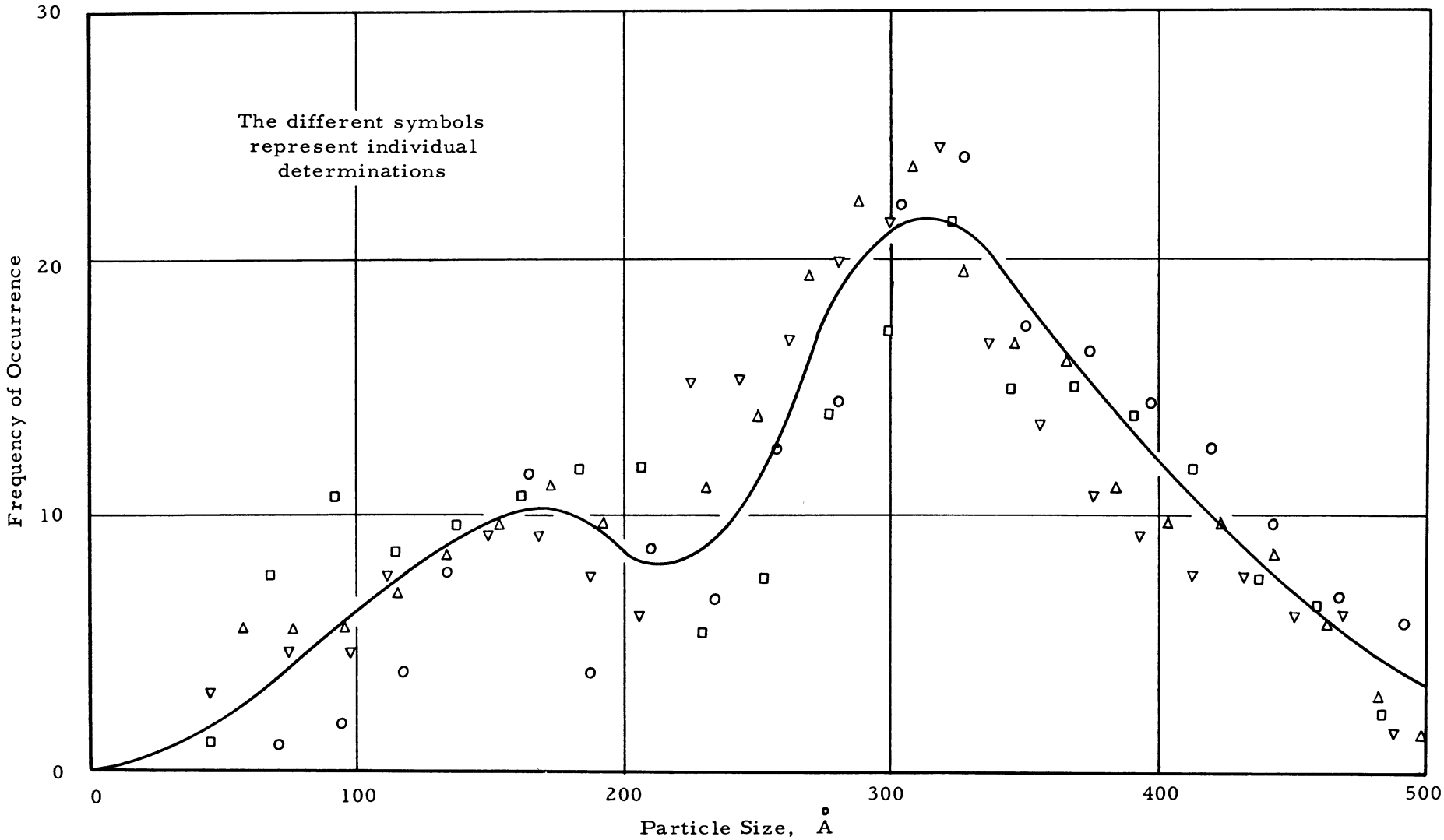

Figure 7. Distribution of γ' Particle Sizes of Sample E. Exposed 26.5 hours at 1400°F, strained 2 percent in 1 hour at 1400°F, exposed an additional 1.5 hours at 1400°F.

