REPORT

ON

INFLUENCE OF A BORON ADDITION ON THE HIGH-TEMPERATURE PROPERTIES OF A CARBON-MOLYBDENUM STEEL

By

J. W. Freeman

PROJECT 2135
FINAL REPORT

February, 1954

THE CLIMAX MOLYBDENUM COMPANY OF MICHIGAN
DETROIT, MICHIGAN

INFLUENCE OF A BORON ADDITION ON THE HIGH-TEMPERATURE PROPERTIES OF A CARBON-MOLYBDENUM STEEL

A special addition of boron-titanium, as "Grainal 79," to low carbon-molybdenum steel was made to a laboratory induction furnace heat. Tests were carried out at 1000°F on this alloy to establish qualitatively the properties relative to standard 0.5-percent molybdenum steel.

Boron content was not reported. The retained titanium, 0.059 percent, together with the room temperature physical properties after normalizing from 1800°F and tempering at 1100°F indicated that an adeqaute amount of boron was present.

The major objective of the investigation was to establish if the boron treatment developed properties sufficient to warrant further development work on boron-treated molybdenum steels.

CONCLUSIONS

A large increase in strength at 1000°F resulted from the addition of boron (or boron + titanium) to 0.5 Mo steel by the "Grainal 79." Strengths in general were several times as high as those usually observed for plain 0.5 Mo steel and twice as high as those experimentally obtained by special heat treatments.

The increase in strength was not accompanied by a decrease in ductility in the rupture test at 1000°F. It was, however, accompanied by increased hardness and short-time tensile strength values, particularly yield point.

Combinations of proper boron additions and heat treatment therefore appear very promising for application to 0.5 Mo steel for the purpose of raising strength at temperatures up to 1000°F. It should be recognized, however, that such steels would probably not be immune to graphitization and might find only limited applicability above 850°F for that reason. In addition, commercial adaptation of boron additions for high-temperature strength has had a rather poor history for other steels in that the laboratory heat properties have not been retained well in commercially produced materials.

EXPERIMENTAL MATERIAL

Stock in the form of heat-treated 7/8-inch round bars was furnished by The Climax Molybdenum Company from their Heat 3108. A 30-pound laboratory induction furnace ingot was forged to 2-inch diameter, turned to 1-7/8 inch diameter, and rolled to 7/8-inch diameter. Their reported chemical composition, heat treatment and room temperature physical properties were as follows:

	C	Cu	B	Si	Zr	Mn	Al	Ti	Fe
Gramal 79	.17	.25	.5	2.94	3.37	6.84	13.01	20.34	bal

Chemical Composition (percent)

C	Mn	Si	Mo	P	S	Ti
0.15	0.54	0.30	0.50	0.032	0.030	0.059

Boron was not reported, probably because boron analysis is difficult and unreliable. It was added as "Grainal 79." The titanium content, together with the response to heat treatment as indicated by the following properties at room temperature, indicated proper boron content.

The bar stock was heat treated by air cooling after 1 hour at 1800°F and tempering 2 hours at 1100°F. The resulting properties at room temperature were reported:

Tensile Strength (psi)	Yield Strength (0.2% Offset) (psi)	Elongation (%)	Reduction of Area (%)	Brinell Hardness
94,500	76,000	24.5	62.5	207/212

PROCEDURE

The influence of boron was evaluated by rupture, creep, and tensile tests at 1000°F.

Rupture Tests

The barstock was split lengthwise and machined into 0.250-inch diameter by 1-inch long gage length specimens. Tests were carried out in accordance with ASTM Recommended Practice E-85.

Three different bars were submitted at intervals for the work. This was reflected in the data in that tests on the second lot did not agree with those from the first and third lots.

The testing program had as its objective the establishment of a reasonably reliable stress-rupture time curve for extrapolation to the prolonged time periods of interest to the steam power, oil and gas turbine industries.

Creep Test

One creep test was conducted at 1000°F. An estimate was made of the stress to give a creep rate of about 0.0001 percent per hour from partially complete rupture test data. The test was carried out in accordance with ASTM Recommended Pract. E-22, using a standard 0.505-inch diameter specimen. The stock was included in the second lot of material submitted.

Tensile Test

One tensile test was conducted at 1000°F in accordance with ASTM Recommended Practice E-21. A standard 0.505-inch diameter specimen, machined from the second lot of test material, was used. Stress-strain data were obtained by step loading and using a modified Martens extensometer with a sensitivity of about three-millionths of an inch.

Completed Test Specimens

All specimens, together with unused stock, were returned to The Climax Molybdenum Company on completion of the tests.

RESULTS

Rupture-Test Properties

The data obtained from the rupture tests at 1000°F are given in the following tabulation and shown as a stress-rupture time curve in Figure 1.

