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QUARTERLY PROGRESS REPORT NO. 4

AN INVESTIGATION OF INTERGRANULAR CORROSION IN STAINLESS STEEL

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INTRODUCTION

This research project has been undertaken under the sponsorship of the Wright Air Development Center of the U. S. Air Force. Its objectives are fourfold:

(a) to determine the effect of temperatures between 1600° and 2000°F on intergranular oxidation or corrosion;

(b) to examine the effects of alloy composition on intergranular oxidation or corrosion;

(c) to determine the nature of the penetrating material in areas of intergranular attack; and

(d) to devise methods of reducing or eliminating intergranular penetration.

MATERIAL

The materials used during this phase of the project were two new type 310 alloy heats, the type 310 heats used in the previous year, Inconel, and three chromel alloys. Of the two new type 310 heats, the 310 RA, obtained commercially as 1/2 x 1 x 12-inch hot-rolled plate, was rolled as described in the experimental procedure for texture studies. Specimens of vacuum-melted 310 stock which will be obtained from WADC will be used for stressed-oxidation studies as well as chromel A. All the alloys have been tested for unstressed oxidation in the same manner as in previous studies (WADC TR 54-120). The 310 type stainless described in the previous report is being used for electron-diffraction studies.

EQUIPMENT

In addition to the equipment used in the previous year, three stress-oxidation units (Fig. 1A) have been constructed. Since the loads needed for the low stresses used are small, a direct-loading instrument is desirable. This type of loading, in addition to making the unit simpler and more easily constructed, gives a more accurate control of stress and results in less eccentricity than a beam-loaded unit. A test of eccentricity using 1/8 x 1 x 18-inch flat-ground stock made into a standard specimen with two SR-4-A1B strain gages offset on each side of the specimen, gave a stress-strain curve with the same slope for each gage position. The stock to be oxidized was found to be slightly warped, making significant stress-strain measurements impossible and necessitating the use of the ground stock for calibration and eccentricity checks. The elevated temperature of testing will undoubtedly eliminate this warping by plastic flow, making the suspension mechanism the governing factor in uniformity of stress distribution.

The furnace windings (Fig. 1A) consist of two sections of No. 12 Chromel wire. More coils are used in the bottom half of the furnace than in the top to correct for draft effects. Separate coils allow for the insertion of shunts to aid in obtaining temperature distribution. A temperature survey shows the two-inch oxidation zone to be essentially flat ($\pm$3°F).

Rough creep measurements can be made by means of the dial indicator (Fig. 1A). The location of the dial on the center line of suspension eliminates the possibility of introducing eccentricity.

PROCEDURE

Specimen Preparation

Stressed-oxidation specimens are prepared as standard sheet specimens as illustrated in Fig. 1B. Special attention is paid to keeping foreign materials and scratches from the portion of the specimen to be measured for intergranular penetration. The material in the reduced section is then sectioned and mounted as in previous intergranular-oxidation measurements.

Texture specimens were prepared by cold rolling the 310 RA alloy 97-98 percent and shearing the material into standard 1/2 x 1-inch oxidation specimens. Control samples to indicate the oxidation in the specimens without a texture were prepared by curring the 1/2-inch stock lengthwise and cold cutting about 10 percent to produce a material with a surface similar to the texture specimen, then cutting the material into standard sizes as indicated above. Both samples were given a 2000°F anneal for four and one half hours in dried argon (dewpoint <-60°F), in an attempt to develop an annealing texture in the highly reduced material. Penetrations were measured after bending and mounting as previously described.

Test Procedure

For unstressed oxidation, the texture, Inconel, vacuum-melted, and chromel specimens were oxidized at temperatures of 1600°, 1800°, 1900°, and 2000°F for periods of 100 hours. The Inconel was also run for 10 and 30 hours. The dewpoint of the air passing over the material was <-40°F and the velocity was 30 ft/sec.

The stress-oxidation equipment is completed and tests are in progress on Chromel A.

ELECTRON DIFFRACTION

Procedure

In accordance with the third overall objective of the project, a program has been initiated which has as its purpose the determination of the composition of the intergranular compounds occurring in the steels under investigation. The method selected for this work was the reflection electron-diffraction technique, which is admirably suited to the study of solid surface layers. The procedure which is being followed on previously oxidized specimens consists of the following steps:

1. As much external scale as possible is removed by scraping without actually disturbing the metal surface itself. The scale thus collected is powdered and identified by X-ray diffraction using the Debye-Scherrer technique.

2. Thickness measurements are made on the specimen at two points on the surface. One of these points will later be subject to etching action, while the other will be protected from etching by Scotch tape, and will thus serve as a reference standard for later thickness measurements. These measurements are made on a Pratt and Whitney supermicrometer accurate to 0.0001 in. The assumption is made that the etching attack on the exposed underside of the specimen is essentially uniform.

3. An electron-diffraction pattern is made of the specimen surface.

4. The specimen is electrolytically etched for from 15 to 30 sec in a mixture of 10 percent perchloric acid and 90 percent glacial acetic acid at a temperature of 15°C and a current density of 6 amp/sq. in. This etching treatment, developed by a group working on the identification of minor phases in heat-resistant alloys*, removes the metal without disturbing the intergranular compounds. The specimen is rinsed in tap water, triply distilled water, and three acetone-benzine rinses, after which it is drained dry.

5. An electron-diffraction pattern is made of the exposed compounds.

6. The exposed compounds are brushed off the surface using a rotary wire brush on a hand power tool. The brush does not damage the surface, and, in addition, is much less likely to cause contamination than is an abrasive compound. The Scotch tape covering the unetched portion of the specimen is removed.

7. Thickness measurements are made of the etched and unetched portions of the specimen as described in step 2. By appropriate subtractions, the amount of metal removed in the etching operation can be determined. A fresh piece of Scotch tape is then applied to the unetched portion of the surface, and steps 4 through 7 are repeated as many times as necessary to reach the depth in the specimen where diffraction patterns from the intergranular compounds no longer appear.

The electron diffraction procedure outlined above will make it possible to present results showing the changes, if any, in the overall composition of the intergranular compounds resulting from oxidation as a function of their depth below the metal-oxide interface. For this program, six heats were selected from the ones studied in the 1953 oxidation runs. These heats were: type 309 + Nb and type 310, heats 64177, 64270, X11306, X11338, and X27258. Only an oxidation time of 100 hr is being considered in the present studies. In the case of the last three above-mentioned heats, specimens oxidized at 1600°, 1700°, 1800°, 1900°, and 2000°F are being examined. In the case of the other heats, no 2000°F specimens are being examined.

Metallography

The metallographic procedure is the same as that used previously with the addition of a final polish. The former objection to a final polish after the three-micron diamond was that the nap of a wet final wheel pulled some of the inclusions and oxide material. By using a thick paste of Linde A

*Brockway, L. O. and Bigelow, W.C., "Development of Procedures for the Identification of Minor Phases in Heat Resistant Alloys by Electron Diffraction," Annual Summary Report on Project 2020, Eng. Res. Inst., Univ. of Mich., to Flight Research Laboratory (WCRRL), WADC, 15 January 1953.

(levigated alumina) on the polishing wheel and thus avoiding the nap effect, an acceptable final polish is obtained. This method was developed during the final weeks of the previous year's experimental program. Each specimen is examined at 1000 diameters using a Bausch and Lomb research metallograph under bright field and polarized light.

Penetration Measurements

Penetration measurements are made in the same manner as in the previous work.

X-Ray Analysis of Scale

X-ray analysis of scale is being continued as in the previous work.

RESULTS AND DISCUSSION

Electron and X-Ray Diffraction

A good deal of the experimental work on the electron and X-ray diffraction studies has been accomplished, but at the present time the results have not been properly evaluated. Therefore, the results of these studies will not be presented at this time.

