

July 30, 1974

SADAO OHTA ET AL

3,826,689

AUSTENITE TYPE HEAT-RESISTING STEEL HAVING HIGH
STRENGTH AT AN ELEVATED TEMPERATURE AND THE
PROCESS FOR PRODUCING SAME

Filed March 9, 1972

2 Sheets-Sheet 1

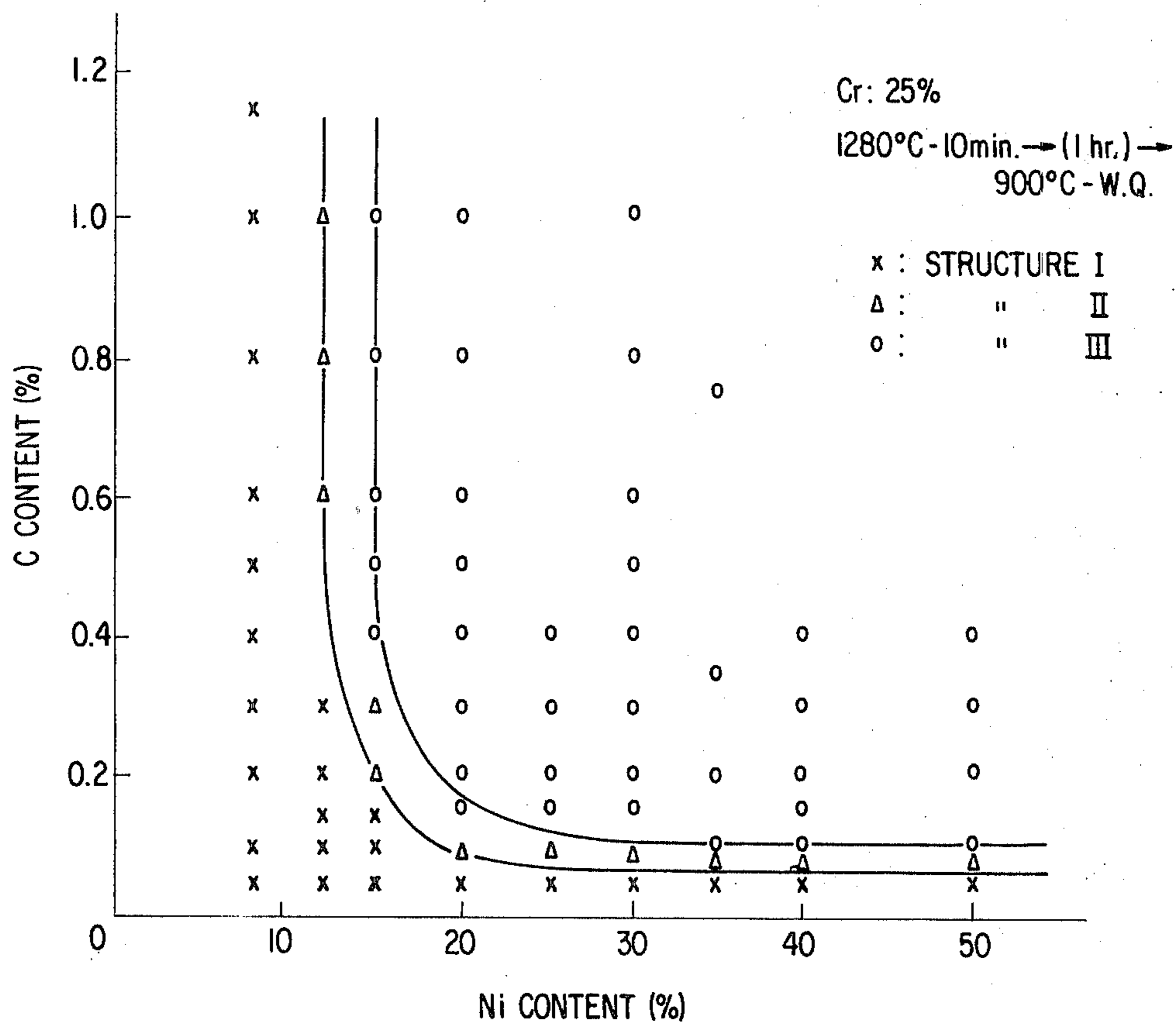


FIG. 1

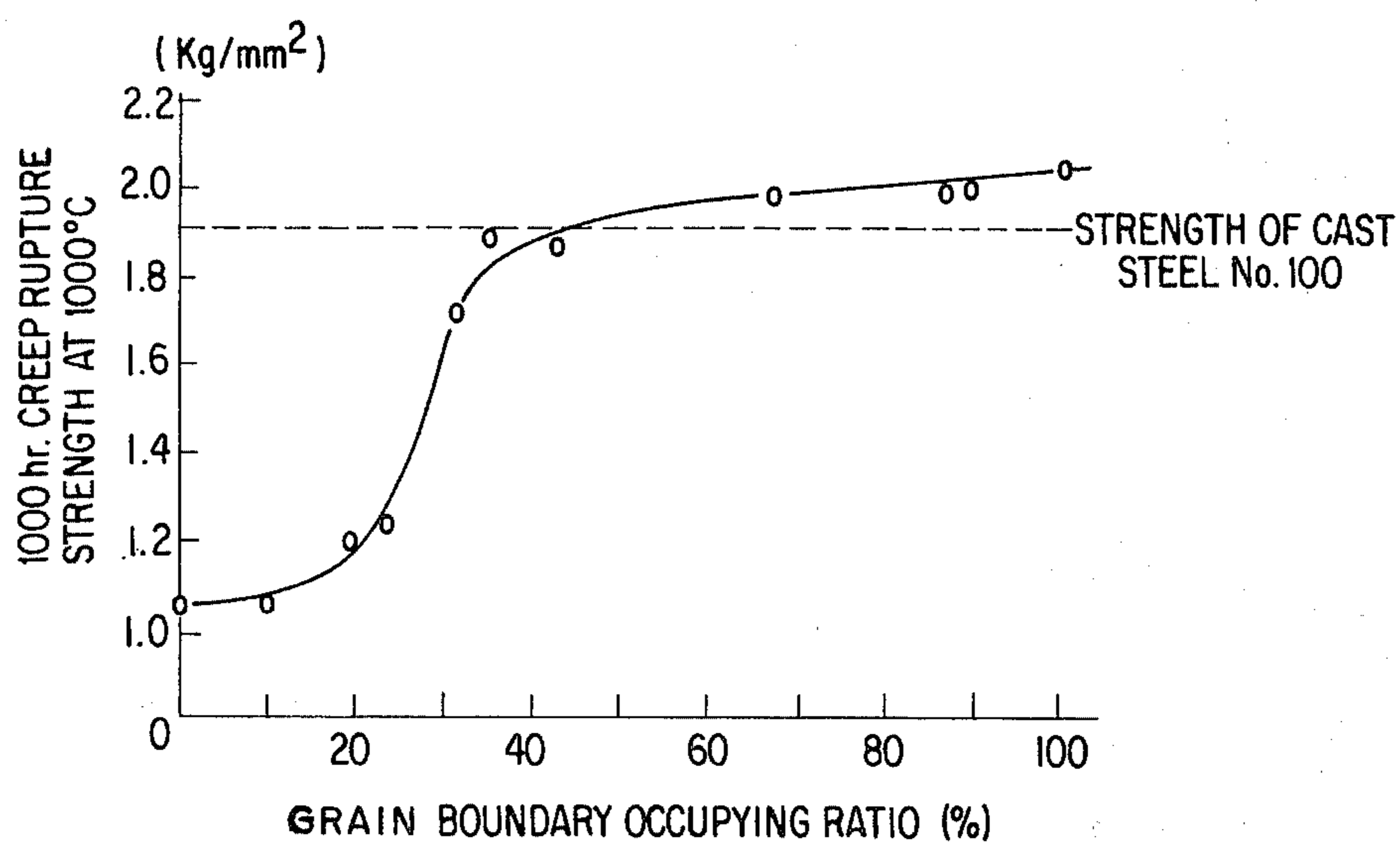


FIG. 3

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2 Sheets-Sheet 2

FIG. 2(I)