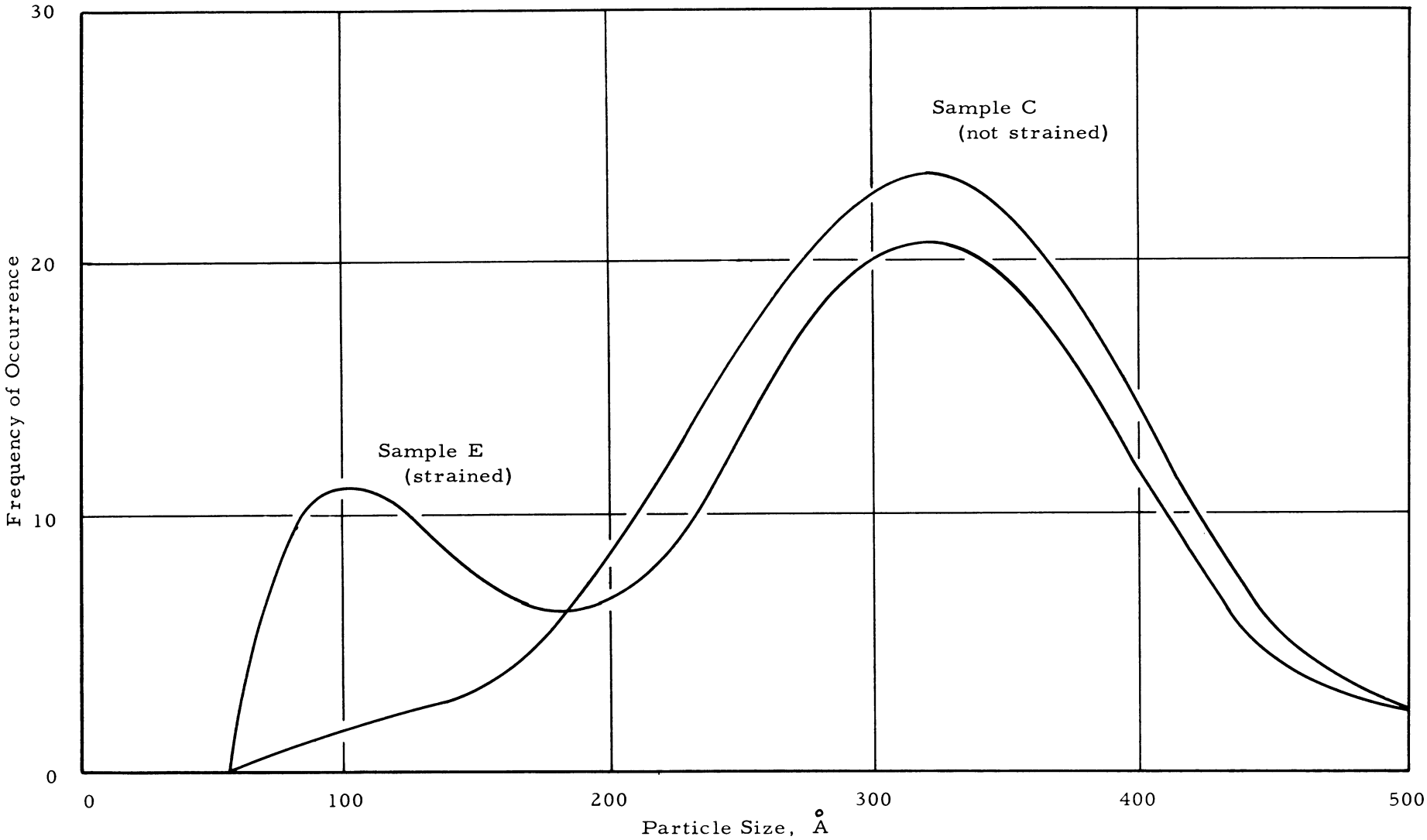

Figure 8. Computer-Fitted Curves to the γ' Particle Size Distributions of Samples C and E.