Penetration Measurements

Figures 2 through 7 give the frequency-vs-depth curves for the Inconel, type 310 texture, type 310 non-texture, and vacuum-melted stock. These curves follow the decay type as noted in report WADC TR 54-120. Figures 8 through 12 are the penetration-vs-frequency and penetration-vs-mean depth curves for these alloys. The method of determining these parameters is described in the above-mentioned report.

Inconel

It can be seen from Fig. 8 that in the Inconel alloy a considerable number of penetrations are formed at the higher temperatures. However, these penetrations are small (Figs. 2 and 9). It is to be emphasized that the smallest mean depth which is reported is 0.00032 in. and corresponds to fissures which fall within the first grid on the number 6 grain size eyepiece used for measurement. A complete discussion of the significance of the mean depth measurement appears in WADC TR 54-120. Some of these fissures at the higher temperatures may be attributed to artifacts since the surface is considerably roughened at these temperatures. The penetrated level is slightly lower than the best 310 alloy previously tested. Since the amount of scale removed during quenching is small and there is very little scale visible microscopically, the lower intergranular penetration level is probably due to a slow oxidation rate.

The length of time of oxidation has little effect on the frequency graph (Fig. 8) or mean depth curve (Fig. 9) in the Inconel alloy. This effect was noted in previous experiments on type 310 alloys (WADC TR 54-120).

Preferred Orientation

The oxidized 97-percent-reduced and annealed material shows a greater number of penetrations (Fig. 10) than the as-received samples. These fissures are not as deep as found in the unreduced material, as can be seen from the mean-depth graph (Fig. 11). The texture treatment changed the physical appearance of the external scale as well as the penetration count. Texture specimens exhibited an adherent reddish-brown scale which was not removed upon quenching or by gentle scraping, while the scales on the non-texture specimens were grey-black and loosely adherent. The fact that the texture specimens were thinner than the 10-percent-reduced stock may account for some of this variation, due to differences in cooling rate. X-ray forward-reflection photographs showed a fair degree of preferred orientation in the texture specimens.

Vacuum-Melted Stock

The vacuum-melted material reveals a smaller number of penetrations and a smaller mean penetration depth than any alloy tested and measured to date. At the temperatures below 2000°F the fissures are all within the first grid while the 2000°F material indicated a slightly deeper mean depth. It is possible that the volume oxidation rate is high, which would account for the low penetration depths. Weight-grain equipment is being assembled to determine this. Chemical analysis and the X-ray data in process is expected to aid in the explanation of this increased penetration resistance.

Chromel

The chromel alloys have been oxidized in the unstressed condition and are in the process of being counted for fissure depths.

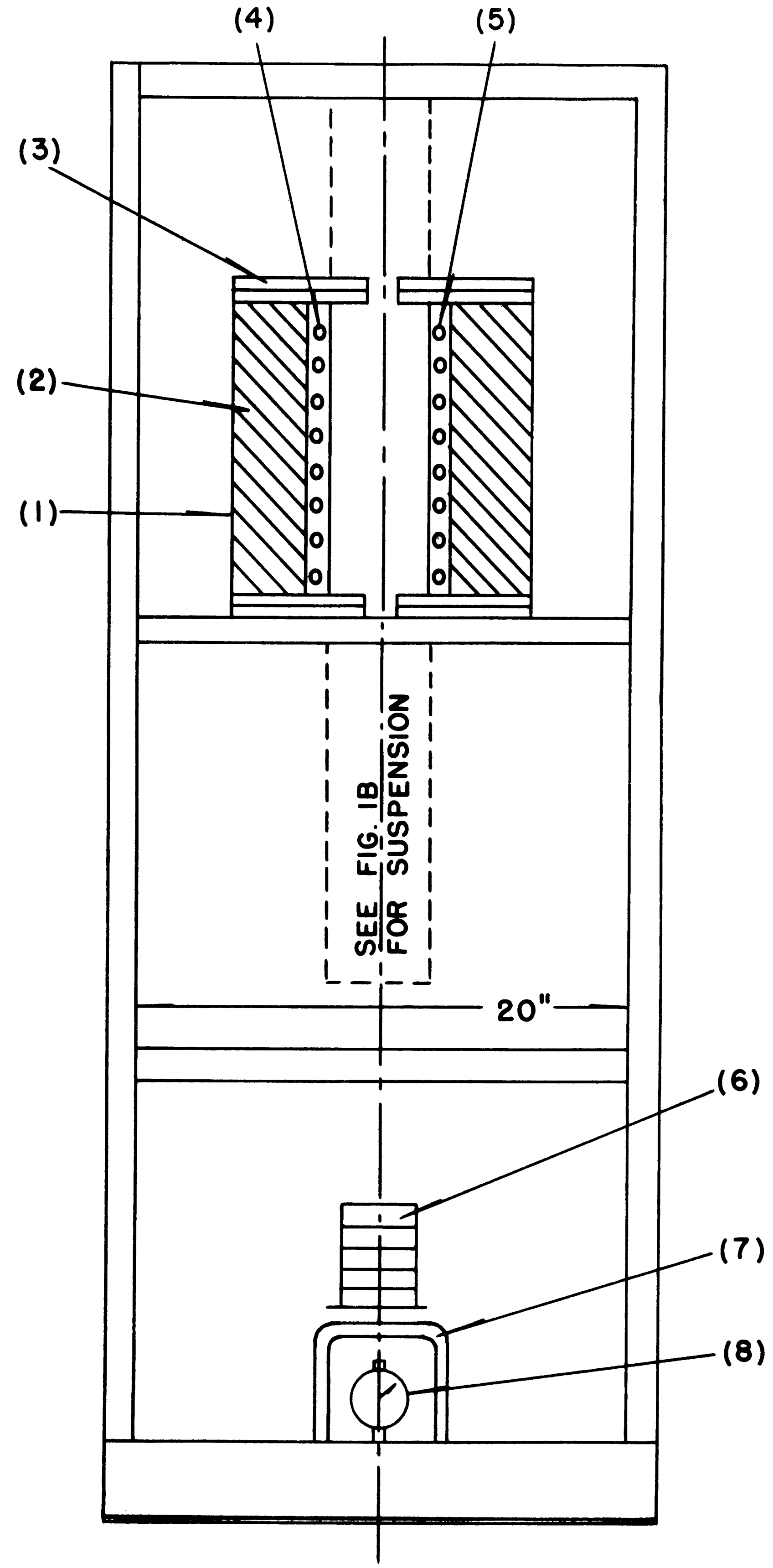

FIG. IA— STRESS OXIDATION UNIT

LEGEND

1- ALUMINUM SHELL
2- VERMICILITE
3- TRANSITE
4- ALUNDUM CEMENT
5- CHROMEL COILS
6- LOAD
7- DIAL GUARD
8- INDICATOR DIAL

FIG. 1B - ASSEMBLY OF SUSPENSION MECHANISM.

