THE UNIVERSITY OF MICHIGAN RESEARCH INSTITUTE
ANN ARBOR, MICH.

SIXTH PROGRESS REPORT

TO

MATERIALS LABORATORY

WRIGHT AIR DEVELOPMENT DIVISION

ON

STUDIES OF HEAT-RESISTANT ALLOYS

by

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Project 02760

Air Force Contract
AF 33(616)-5466
Task No. 73512

September 30, 1959

SUMMARY

Progress is reported for research carried out under Air Force Contract No. AF 33(616)-5466 covering the period of June 30, 1959 to September 30, 1959.

Results are given of tests on "A"Nickel to establish the conditions necessary for the formation of substructures that can be delineated by an etch-pitting technique. It was determined that tensile straining at 1600°F at strain rates of 10 to 100 percent per hour produces substructures that can be delineated quite clearly by electrolytic etching in a 40-percent aqueous solution of H_3PO_4. Further, it was established that substructures produced in this manner can be measured by a lineal intercept method with satisfactory reproducibility. Also, it was found possible to measure a coarsening of the substructure that occurred during creep in a specimen prestrained at 1600°F. Limitations on the etch-pitting method of measuring substructures are discussed.

During this period, the choice of refractory metals to be studied was reviewed with representatives of the Materials Laboratory and the decision was made to use niobium and, if time and funds permit, an alloy of niobium. The adaptation of the rolling mill to permit rolling in an inert atmosphere is discussed in this report.

INTRODUCTION

This report, the Sixth Progress Report issued under Air Force Contract AF 33(616)-5466, covers work done from June 30, 1959 to September 30, 1959.

The research described in this report is part of an investigation being carried out at the University of Michigan for the Materials Laboratory, Wright Air Development Division. The over-all purpose of the investigation is to establish basic relationships between the structure and creep-rupture properties of heat-resistant alloys. The present phase of the work concerns the effect of hot working on the structure and properties of simple, single-phase materials.

As discussed in Reference 1, a good deal of the research effort is being placed on the evaluation of substructure and impurity effects in nickel, using commercial "A"Nickel and high-purity (about 99.95 percent) nickel as the experimental materials. Also, the influence of hot rolling on the structure and properties of pure niobium is being evaluated. If time and funds permit, a niobium-base alloy will be added to the study.

SUBSTRUCTURE AND IMPURITY EFFECTS IN NICKEL

Development of Measurable Substructures

As discussed in Reference 1, it was determined that two conditions were necessary to develop substructures which could be delineated by etch-pitting for measurement under the microscope.

1. Opportunity must be provided for polygonization; relatively slow rates of deformation at relatively high temperatures appeared to be most promising.

2. The "A"Nickel could not be exposed to temperatures below 1500°F before substructures were developed or the decorator effect of the carbon would be lost by precipitation and etch pits would not develop.

With this as a background, experiments were undertaken to develop a range of measurable substructures in the "A"Nickel.

Prestraining to Develop Substructures: Samples were heated to 1600°F and strained in tension at rates of 100, 30, and 10 percent per hour to a deformation of 5.28 to 6.18 percent. All of these developed substructures which could be delineated by etch pits with the H_3PO_4 etchant. In Figure 1, these structures are compared to that of the sample rolled to a 5.8 percent reduction at 1800°F.

The specimen strained 100 percent per hour at 1600°F exhibited substructures in all of the grains. The occurrence of the grid-type structure was less frequent than in the rolled sample, and a semi-equiaxed substructure was visible in the remaining grains. As the strain rate was reduced to 30 and 10 percent per hour, the prominence of semi-equiaxed substructures increased and the amount of the grid-type structure decreased.

The grid-type substructure was visible in only some of the grains. This appears to be due to the high orientation dependence of the etching characteristics of this type of substructure. The dislocations in the slip planes must be nearly perpendicular to the plane of the polished surface before etch pits will outline the boundaries (Ref. 2). Thus the substructure is only visible in those grains which are properly oriented to cause the dislocations in the slip planes to be perpendicular to the polished surface. This response to etching arises from the dislocations' being lined up in the direction of the slip plane. In the semi-equiaxed substructures, the boundaries are composed of dislocations that are more randomly oriented. Thus there are sufficient dislocations properly oriented in the sub-boundaries to develop etch pits in all grains. Thus the structure is visible in all grains.