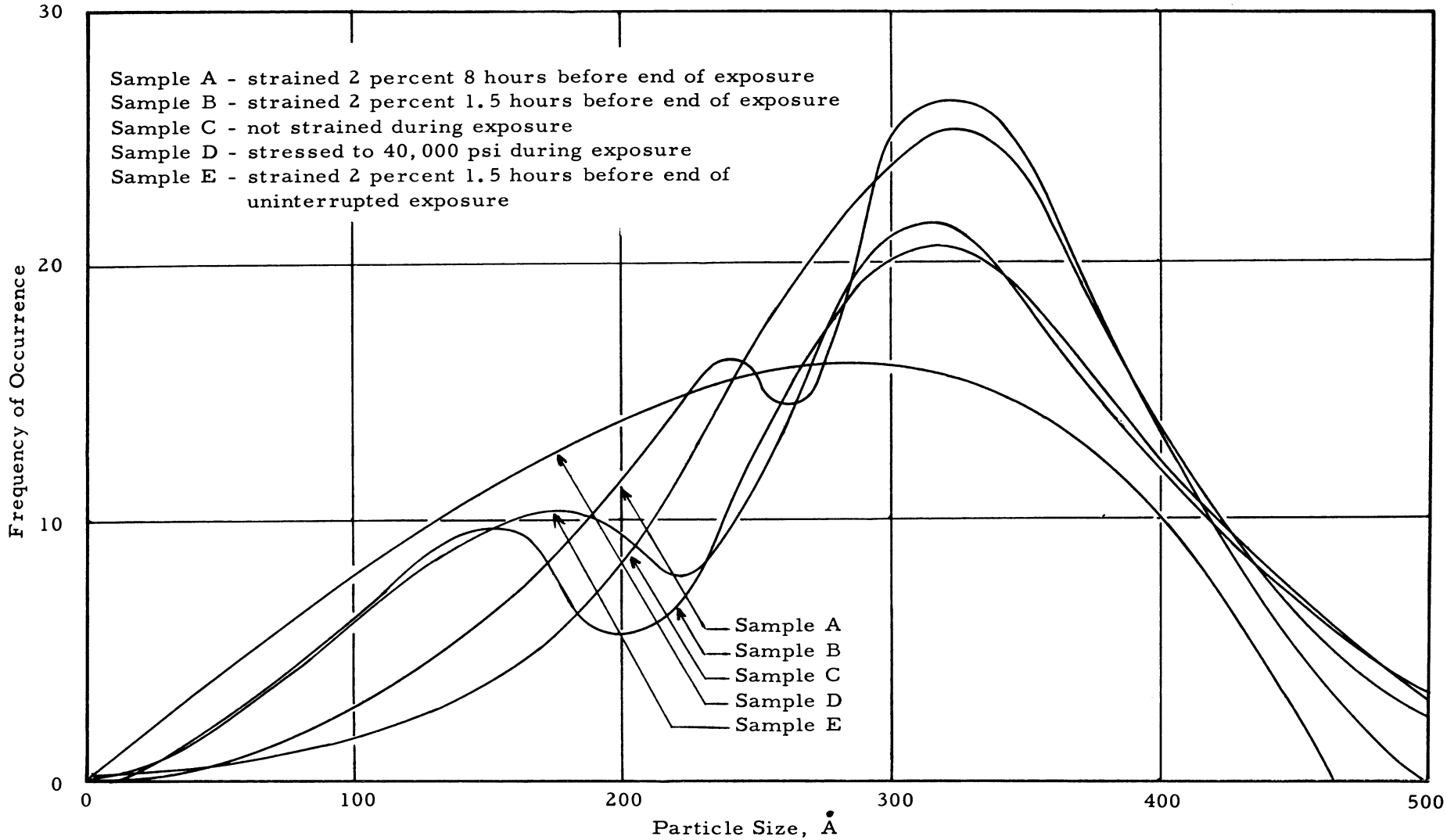

Figure 9. Distribution of γ' Particle Sizes of Samples A, B, C, D and E.