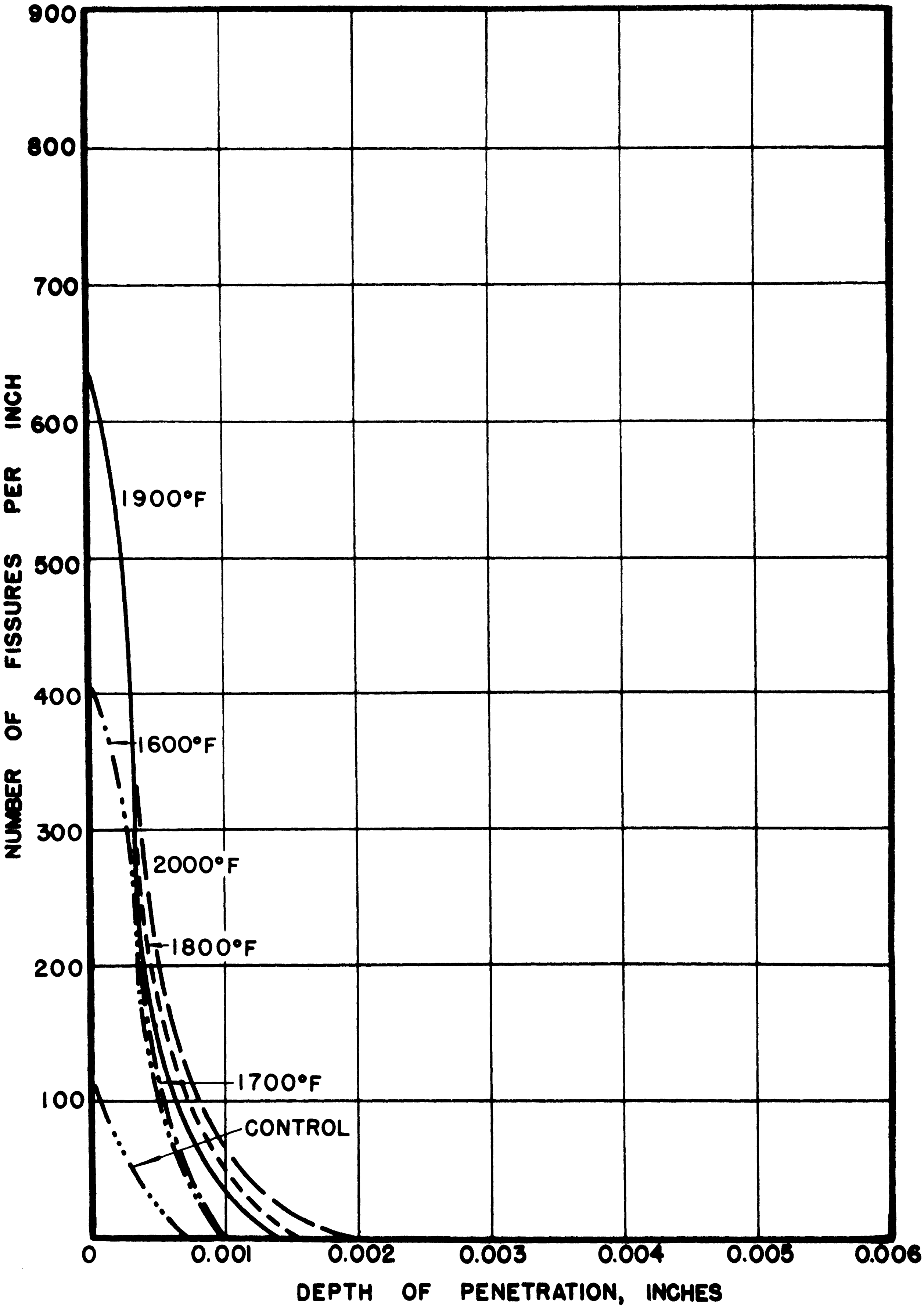

FIG. 2 – PENETRATION VS. DEPTH BELOW SURFACE.
INCONEL ALLOY, RUN 30A. 10 HOURS.

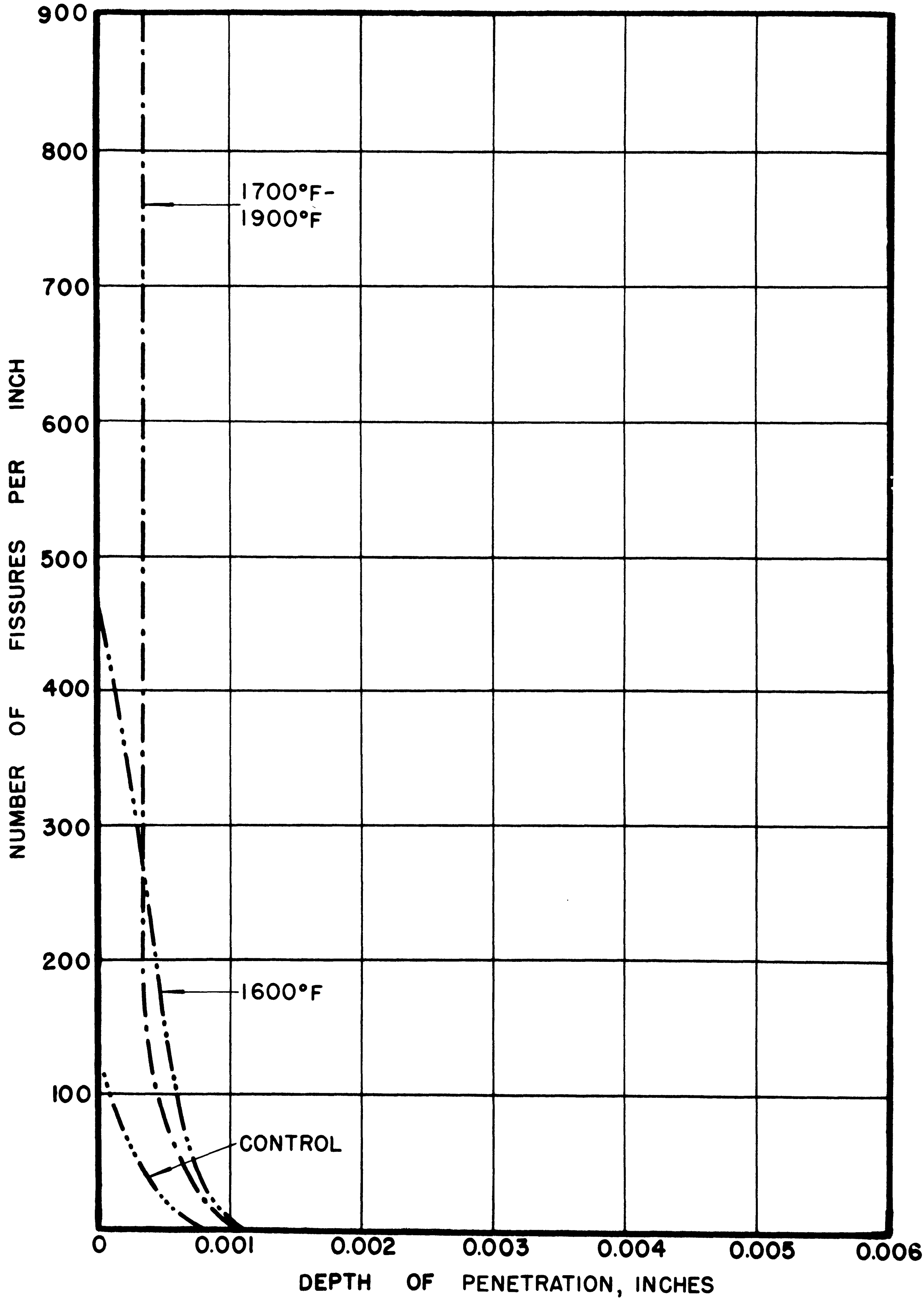

FIG. 3 — PENETRATION VS. DEPTH BELOW SURFACE.
INCONEL ALLOY, RUN 30B. 30 HOURS.