Substructure Measuring Technique

Careful microscopic examination of several "A"Nickel specimens containing substructures lead to two important conclusions regarding the choice of a technique for obtaining quantitative subgrain size measurements. First, the grain-to-grain variation in subgrain size and shape was found to be quite large, indicating that a large number of grains would have to be examined to obtain a reliable mean subgrain size. Second, rather frequent discontinuities were found in the sub-boundary network which would make it virtually impossible to count the number of subgrains in a prescribed area; this suggested that a lineal intercept method would be best.

Principle: Briefly, the principle of the intercept method (Ref. 3) as applied to the present problem is that the mean subgrain diameter in a given specimen is equal to the reciprocal of the number of intercepts per unit length that occur between the subgrain boundaries and a set of straight lines passing through the specimen in all possible directions. It was reasoned that this idealized condition could be adequately approximated by using a set of parallel lines in a single plane, such as the polished plane of a metallographic specimen, so long as a large number of randomly oriented grains were traversed by the lines. As discussed later, experiments with samples strained 5 to 6 percent at 1600°F showed that independent observers could check their counts of subgrain boundaries within ± 6 percent when the lines traversed about 350 grains. This was considered to be adequate for the purposes of the investigation.

Practice: In practice, the 1/4-inch diameter specimens were halved longitudinally, polished on a Syntron vibratory polisher, etched electrolytically in a 40 percent aqueous solution of H_3PO_4, and examined on a microscope equipped with a travelling stage and an eyepiece containing a cross hair. The stage carried the specimen measured distances while the observer actuated a counter each time a subgrain passed beneath the cross hair. The grain and twin boundaries were also counted so that this information would be available if needed later. The microstructure of the "A"Nickel exhibited banding resulting from chemical segregation. As far as could be seen, the substructures were constant across these bands. However, the traverses were made completely across the width of the specimens at an angle of 22.5 degrees to the tension axis and thereby across the bands, to avoid possible bias from this condition.

Limitations: It was found that one of the severest limitations of this method was the difficulty of reproducing the polishing and etching conditions. The cold working or smearing of the surface metal that occurred with ordinary methods of mechanical polishing was found to cause serious non-uniformity of etch pitting. The geometry of the specimens prevented the use of existing electropolishing equipment, so a Syntron vibratory polisher was tried. Satisfactory results were obtained so long as the coarse and fine grinding operations were carried out properly.

The etching problem stemmed from the fact that the number of visible sub-boundaries increased with the degree of etching. That is, additional boundaries were still appearing even after the point had been reached where the most closely spaced boundaries began to overlap and be irresolvable. It was then necessary to standardize the degree of etching at that point. A carefully-prepared specimen was set aside as a standard, and all the other specimens were slowly etched and frequently compared with the standard at both high and low magnifications until the sub-boundaries in both specimens appeared to be etched equally. To test the suitability of this technique, several sub-boundary counts were made on three specimens by two observers. The results are presented in Table I and Figure 2 along with single counts on specimens with low and high prestrains. The data indicated that the reproducibility was adequate.

There is, in addition, the problem of the degree to which all boundaries will be etched under the procedures used. Even under favorable conditions, there appears to be some boundaries present which cannot be etched. Those boundaries which do not respond to etching are presumably the ones that meet the polished surface at oblique angles. Thus the measurements will provide numbers which will be proportional to but not equal to the true boundary density. Thus far, no reason has been found to suspect that the numbers are not proportional although this factor will have to be checked during future work.

In addition to these major problems, certain other aspects of the etching behavior influenced the sub-boundary counts. Methods of handling these problems will be discussed in detail where actual data are presented in the future. Except when specimens had been exposed to prolonged creep, there was a narrow zone on either side of the grain boundaries which appeared to be depleted of the decorator element with the result that the sub-boundaries did not etch. Fortunately, the zones of depletion covered only a small fraction of the total area. Surface decarburization also resulted in an area near the surface where sub-boundaries could not be etched. Although it has not been recognized as occurring, there is a possibility that during prolonged creep at temperatures below 1500°F, a general depletion of carbon might occur slowly due to precipitation and/or growth of existing precipitates.