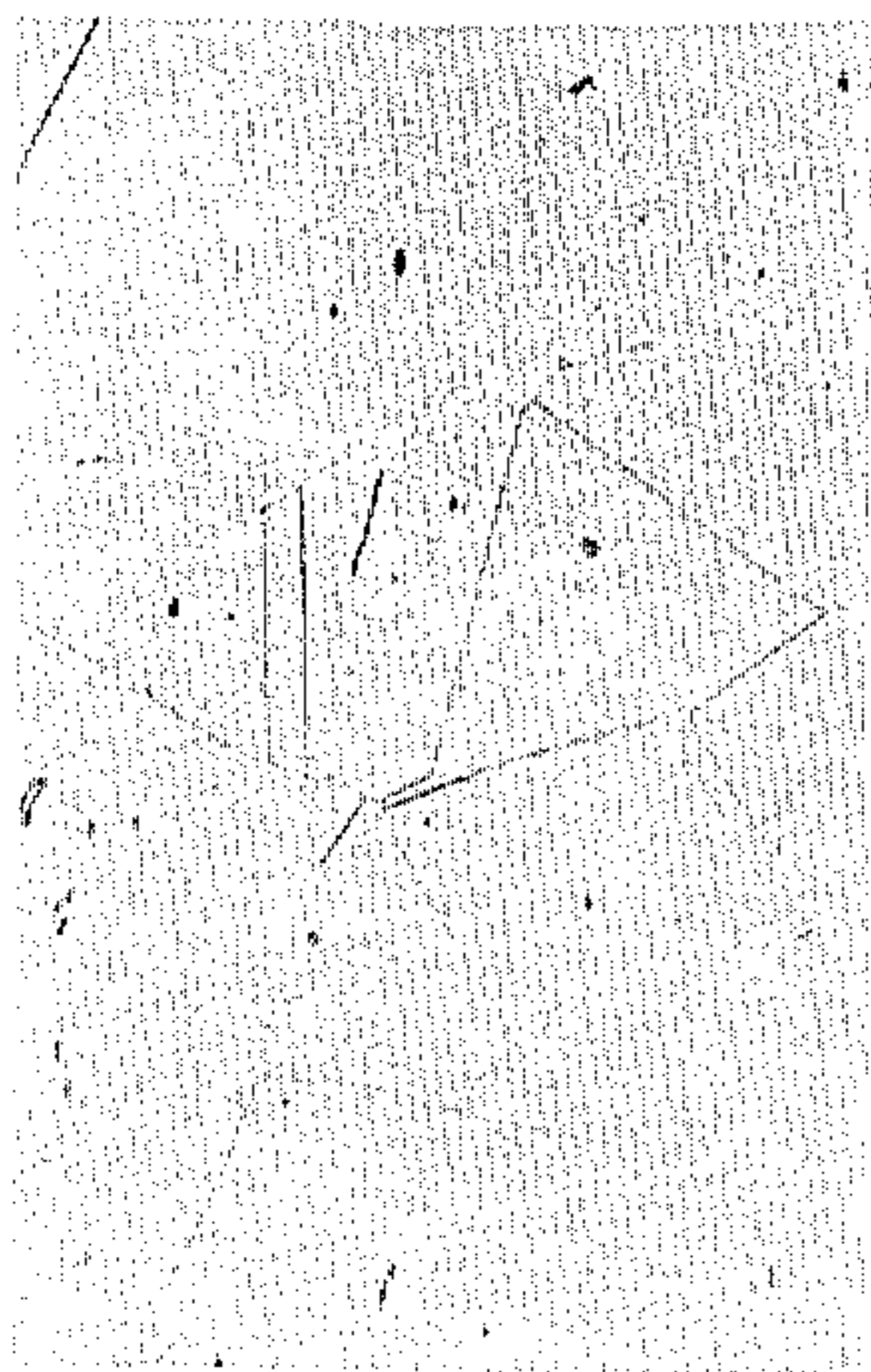


FIG. 2(II)