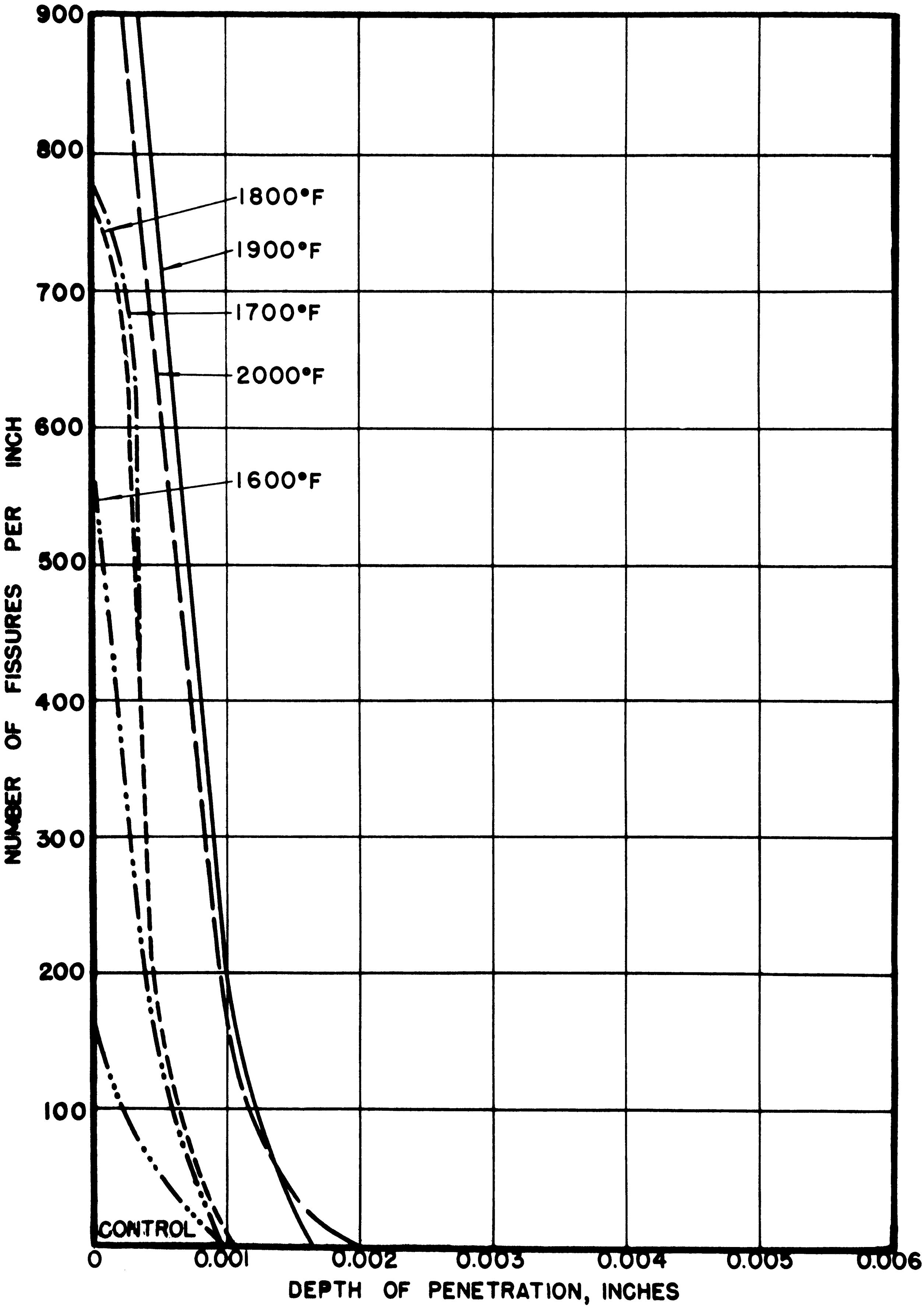

FIG. 4 – PENETRATION VS. DEPTH BELOW SURFACE.
INCONEL ALLOY, RUN 30C. 100 HOURS.

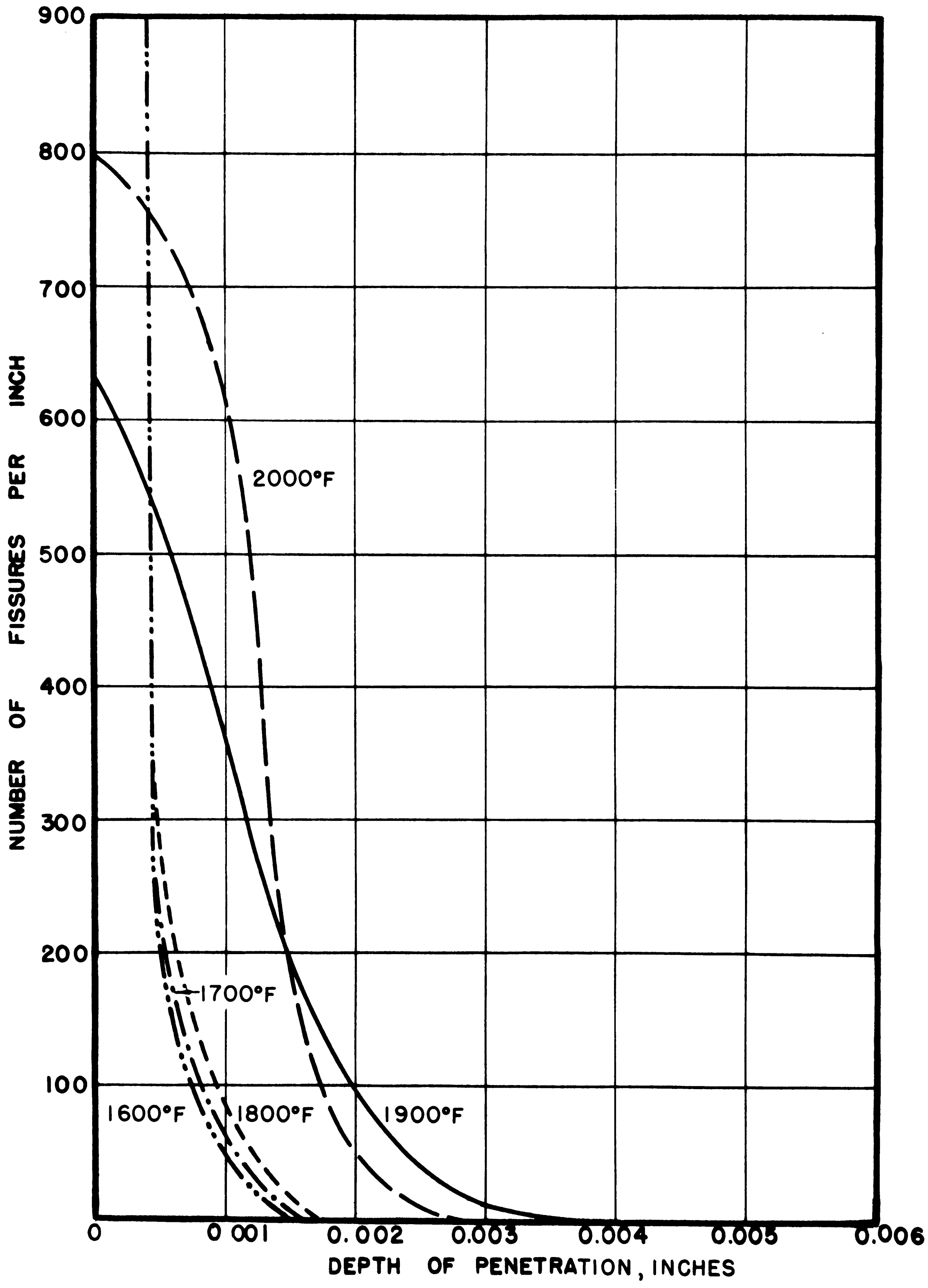

FIG. 5 – PENETRATION VS. DEPTH BELOW SURFACE.
TYPE 310 ALLOY, HEAT 31372.
AS RECEIVED. RUN 33.