Material Lot	Stress (psi)	Rupture Time (hours)	Elongation (% in 1 in.)	Reduction of Area (%)
1st	60,000	10.2	20.5	72.0
1st	57,000	97.7	13.0	33.0
1st	54,000	183.6	8.0	20.3
3rd	50,000	460.5	4.0	11.8
3rd	47,000	723.9	8.0	10.2

The rupture strengths indicated by Figure 1 were as follows:

Stress (psi) for Rupture in Indicated Time Periods				
10-hours	100-hours	1000-hours	10,000-hours*	100,000-hours*
60,000	57,000	46,000	37,000	30,000

* Extrapolation of Figure 1.

The elongation and reduction of area decreased with time for fracture from the tensile test. The elongations of the specimens which fractured between 100 and 1000 hours ranged from 13 to 4 percent. The 4 percent value was obtained from the intermediate time test which lasted 450 hours. The elongation for fracture in time periods less than 10 hours was more than 20 percent.

In addition, three tests were run on specimens from the second lot of material supplied with the following results:

Stress (psi)	Rupture Time (hours)	Elongation (% in 1 in.)	Reduction of Area (%)
50,000	167.3	23	56
50,000	164.6	26	52
46,000	272.7	26	50

These times for rupture were considerably less than those shown by previously tested material. This is shown by Figure 2, which compares the two sets of data. It will also be noted that elongation and reduction of area values were much higher. The specimens were returned to The Climax Molybdenum Company who reported that the grain size was much finer than it should have been for material normalized at 1800°F, and it was presumed that their heat treating temperature had inadvertantly been low. At this time, additional test material (3rd lot) was submitted as having been properly heat treated. The results from this material are those indicated previously for the 3rd lot of material and had properties which agreed with those of the first material submitted.

Creep-Test Properties

The creep test at 1000°F under 34,000 psi gave a minimum creep rate of 0.00021 percent per hour and a slightly higher rate from 600 to 1000 hours of 0.00024 percent per hour. The time-elongation curve is shown as Figure 3. These creep rates indicate a creep strength of about 30,000 psi for a rate of 0.0001 percent per hour (0.1 percent per 1000 hours).

The slight change in creep rate during the test was probably due to structural changes during the test. Boron and titanium treated steels frequently show this behavior.

The specimen used for the 34,000-psi creep test was taken from the second lot submitted. Because the bar from this lot used for rupture tests was apparently improperly heat treated, there was a question as to whether the creep test was representative of the steel properly normalized from 1800°F. The Climax Molybdenum Company examined the completed test specimen and reported that the grain size was normal.

The creep strength observed bears this out. Normally the stress for a rate of 0.0001 percent per hour should be 70 to 80 percent of the 10,000-hour rupture strength. The observed value of 37,000 psi for rupture in 10,000 hours would therefore indicate a stress of about 30,000 psi for a rate of 0.0001 percent per hour, as was indicated by the test.

A stress of 34,000 psi was selected when the rupture tests were still incomplete and indicated a 10,000-hour strength of 45,000 psi. On this basis, 34,000 psi was expected to give a rate between 0.00001 and 0.0001 percent per hour. The incomplete rupture data indicated higher strength than was actually found. Consequently, the stress of 34,000 psi gave a higher rate of creep than was desired.

Time-elongation curves from the rupture tests are shown by Figure 4. The curves are restricted to those from properly heat-treated stock. The minimum creep rates from the longer tests, together with the creep test result, were used to plot the stress-creep rate curve of Figure 5. It will be noted that they appear to agree with the creep test rate.

Tensile Test

One test was conducted at 1000°F, with the following results:

tensile strength -- 68,500 psi
0.2% offset yield strength -- 60,000 psi
0.1% offset yield strength -- 55,000 psi
proportional limit -- 32,500 psi
elongation -- 23.5% in 2 inches
reduction of area -- 75.5%

The stress-strain curve is shown as Figure 6. It will be noted that the tensile strength was substantially lower than the value reported for room temperature, whereas the yield strength was not lowered nearly as much. Ductility values were the same as both temperatures.