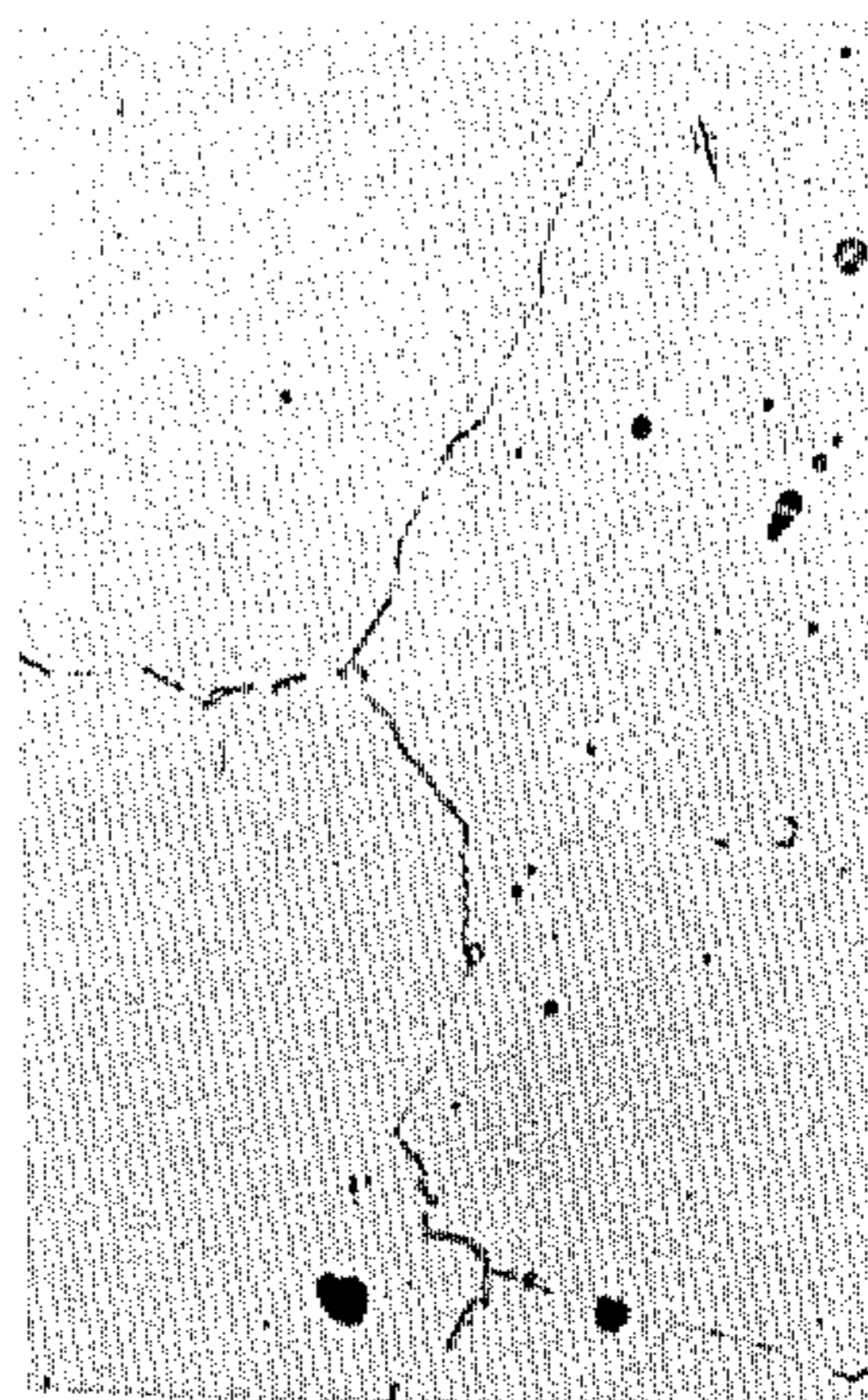


FIG. 2(III)