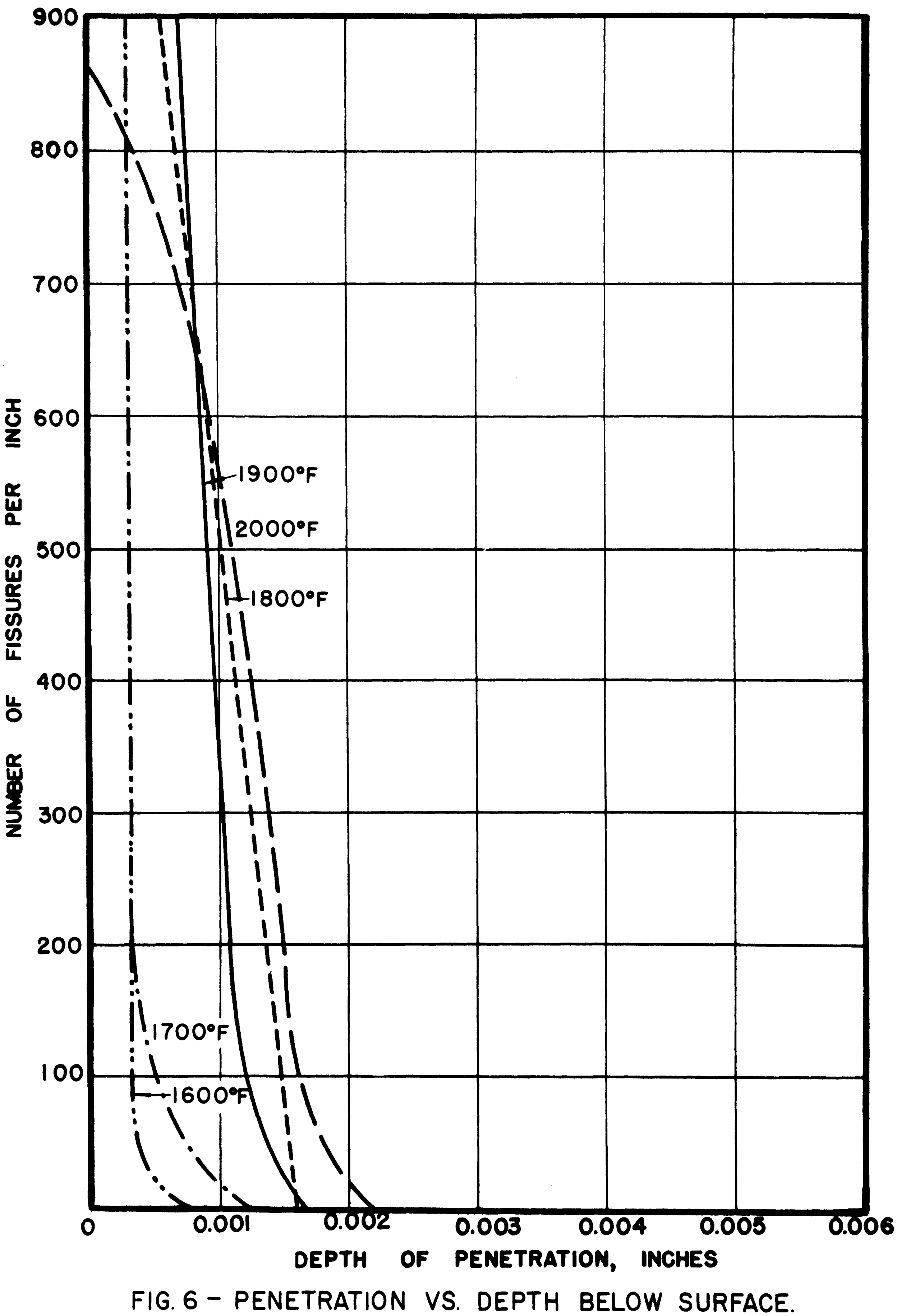

FIG. 6 – PENETRATION VS. DEPTH BELOW SURFACE.
TYPE 310 ALLOY, HEAT 31372.
REDUCED 97% & ANNEALED. RUN 33.

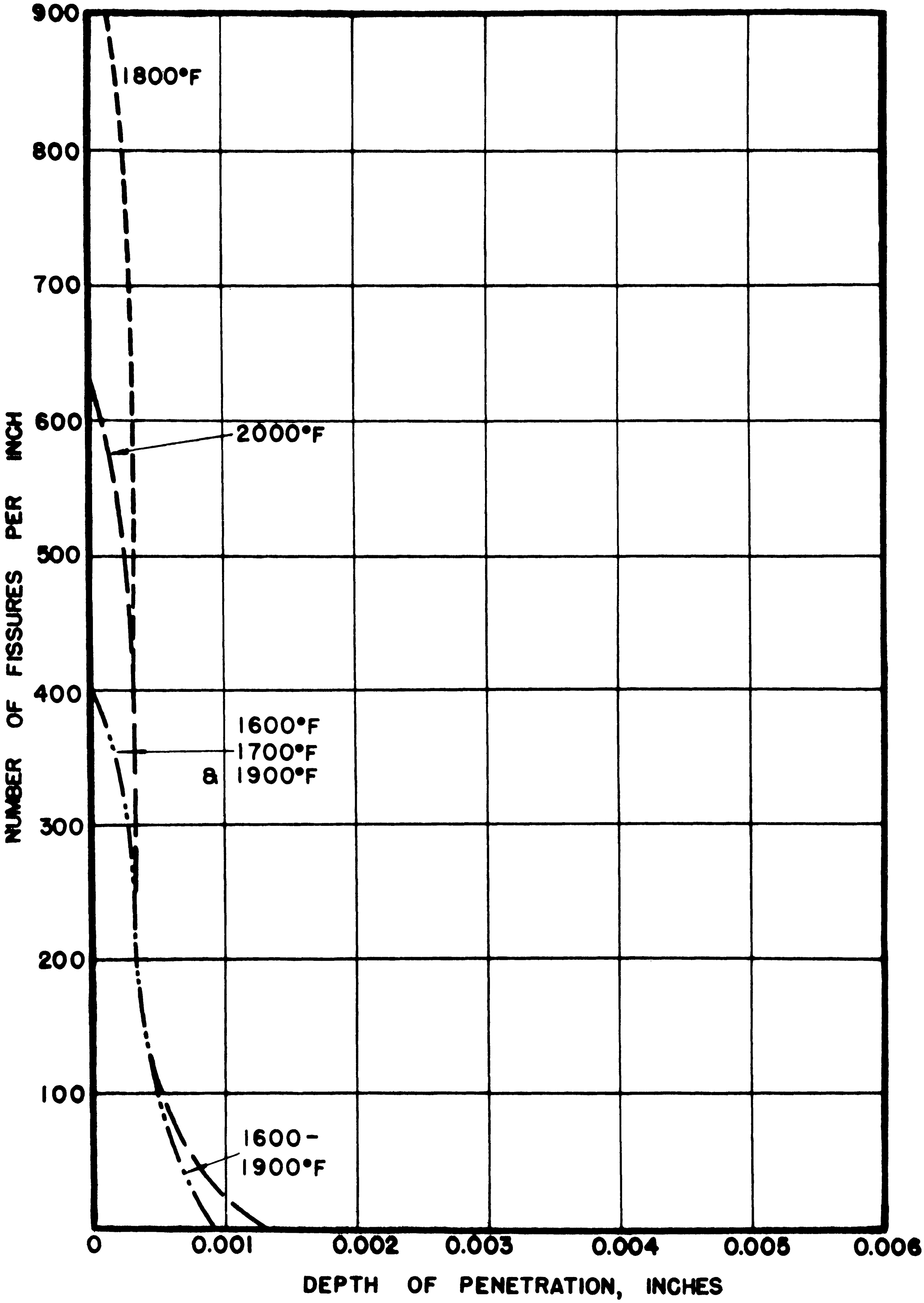

FIG. 7 - PENETRATION VS. DEPTH BELOW SURFACE.
TYPE 310 ALLOY, VACUUM MELTED. RUN 33.