DISCUSSION

The strength of boron-treated 0.5 Mo steel, Heat 3108, at 1000°F is substantially higher than ordinary 0.5 Mo steel on the basis of the three tests used to evaluate its properties. For instance, ASTM Special Technical Publication No. 100 lists the following ranges in strength as typical of 0.5 Mo steel at 1000°F:

Property	Range for 0.5 Mo Steel	0.5 Mo + Boron (Heat 3108)
Tensile strength, psi	46,000 - 67,000	68,500
Yield strength, psi	14,000 - 34,000	60,000
Elongation, %	23 - 47	23.5
1000-hr rupture strength, psi	22,000 - 38,000	46,000
10,000-hr rupture strength, psi	12,000 - 22,000	~37,000
0.1% per 1000-hr creep strength, psi	7,000 - 18,000	~30,000

It should be recognized that the above ranges in strength for plain 0.5 Mo steel include data for annealed and highly tempered material. Restriction of the data to material deoxidized only with silicon and to aluminum deoxidized steel normalized from above the coarsening temperature of the austenite would have brought the level up nearly to the top side of the range. So far as the writer knows, however, the strength of plain 0.5 Mo steel cannot be brought up to the level obtained in this investigation for Heat 3108 by heat treatment alone.

The ductility values obtained in the rupture tests on the boron-treated material were similar to those commonly found for annealed plain 0.5 Mo steel.

It seems reasonably certain that a combination of proper boron (or boron + titanium) addition and heat treatment can result in nearly doubling the strength of 0.5 Mo steel at temperatures up to 1000°F. The increase is much greater than that for the usual commercial heat treatments used for plain 0.5 Mo steel. It should be recognized that the entire increase may not be due to boron alone, because it is known that titanium additions can also give a substantial increase in strength at high temperature.

The high strengths certainly warrant further consideration of the development of low alloy steel with small boron additions. In such developments, however, consideration should be given to the following possible difficulties based on commercial experience:

1. Plain 0.5 Mo steel appears to have limited applicability in the future at temperatures above 850°or 900°F, due to graphitization during service. There seems to be little hope that the "Grainal 79" addition would eliminate this difficulty.

2. The hardness level and tensile properties are considerably higher than has been customary for tubes and pipes used at high temperatures. It remains to be seen how much difficulty this might cause from stress concentrations encountered in service, and the attendant problems of obtaining acceptance by users.

3. All experience in attempting to apply boron additions under production conditions to steels for high temperature service has indicated difficulties which have not been solved. The reasons are not clear. The amounts added in this case were probably considerably less than in most cases which have come to the writer's attention. The influence of this on control in large heats is not well established. There are cases of this type where the desired effects have not been obtained in large heats, even though they were easily obtained in laboratory heats.

4. The experience of low strength from improperly heat treated bars from the second lot suggests that the critical nature of the response to heat treatment should be explored.

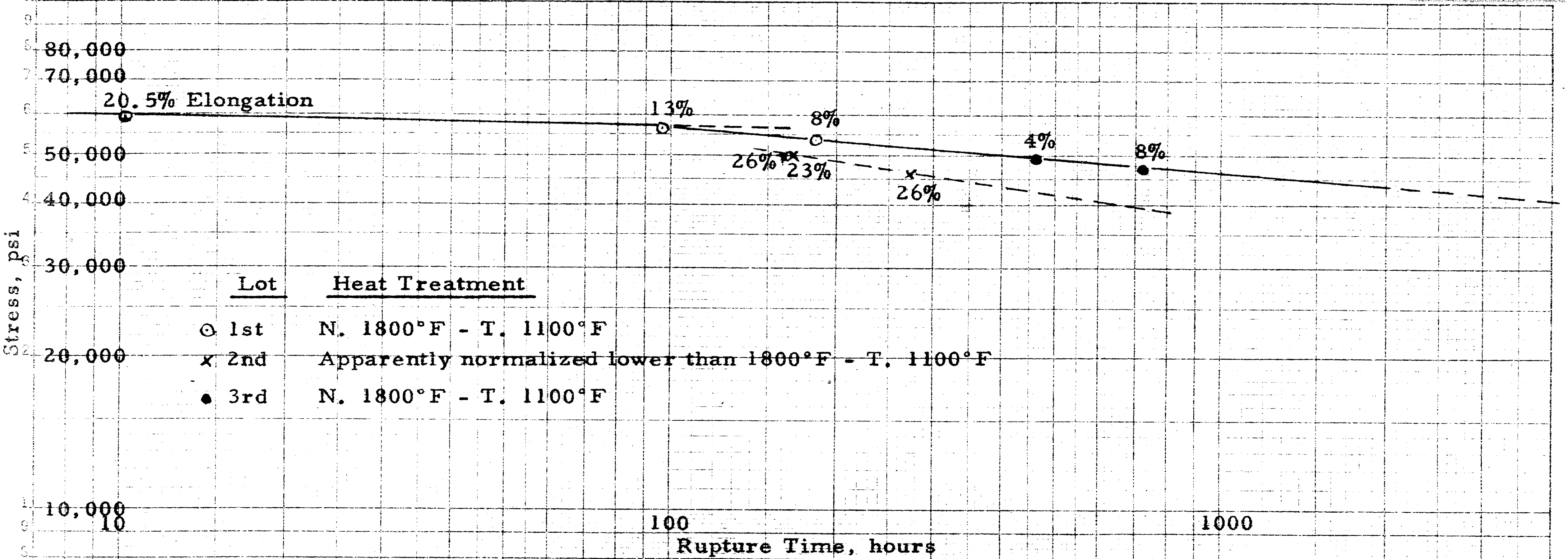

Figure 2. - Comparison of Rupture-Test Results at 1000°F from Material Properly Normalized from 1800°F and the Second Lot of Material Which Apparently Was Normalized from a Lower Temperature.