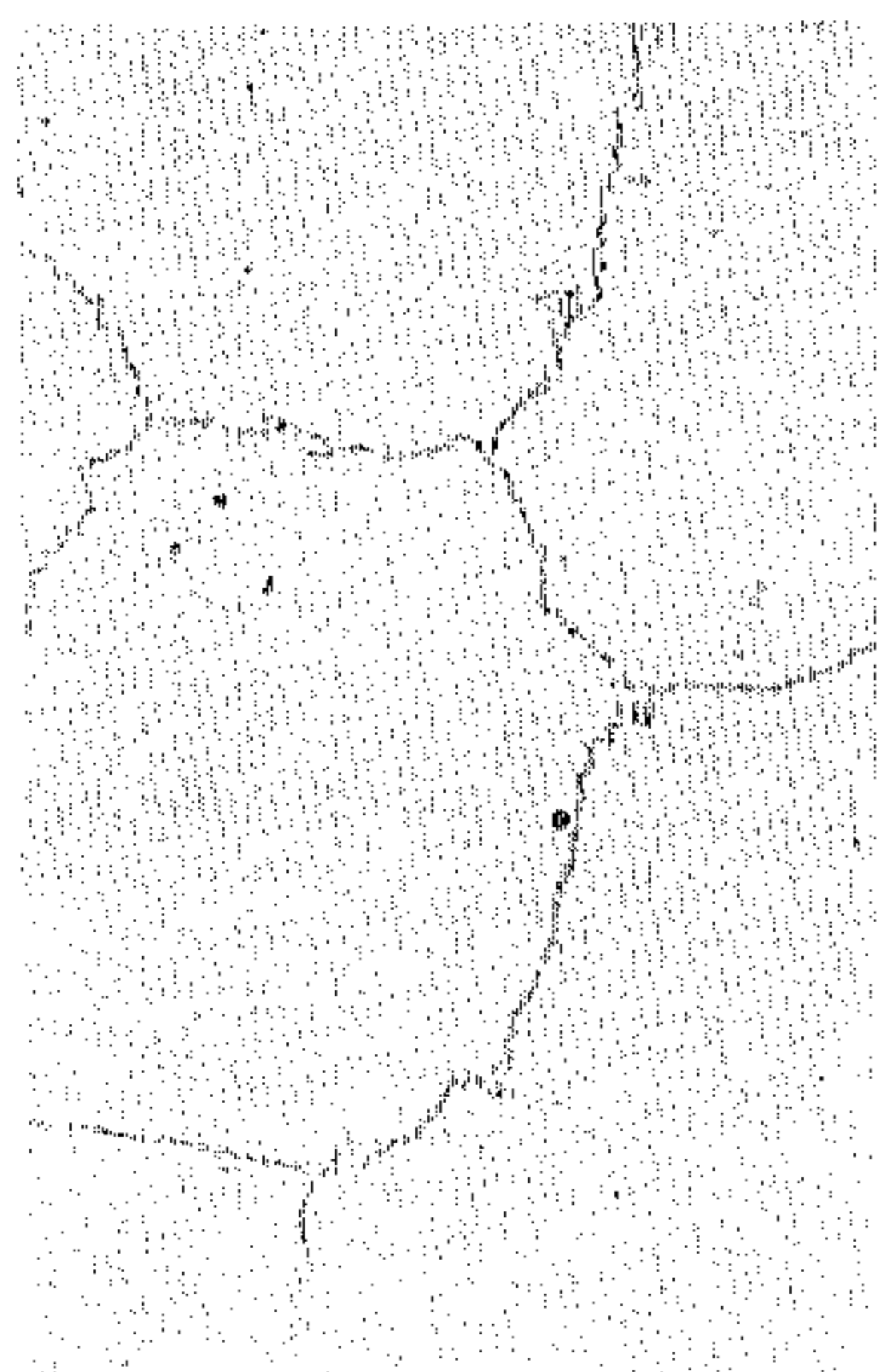
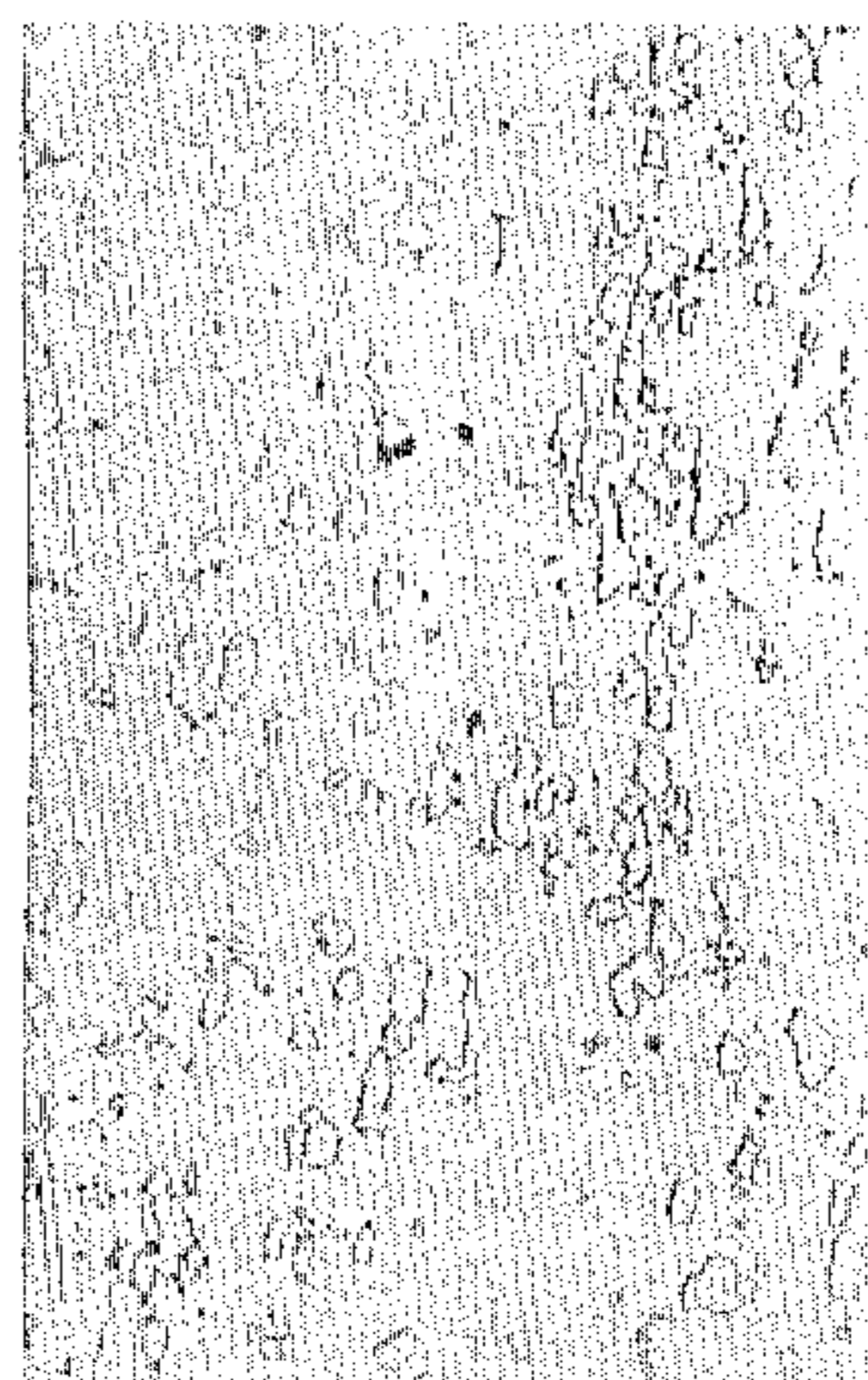