Due to these limitations, therefore, the method of quantitatively measuring the substructures has limited applicability. The specimens to which it is applied must be those in which the conditions are correct for the proper delineation of the substructure by etch pits using the H_3PO_4 etching method. It must be remembered that the numbers obtained will be proportional --not equal-- to the true substructure size. The procedure developed is believed to be an improvement on prior methods even though it has severe limitations. As data are obtained, it will be necessary to test the results carefully to be sure that one or more of the limiting features are not causing misleading indications. Furthermore, it points to the desirability of improving the methods of producing substructures and developing of an etch which is not dependent on the presence of impurities.

Control of Pre-induced Substructures: These results indicated that substructures produced by tensile straining at 1600°F at 30 percent per hour could be delineated and measured quantitatively. The next problem then was to find a way to vary the substructure size while still retaining the requirements of being able to measure the size. To determine the effect of the amount of deformation, samples were strained at 30 percent per hour at 1600°F to strains of 1.7 and 19.8 percent. The substructure size was observed to decrease with increasing strain. The results (Table I) indicated the following:

1. As deformation was increased, an increasing number of sub-boundaries became visible.

2. The major effect of increasing amounts of strain was therefore to

reduce the mean distance between sub-boundaries. Reference to the photomicrographs of Figure 1 shows that for strains of 4 percent or greater, many small subgrains are outlined. However, for deformations below about 2 percent, it was observed that the boundaries tend to be discontinuous and often fail to completely outline distinct small subgrains.

3. The mean number of sub-boundaries in the specimen strained 19.7 percent was not appreciably higher than in the specimen strained 6.18 percent (Fig. 2).

4. Increasing the strain from 6.18 to 19.7 percent resulted in partial recrystallization. The newly-recrystallized grains were nearly free from sub-boundaries. Consequently, the over-all average number of sub-boundaries was below that observed in the unrecrystallized grains.

These results are difficult to appraise. As nearly as can now be estimated, increasing strain develops an increasing number of the small subgrains defined by the microstructure of the sample stretched 6 percent. This is in the main deduced from Weissmann's discussion of his X-ray diffraction data for 3rd order substructural units (Ref. 4). It also stems from a scepticism that discontinuous boundaries are properly outlining the subgrains. It, however, seems reasonable to assume that the number of sub-boundaries present is related to the number of subgrains present. Moreover, for the higher deformations, there seems to be some evidence that the size of the subgrains actually decreases slightly with increasing strain.

Prestrain + Creep

At this point, it appeared desirable to determine what happened to the pre-induced substructures during creep. This stemmed mostly from data in the literature indicating the formation of an equilibrium substructure size which depends mainly on the stress, apparently independent of the temperature and rate of creep. In particular, it was necessary to know whether or not the decorator atoms would move with changes in the substructure and continue to allow its delineation by the H_3PO_4 etch-pitting method.

Four tests were carried out:

Prestrain at 1600°F at 30% per hour (% El.)	Data on Subsequent Creep			
	Temp. (°F)	Stress (psi)	Time (hrs)	Strain (%)
6.06	1200	6,950	93	1.37
5.93	1350	3,325	70	1.42
5.32	1500	3,325	18	1.20
0	1500	3,325	20	3.48

The substructure change that occurred during creep at 1200°F was not readily noticeable to the untrained eye although counts of sub-boundaries indicated a 23-percent decrease. The size of the subgrains had noticeably increased when inspected under the microscope for the tests at 1350° and 1500°F. Moreover, they were similar in size. The test on material without prestrain, exhibited a substructure very similar to the material prestrained and tested at the same stress level at 1350° and 1500°F. It seems, therefore, that the decorator elements do move with the sub-boundaries and continue to outline the substructure during creep. This, however, must be checked carefully to be sure that the tendency for the precipitation of carbon will not bring the carbon available for decoration below the required level to outline all the subgrains.

Another result from these tests was the suggestion that initial substructure could be varied and controlled better by prior creep than by tensile prestraining. Accordingly, it was decided that the first step during the next period would be to check this method out.