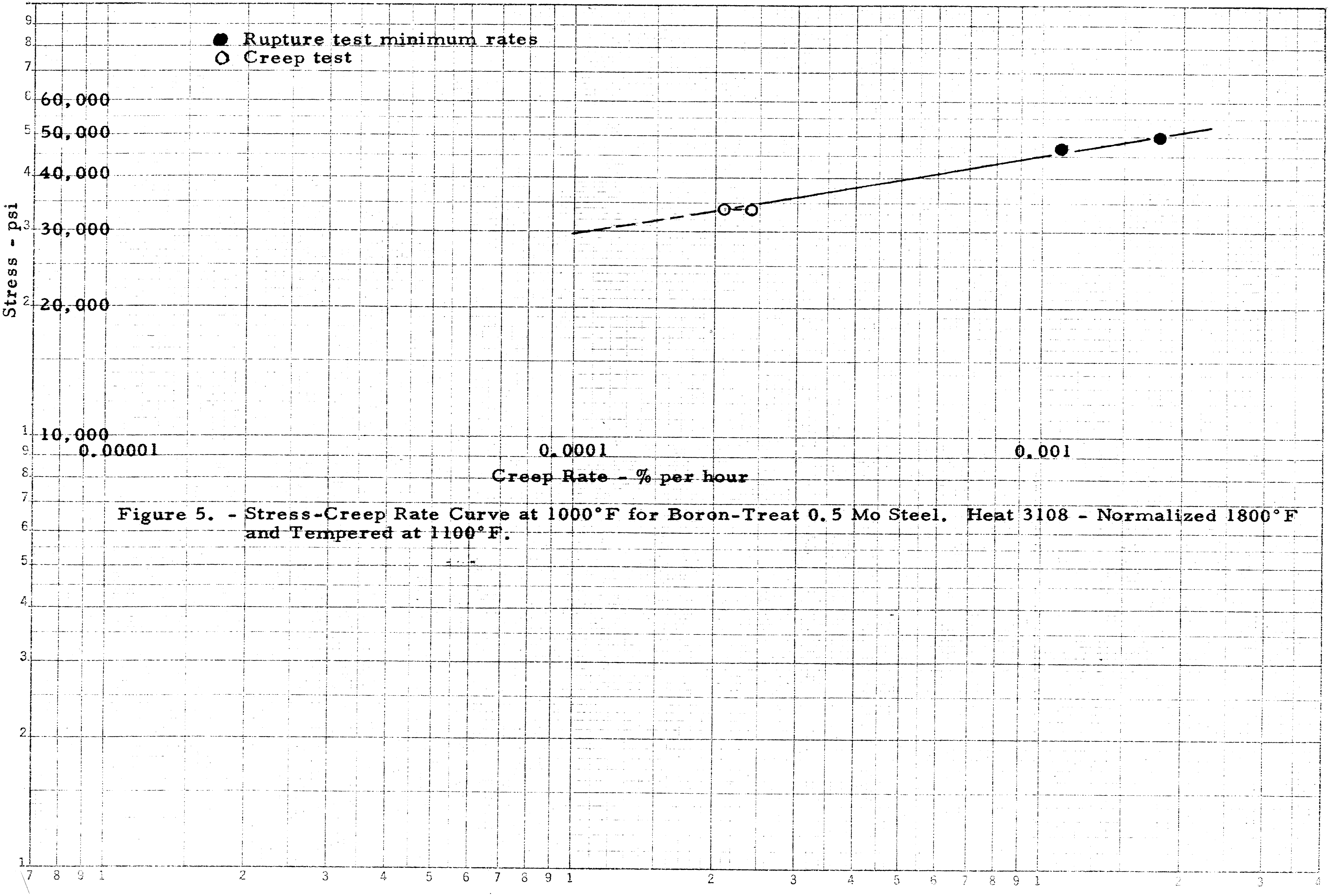

Figure 5. - Stress-Creep Rate Curve at 1000°F for Boron-Treat 0.5 Mo Steel. Heat 3108 - Normalized 1800°F and Tempered at 1100°F.