FIG. 2(IV)



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AUSTENITE TYPE HEAT-RESISTING STEEL HAVING HIGH STRENGTH AT AN ELEVATED TEMPERATURE AND THE PROCESS FOR PRODUCING SAME

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5 Claims

ABSTRACT OF THE DISCLOSURE

An austenite type heat-resistant steel, containing in weight percent from 0.1 to 1% carbon, from 0.01 to 3% silicon, from 0.01 to 10% manganese, from 13 to 35% chromium, from 15 to 50% nickel, and the balance essentially impurities and iron, or additionally other elements such as Co, W, Mo, Nb, Ti, Al and/or N, which is characterized by high strength at elevated temperatures, and which is adaptable to forming by forging or centrifugal casting processes, is provided herein.

BACKGROUND OF THE INVENTION

Field Of The Invention

This invention relates to an austenite type heat-resistant steel which is capable of use at elevated temperatures of over about 750° C. This invention further relates to a process for producing the same.

Description Of Prior Art

Recent developments in the petrochemical industry, particularly in the production of ammonia, methanol, ethylene or the like, has resulted in a demand for steels which are capable of withstanding high temperatures, in the order of over 750° C., for extended periods of time.

Heretofore, 0.05C-25Cr-20 Ni stainless steel and 20Cr-32Ni-0.5Al-0.5Ti-Fe alloy (Incolloy 800 alloy) have found wide use for applications involving temperatures of below 850° C. These alloys, however, have suffered from a variety of shortcomings. For one, since these alloys contain a relatively low carbon content, their strength is considerably reduced and they are generally incapable of withstanding a sustained load at such elevated temperatures. Although these shortcomings can be avoided to some extent when high carbon-high chromium-high nickel stainless steels are used as castings produced by the centrifugal casting process, the use of that technique does not alleviate the entire problem. Tubes produced by the centrifugal casting process are characterized by high strength at elevated temperatures, but they cannot be formed into small diameter shapes of less than 75 mm. O.D. and wall thicknesses of below 6 mm. Moreover, they cannot be formed into tubes of lengths of over 2 m. with diameters of 75 mm. O.D. nor tubes of lengths of over 4 m. with diameters of over 120 mm. O.D. Furthermore, tubes formed by that method have generally inferior inner surfaces and, of course, that technique cannot be used to produce sheets.

Previous attempts have been made to improve the high temperature strength of high carbon-high chromium-high nickel stainless steel, by use of a solution heat treatment in which, after the steel has been hot or cold worked, it is heated to a temperature of from 1,000° to 1,300° C., and then water quenched. These efforts, however, have met with only limited success in terms of creep rupture strength, and the strength is only slightly improved as compared with steels of low carbon contents, such as

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0.50C-25Cr20Ni stainless steel or 20Cr-32Ni-0.51Al-0.5 Ti-Fe alloy.

Other attempts at improving high temperature strength properties include the addition of Co, W, Nb, Ti, Al or the like, to the forging alloys, for instance, to such steels as high Cr-high Ni stainless steel having less than 0.1% level of carbon. This has been shown to be satisfactory in certain instances to provide strength characteristics comparable to that of high C-high Cr-high Ni stainless cast steels. Nevertheless, those alloys are generally characterized by poor hot or cold workability, so that they are difficult to form into long length, small diameter tubes.

A need continues to exist, therefore, for a high temperature, heat resistant steel having high strength properties at the higher temperature ranges which possesses good workability.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a high Cr-high Ni heat resistant steel having high strength properties at temperatures of above 750° C.

It is another object of the invention to provide high Cr-high Ni heat resistant steel which is suitable for use in forgings, rollings, or extruded forms with the superb characteristics which permit the production of tubes having improved wall thickness and length and the production of sheets.

It is a still further object of the present invention to provide a process for producing such a high Cr-high Ni heat resistant steel.

These and other objects, as will hereinafter become more readily apparent, have now been attained by the discovery that the high Cr-high Ni heat resistant steel having high strength characteristics at elevated temperatures and which has desirable forging, rolling or extrusion characteristics, can be obtained by the use of a novel alloy. In particular, it has now been discovered that the creep rupture mechanism of a steel used at elevated temperatures ranging from 800° C. to 1,000° C. appears to differ from that of a steel used within a temperature range of from 600° to 700° C. At temperatures above 750° C., say, at 1,000° C., in order to attain improved creep rupture strength, it is necessary for the carbide to precipitate on the grain boundaries in a continuous or partially-continuous form. The ratio of the carbides occupying the grain boundaries (the grain boundary occupying ratio) should nevertheless be over 30%, preferably over 50%. These facts have led to the discovery of an alloy steel wherein the carbides appearing on the grain boundaries are precipitated in continuous or partially-continuous form. This steel alloy contains carbon, silicon, manganese, chromium, nickel, and the balance essentially impurities and iron.