High-Purity Nickel

Investigation of the possible sources of "pure" nickel indicated that the most practical method would be to use carbonyl nickel powder. A typical analysis of this material is as follows (weight percent):

Ni --- 99.80
Fe --- 0.005
C --- 0.09
O --- 0.10
S --- Nil

The main impurities are carbon and oxygen. Private communications have indicated that the powder can be consolidated to produce 99.94% nickel by melting under an argon blanket with final deoxidation with magnesium and vacuum melting. The high oxygen reduces the carbon to a very low value (<0.005%); the magnesium removes the remainder of the oxygen; and melting in vacuo removes the excess magnesium.

Several attempts were made using recommended procedures. However, the vaporization of magnesium was not controlled well enough by this procedure and most of the charge was blown out of the crucible.

REFRACTORY METALS

Material Selection

During the period the question of the refractory metals to be studied was reviewed with representatives of the Materials Laboratory and the decision was made to use niobium. Double-electron-gun-melted bar stock will be used. If time and funds permit, an alloy of niobium will also be included.

Experimental Program

The niobium bar stock will be hot rolled over a range of reductions and temperatures which will meet the following requirements:

1. No recrystallization during rolling.
2. Recrystallization initiated after considerable reduction.
3. Complete recrystallization with relative small reductions. The hot rolling will be carried out isothermally and on definite schedules of temperature variation with reduction.

The influence of the hot-working conditions on creep-rupture properties will be established at two temperatures. One will be at a relatively low temperature where the as-rolled structures are quite stable. A higher temperature will also be used where recovery effects are quite rapid.

This program will give results which can be correlated with those for nickel. The face-centered-cubic nickel was previously shown to have a considerable dependence on internal strain for strength at the relatively low test temperature. At the higher test temperature, strength increased markedly with percent reduction independent of the temperature of reduction up to the point where recrystallization during rolling or during testing limited the strengthening. The results should be particularly significant from a basic viewpoint because they should show the influence of the very low strain hardening capacity of the body-centered-cubic niobium in contrast to nickel. Secondly, it should be shown whether or not substructures are influential in the absence of strain hardening in a body-centered-cubic structure.

Adaptation of Rolling Mill

Following extensive consultation and design work, a system was developed which will permit rolling in an argon atmosphere. A sheet steel enclosure will be sealed around the rolls. This chamber will be purged of air by evacuation with an air-operated ejector pump, and then filled with argon to a slight positive pressure. A furnace for heating in argon will be attached to the chamber and equipped with a lock through which bars can be charged from the room. The bars will be manipulated from the furnace through the mill using hand tongs. The operators will work through a "glove box" attachment employing rubber gloves sealed to the chamber. Construction of the enclosure has begun.

Two furnaces will be employed. One will be a wound resistor type electric furnace constructed with Hoskins Alloy 875 wire permitting operation up to about 2200°F. It is anticipated that this will be adequate for part of the work on niobium. In addition, requests for quotations have been placed for several types of furnaces capable of heating to the range of 3500°-5000°F. As soon as these quotations have been studied, a recommendation will be made to the Materials Laboratory for a choice of furnace.

In establishing the technique to be used for rolling, and in designing the equipment with which to implement this technique, many decisions have been necessary among the available alternatives. There is no experience to set as a guide. The opinions of qualified individuals working in the field often conflict. These problems are of such an unusual nature that it is difficult to select an adequate compromise, particularly in view of the limited available funds. For example, one of the groups consulted had fairly convincing evidence that the use of a glass coating could provide an excellent, low-cost method with very high temperature capability for the solution of the atmosphere problem. That this technique was unsuitable for experimental work involving a variety of materials and stock sizes was certain only after considerable study.

All things considered, the proposed design for an enclosed chamber with the furnace integrally attached is believed to present the best solution to the fabricating problem.

REFERENCES

1. A. P. Coldren and J. W. Freeman, "Studies of Heat-Resistant Alloys", Fifth Progress Report to Wright Air Development Division Under Contract No. AF 33(616)-5466 (June 30, 1959).