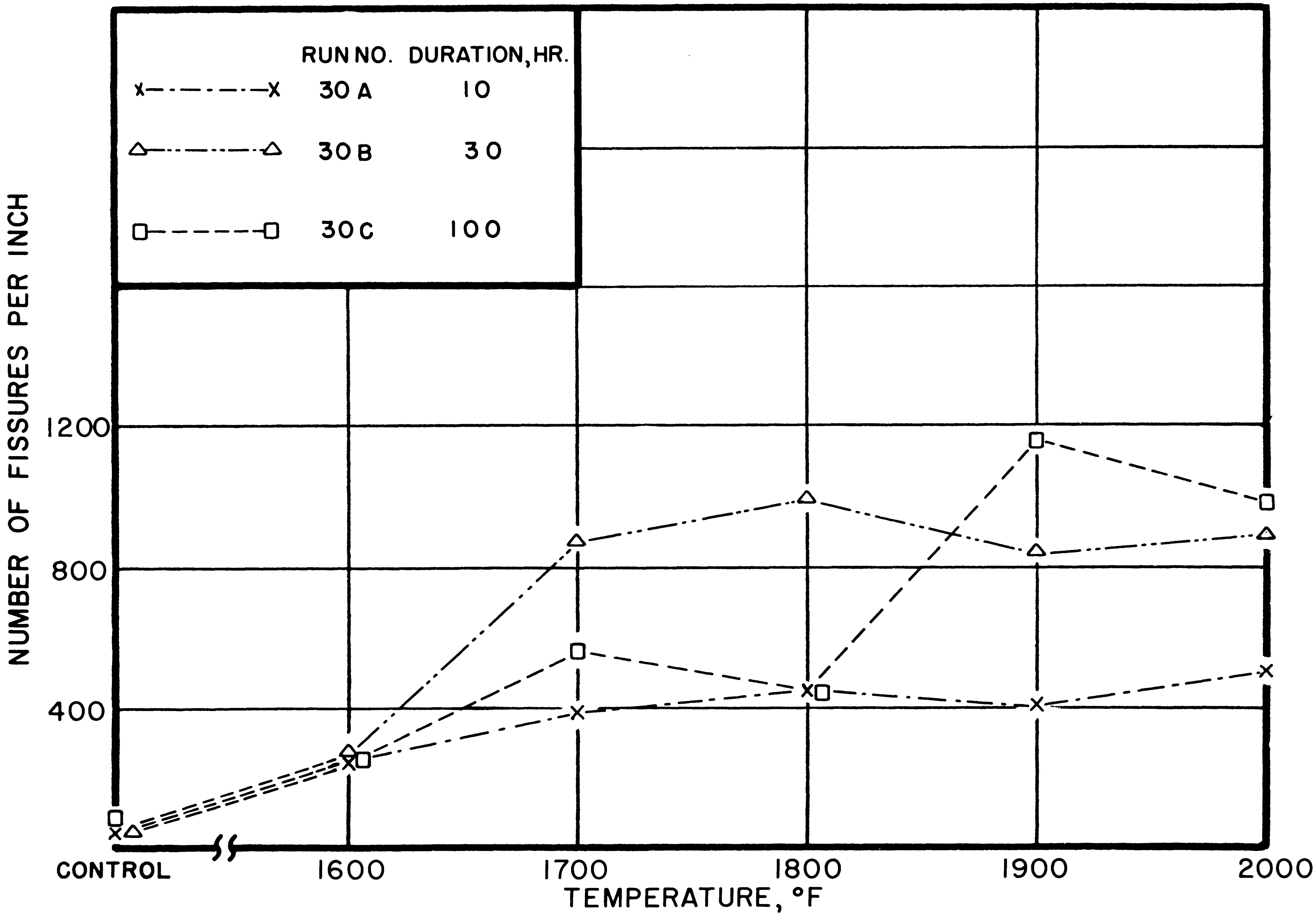

FIG. 8 – SUMMARY PENETRATION FREQUENCY CURVES.
INCONEL ALLOY. EFFECT OF TIME.

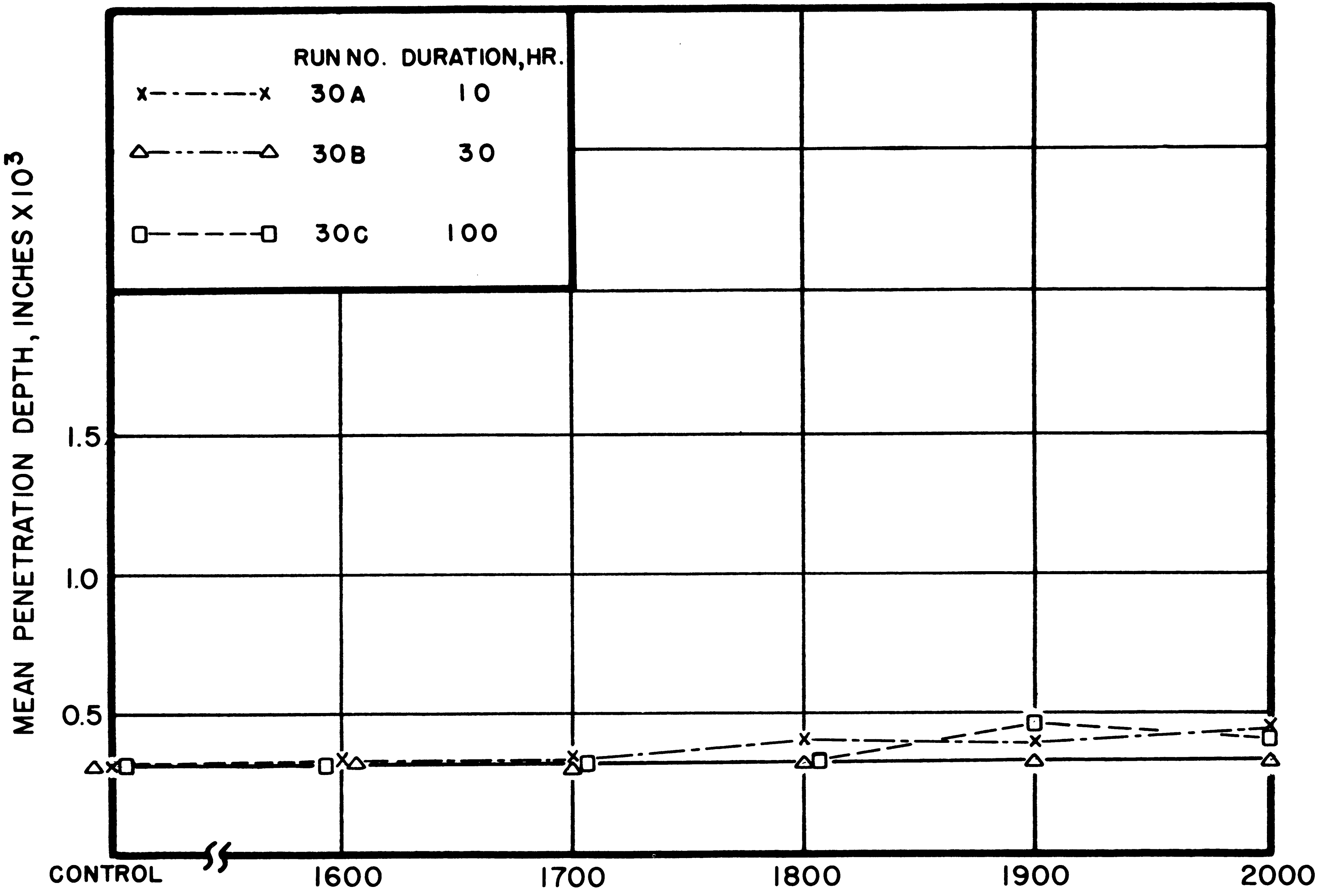

FIG. 9 - SUMMARY PENETRATION DEPTH CURVES.
INCONEL ALLOY. EFFECT OF TIME.