This steel alloy is produced by a novel process which includes a unique heat treatment technique wherein the steel is heated to a temperature in the range of from 1,150° C. to the solidus temperature, and it is then cooled to a temperature of 950° C. or higher. Subsequent to this solution heat treatment, after the casting or working of the steel, the slow cooling is followed by water quenching.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of austenite type stainless steel compositions containing from 0.004 to 1.2% carbon, about 25% chromium and from 8 to 50% nickel;

FIG. 2 are photomicrographs of selected composition structures wherein FIGS. I and II are provided for purposes of comparison with structure III of the present invention. FIG. IV shows a structure having a carbide precipitate dispersed within the grains; and,

FIG. 3 is a graphical representation of the ratio of grain boundary occupation of carbide and its effect on creep strength.

DETAILED DESCRIPTION OF THE INVENTION

In greater detail, the present invention provides an austenite type heat resistant steel having high strength properties at elevated temperatures, and containing, in weight percent, from 0.1 to 1% carbon, from 0.01 to 3% silicon, from 0.01 to 10% manganese, from 13 to 35% chromium, from 15 to 50% nickel, and the balance essentially impurities and iron. This alloy is characterized by a precipitation of carbides on the grain boundaries in a continuous or partially-continuous form.

The present invention further provides an austenite type heat resistant steel containing, in weight percent, in addition to the alloy elements referred to above, at least one element selected from a group of less than 30% cobalt, less than 10% tungsten, less than 10% molybdenum, less than 5% niobium, less than 5% titanium, less than 5% aluminum and less than 0.5% nitrogen.

Furthermore, the present invention presents a process for producing an austenite heat resistant steel having the above-defined composition which is subjected, subsequent to casting or working, to a heat treatment at a temperature of from 1,150° C. up to the solidus temperature, followed by slow cooling from said temperature to a temperature of 950° C. or higher, for a time of from 5 seconds to one hour, and thereafter water quenching.

Referring now to FIG. 2, photomicrographs of austenite type stainless steel structures having a variety of compositions containing from 0.004 to 1.2% carbon, about 25% chromium and from 8 to 50% nickel are shown. Those compositions were subjected to heat at a temperature of 1,280° C. for 10 minutes, slow cooling from 1,280° C. down to 950° C. for one hour, and then water quenching to room temperature.

Table I further describes the structures shown in FIG. 2 and indicates the creep rupture strength of the various austenite type compositions.

FIG. 2 (I) shows a structure having no carbide precipitate on the grain boundaries; (II) shows carbide precipitate aligned partially on the grain boundaries, with a grain boundary occupying ratio of up to 30%; (III) shows a structure having a continuous carbide precipitate on the grain boundaries, and (IV) shows a structure having a carbide precipitate dispersed within the grains. As shown in Table I, sample No. 101 of the structure (I) where no carbide precipitation occurred on the grain boundaries, comparatively inferior creep rupture strength was obtained. In Sample No. 102 of structure (II), carbide was precipitated only in partial alignment with the grain boundaries and likewise showed a comparatively low creep rupture strength. In contrast, Samples Nos. 102 to 109 of the structure (III), wherein carbide precipitation occurs on the grain boundaries, improved creep rupture strength was obtained.

FIG. 3 shows the result of a series of tests made to clarify the effect of the quantity ratio of carbide precipitation on the grain boundary on the creep rupture strength of steels containing 0.4% carbon, 25% chromium, and 20% nickel.

This figure clearly indicates that the higher the quantity ratio of carbide precipitation in grain boundary, the higher will be the creep rupture strength. If the quantity ratio falls to less than 20%, however, the creep rupture strength will be only moderately increased. If the quantity ratio in the grain boundary is more than 30%, the creep rupture strength will be greatly improved and will be substantially equal to that of cast materials. Moreover, the creep rupture strength will be superior to that of cast materials if quantity ratio in the grain boundary exceeds 50%.

From the above results, it is concluded that the ratio of grain boundary occupied by carbides should be over 30%, and preferably over 50%.

With particular reference to the alloying elements such as C and Ni which play an important role from the structural viewpoint, it can be appreciated from FIG. 1 that

if the carbon level is less than 0.1%, such as in structures (I) and (II), the creep rupture strength will be extremely inferior, whereas if the carbon level is over 0.1% as shown in (III) of Table I, the creep rupture strength will be greater. However, if the carbon level is over a certain limit, the creep rupture strength will be reduced conversely, as shown in Table I. Furthermore, the higher the carbon content, the lower the cold workability. With these factors in mind, the upper limit of the carbon content has been set as 1%.