2. R. W. Guard, "The Role of Polygonization in Creep", Preprint Copy of WADC Technical Report Covering Work Done for the Aeronautical Research Laboratory Under Contract AF 33(616)-3263, Appendix A (December, 1959).

3. C.S. Smith, "Grain Shapes and Other Metallurgical Applications of Topology", Seminar on Metal Interfaces, ASM (1951) p. 65.

4. S. Weissmann, "Quantitative Study of Substructure Characteristics and Correlation to Tensile Properties of Nickel and Nickel Alloys", J. Appl. Phys., 27 (1956) 1335.

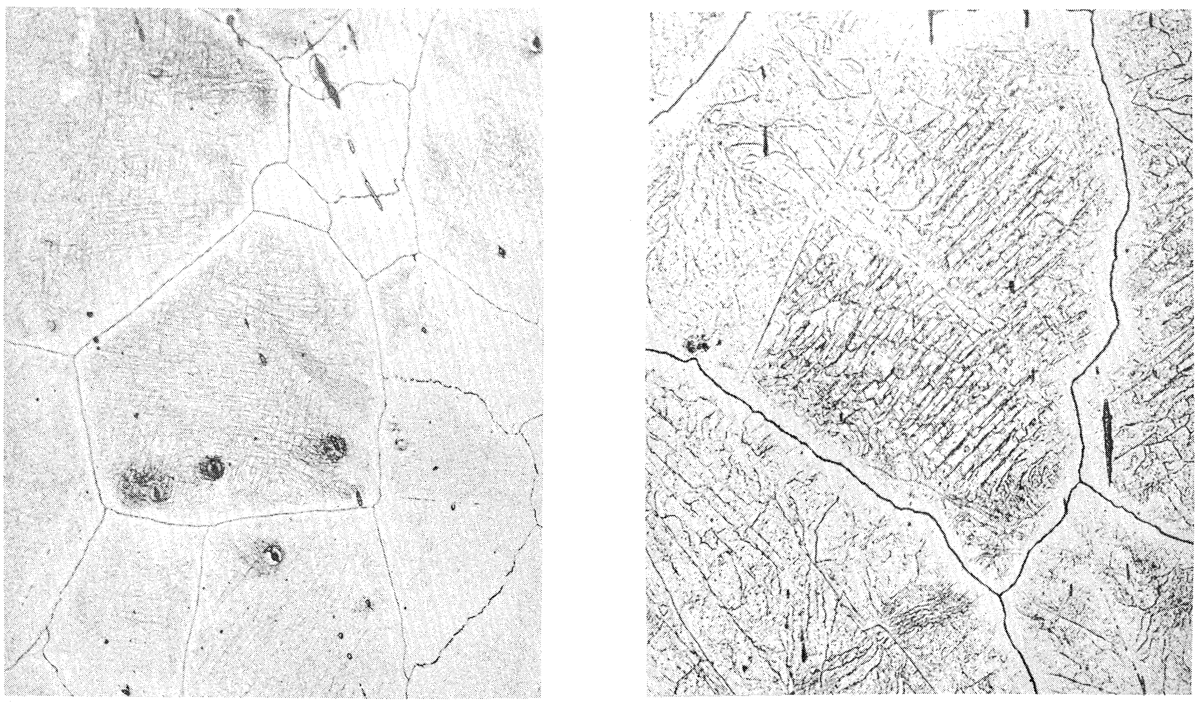
TABLE I

QUANTITATIVE SUBSTRUCTURE DATA

Spec.	Prestrain* and/or Creep Conditions	Spec. Prep. No.**	Boundary Counts (No. intercepted per lineal inch)					
			Sub-boundaries		Twin Boundaries		Grain Boundaries	
			Observer A	Observer B	Observer A	Observer B	Observer A	Observer B
PSE-7	5.28% Prestrain	1	2,297	2,270	22.2	33.2	120.4	126.8
		2	--	2,260	--	37.2	--	118.2
		3	--	2,080	--	21.8	--	119.5
		3	--	2,090	--	21.7	--	121.0
PSE-5	6.18% Prestrain	1	2,368	--	32.7	--	127.3	--
		2	--	2,510	--	29.7	--	122.0
		3	--	2,430	--	32.6	--	110.3
PSE-4c	6.06% Prestrain + 1.37% Creep at 1200°F and 6,950 psi	1	1,821	--	21.0	--	118.3	--
		1	1,876	--	18.2	--	120.0	--
		2	--	1,855	--	31.8	--	113.7
PSE-8	1.74% Prestrain	1	--	862	--	46.4	--	111.7
PSE-12	19.7% Prestrain	1	--	2,440	--	27.3	--	131.2