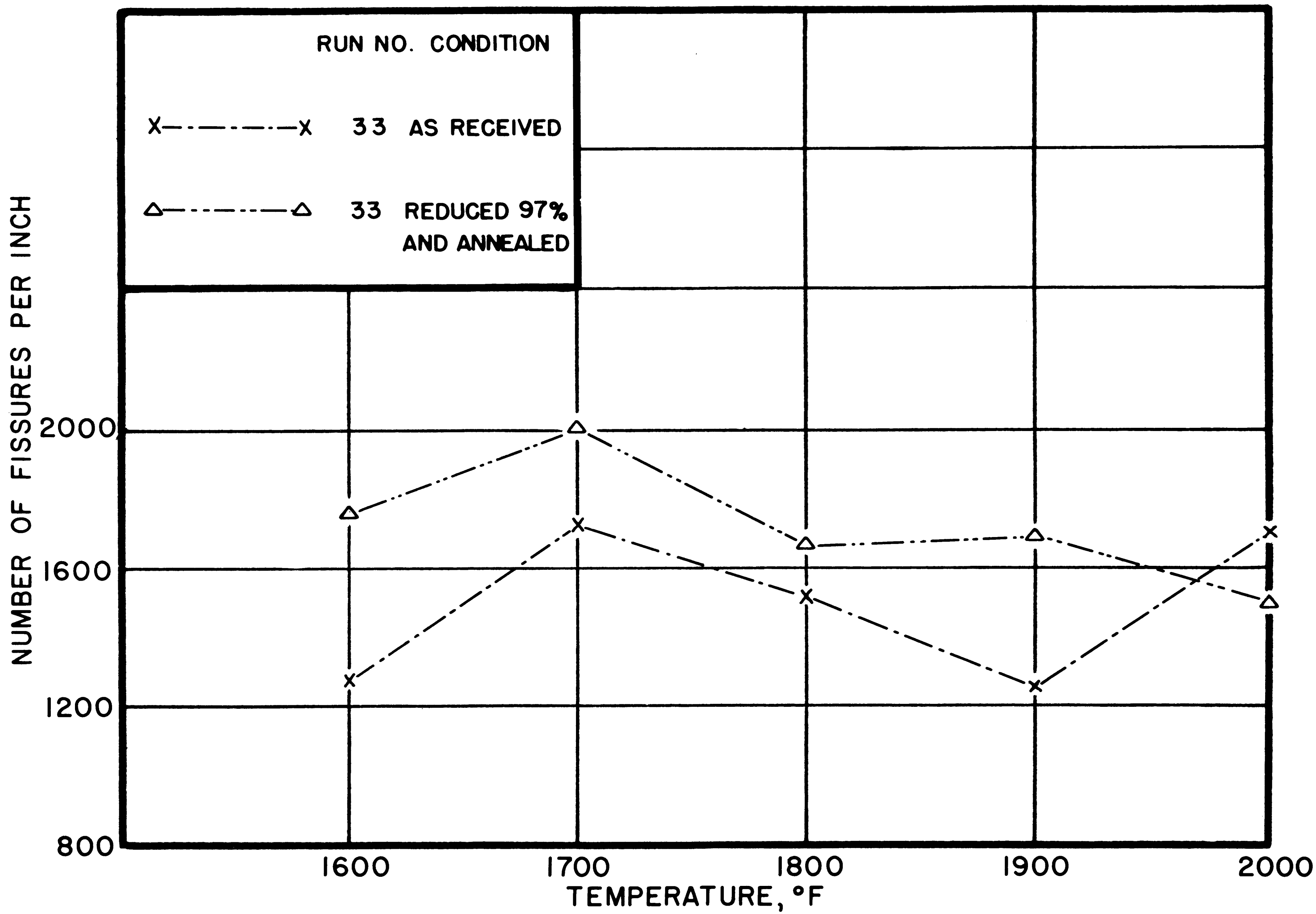

FIG.10-SUMMARY PENETRATION FREQUENCY CURVES.
TYPE 310 ALLOY, HEAT 31372. 100 HOURS DURATION.
EFFECT OF PREFERRED ORIENTATION.

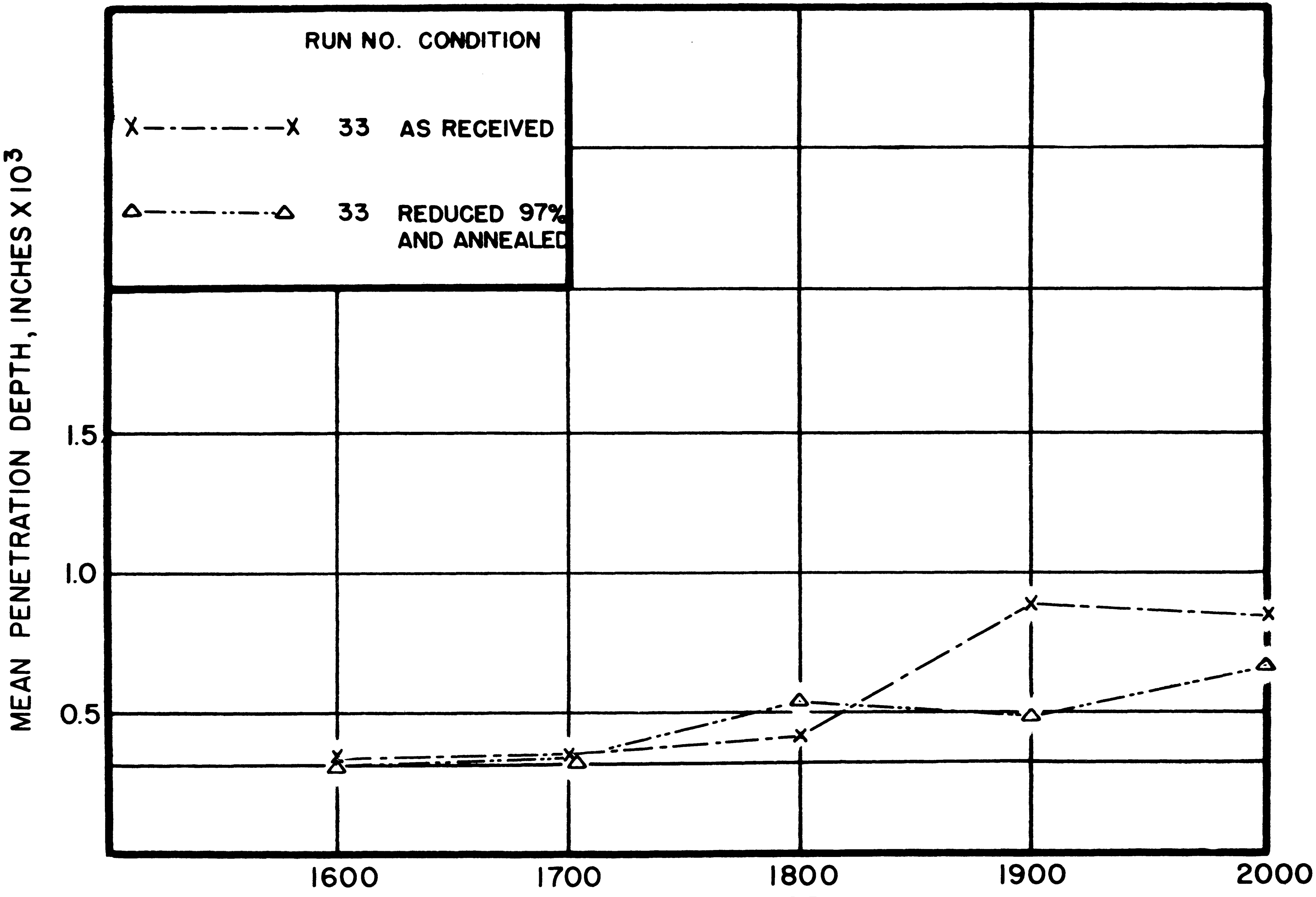

FIG. 11—SUMMARY PENETRATION DEPTH CURVES.
TYPE 310 ALLOY, HEAT 31372. 100 HOURS DURATION.
EFFECT OF PREFERRED ORIENTATION.