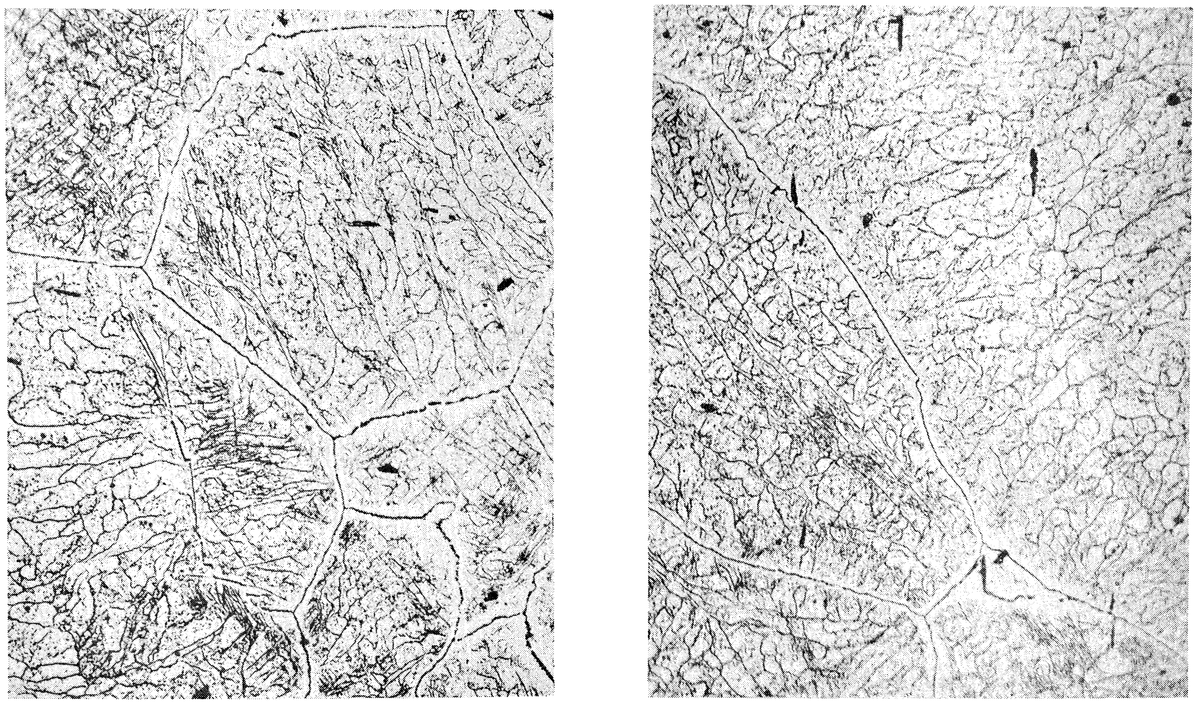
* - All prestraining was carried out at 1600°F at a strain rate of 28.9 ± 2.7% per hour.

** - "Preparation" includes grinding, polishing and etching; hence, a change in "Preparation No." means that the specimen was reground and then polished and etched.



(a) Rolled 5.8% Reduction of Area at 1800°F.

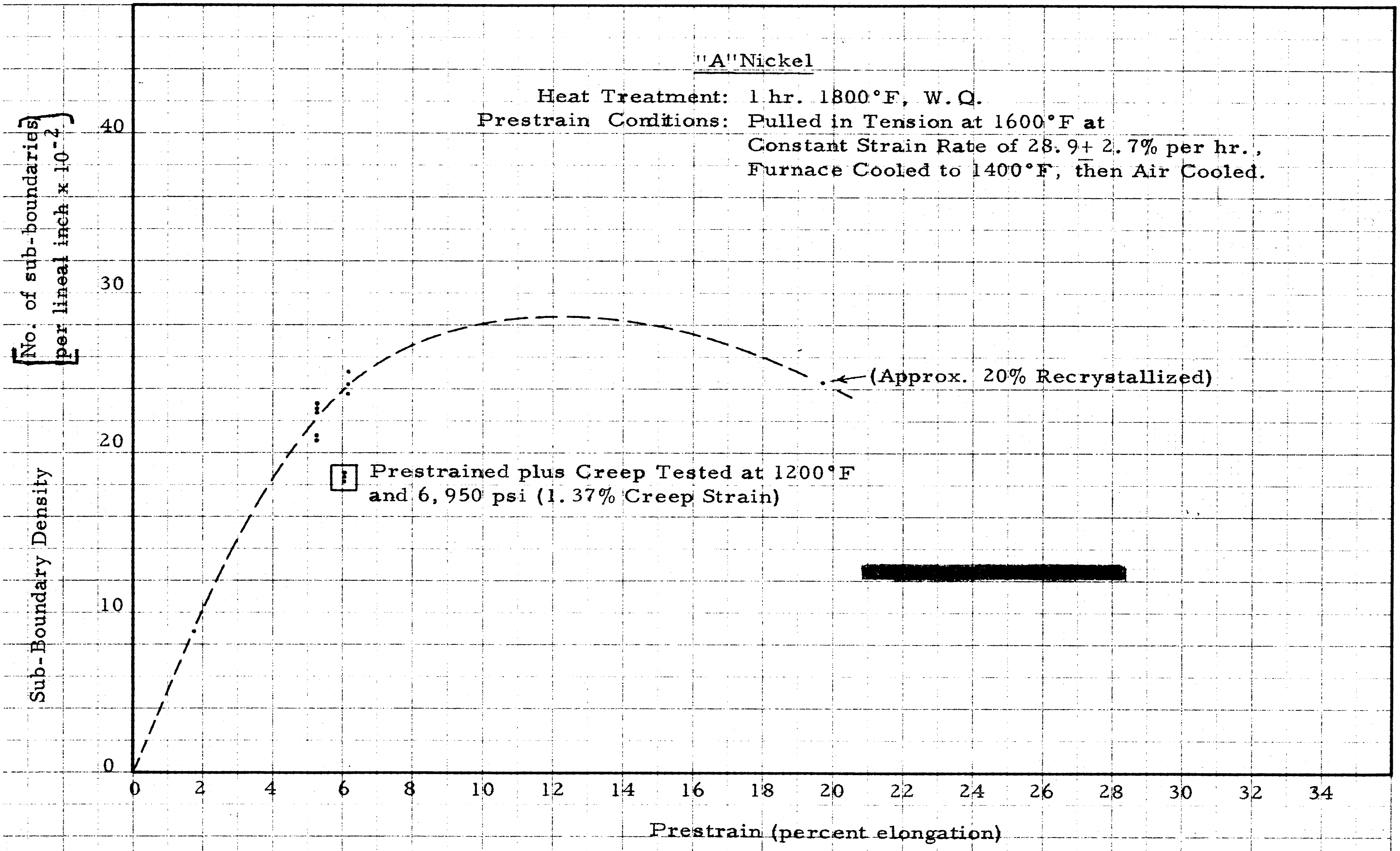
(b) Strained in Tension to 4% Elongation at 1600°F at a Constant Strain Rate of 100%/hr.



(c) Strained in Tension to 5.3% Elongation at 1600°F at a Constant Strain Rate of 30%/hr.

(d) Strained in Tension to 4% Elongation at 1600°F at a Constant Strain Rate of 10%/hr.

Figure 1. Substructures in "A"Nickel Delineated by Etch-Pit Technique. The conditions of substructure formation are as indicated. All micrographs are at a magnification of 250 diameters.



[redacted]

Figure 2. - Metallographic Counts of Subgrain Boundaries in Commercially-Pure Nickel. Sub-Boundary Densities Were Obtained by Lineal Intercept Method. Each Point is an Average for a Total Length of Traverse of About 3 Inches, Crossing About 350 Grains.

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