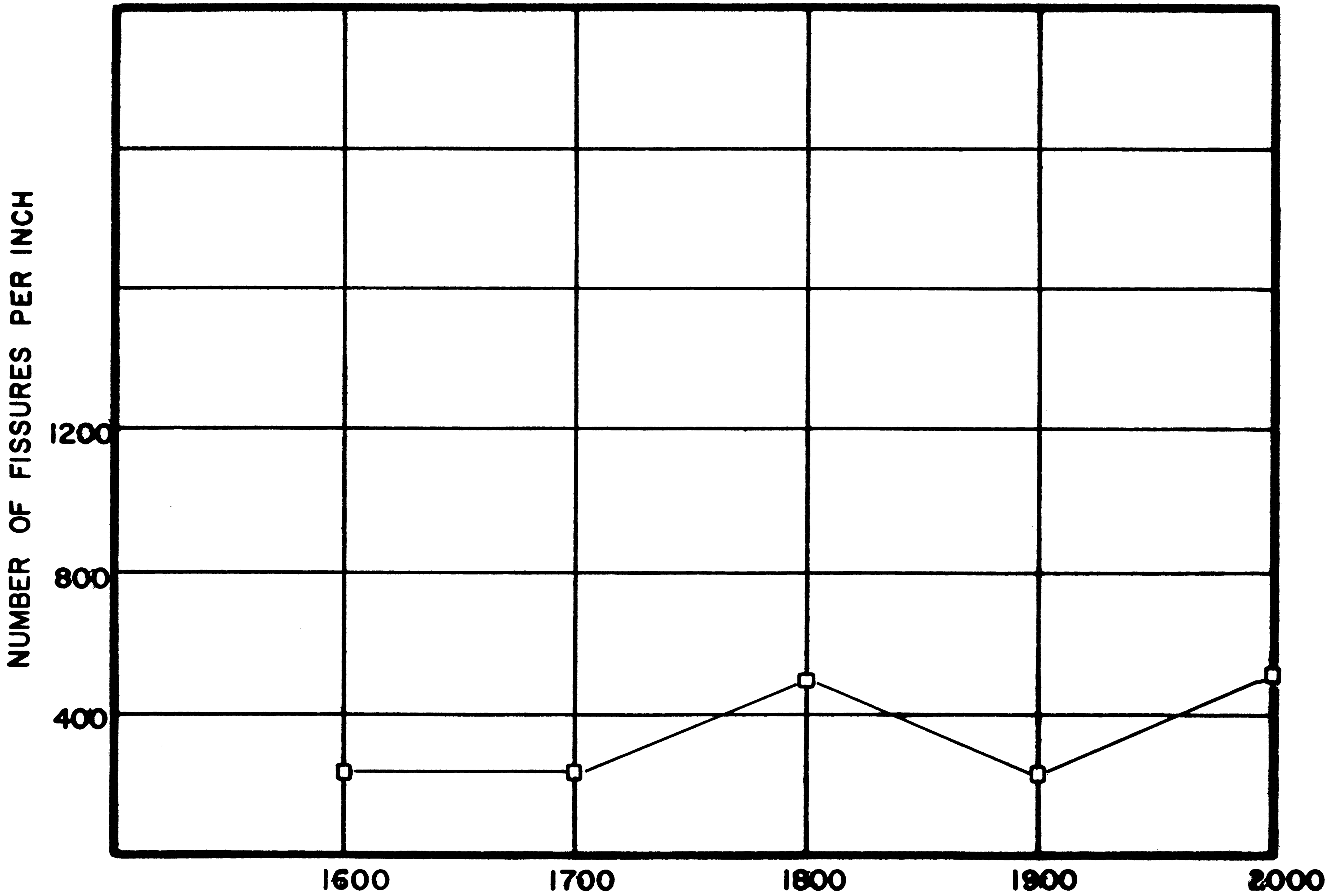

FIG. 12 - SUMMARY PENETRATION FREQUENCY CURVE
TYPE 310 ALLOY, VACUUM MELTED.

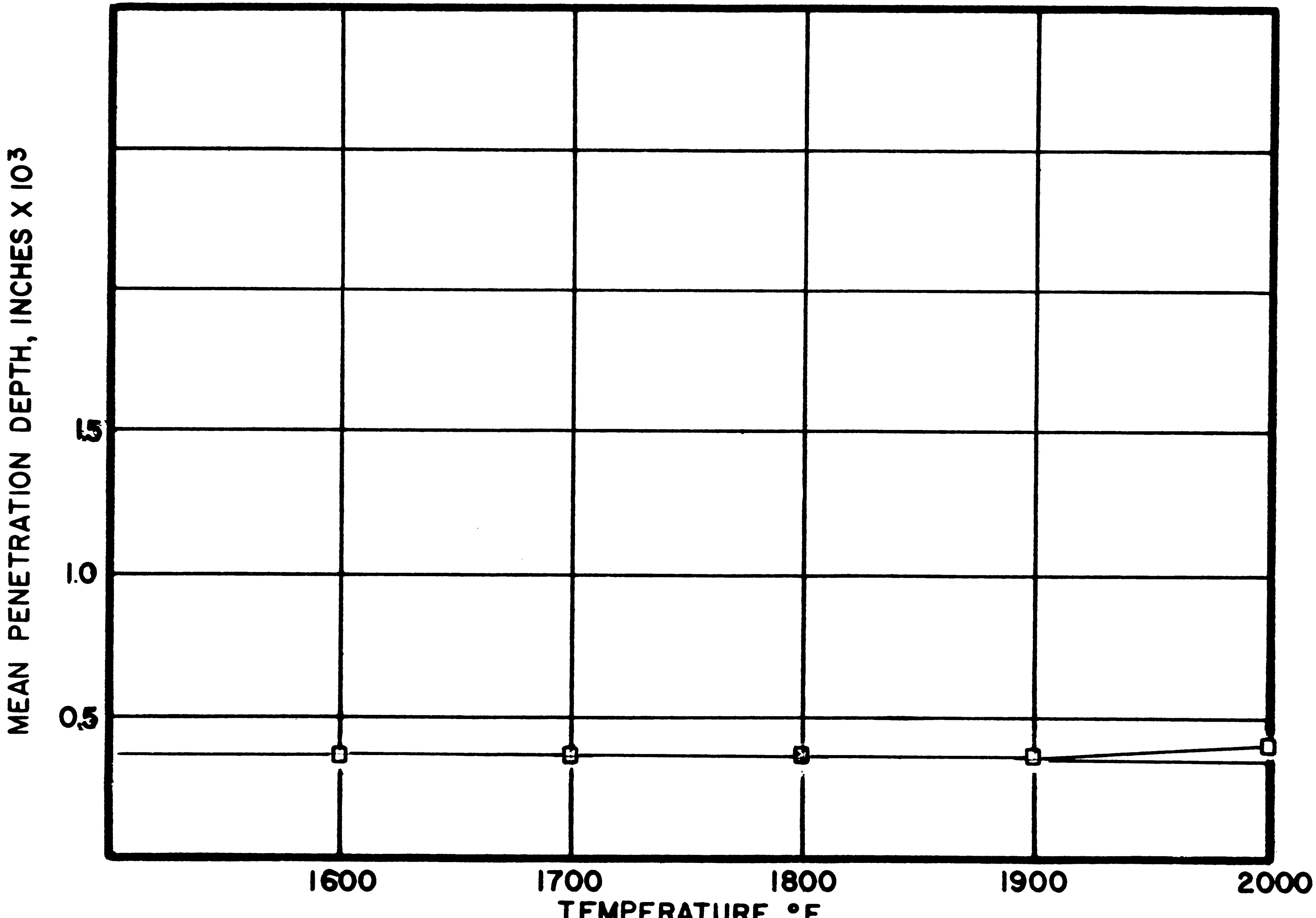

FIG. 13 – SUMMARY PENETRATION DEPTH CURVES
TYPE 310 ALLOY, VACUUM MELTED STOCK