The amount of Ni can vary from between 15 and 50%. Table 2 shows the creep rupture strength at 1,000° C., of a stainless steel containing about 0.4% carbon, about 45% chromium, and from 8 to 45% nickel. This steel had been subjected to heat treatment at 1,280° C. for 10 minutes, and was then slowly cooled from 1,280° C. down to 950° C. for one hour, followed by rapid cooling to room temperature. Samples 201 and 202 represent structure (I) characterized by a low creep rupture strength, while samples 203 to 208 containing over 15.7% Ni, represent structure (III) which is characterized by greatly improved creep rupture strength. The higher the nickel content, the higher will be the creep rupture strength. However, if the nickel content exceeds 50%, no further improvement in strength will be obtained, and it will only be adding to the costs.

TABLE 1

Sample number	Alloy element, percent			Structure	1,000 hr. creep rupture strength (kg./mm. ²) at 1,000° C.
	C	Cr	Ni		
100	0.40	24.91	19.92	I	1.90
101	0.04	25.18	20.40	II	0.90
102	0.08	25.32	19.99	III	0.95
103	0.14	24.69	20.38	III	1.65
104	0.20	25.04	19.57	III	1.70
105	0.31	25.46	20.59	III	1.90
106	0.43	25.82	20.41	III	1.95
107	0.65	25.18	20.23	III	1.90
108	0.82	25.45	19.74	III	1.90
109	0.95	24.71	20.16	III	1.80
110	1.15	25.38	20.21	III	1.65

TABLE 2

Sample number	Alloy element, percent			Structure	1,000 hr. creep rupture strength (kg./mm. ²) at 1,000° C.
	C	Cr	Ni		
201	0.39	25.24	8.29	I	0.85
202	0.42	25.56	13.51	I	0.90
203	0.47	25.38	15.70	III	1.85
204	0.43	25.80	20.46	III	1.95
205	0.35	25.42	24.82	III	2.05
206	0.39	24.75	30.67	III	2.00
207	0.42	24.96	35.53	III	2.10
208	0.37	25.18	45.40	III	2.00

Silicon may be used within the range of 0.01 to 3%. Silicon is added to the molten steel during production for the purpose of deoxidation. Although silicon improves the oxidation resistance of the steel for use at elevated temperatures, greater than 3% will impair weldability and workability, and enhance the formation of a sigma phase.

Manganese may be present in amounts of from 0.1 to 10%, also, for the purpose of deoxidation during steel making. Manganese tends to stabilize the austenite and to prevent the formation of a sigma phase. If more than 10%, however, is used, oxidation resistance is reduced.

Chromium may be present in amounts of from 15 to 35%, also to improve the oxidation resistance of the steel. For product use at temperatures of over 750° C., the chromium content should be at least 15%. However, if greater than 35% is used, such larger amounts can cause difficulties in hot or cold working, and also increase the tendency of sigma phase formation.

To further improve the creep rupture strength at elevated temperatures, Co, W, Mo, Nb, Ti, Al and/or N, may be further added.

Cobalt should be present in amounts of less than 30%. Cobalt will completely dissolve in the matrix of high

Cr-high Ni austenite to greatly improve the creep rupture strength. If the level exceeds 30%, the cost of the steel will be increased unfavorably.

If tungsten is used, the quantity present is limited to amounts of below 10%. Tungsten, together with molybdenum, dissolve at the solution heat treatment temperature in the austenite matrix, with a part thereof precipitating in the form of carbides during the slow cooling. The greater amount, however, will remain in solid solution, so that during use, it will precipitate as fine carbide particles within the grains to thereby increase the product strength. However, even if the level is increased beyond 10%, there will be no substantial increased effectiveness, and the hot or cold workability can be impaired.

in FIG. 2 (IV). As can be observed, no precipitate occurred on the grain boundaries. It is advantageous, in a sense, that the higher the temperature of the solution heat treatment, the shorter will be the time required for the solution of the carbides. However, if the temperature reaches the solidus line of the steel, the steel is likely to melt. Accordingly, the temperature of the solution heat treatment is limited to the range of from 1,150° C. to the solidus line.

Table 4 compares the structures of steels according to the present invention with certain controls. Those samples were heated at 1,280° C. for 10 minutes after forging, and then slowly cooled to 950° C. for a time ranging from 1.1 second to 1.5 hour.

TABLE 4

Sample number	Alloy element, percent			Cooling time from 1,280° C. down to 950° C. (X)										
	C	Cr	Ni	1.1 sec.	2.4 sec.	4.1 sec.	5.7 sec.	15.6 sec.	28.3 sec.	1.1 min.	4.3 min.	2.85 min.	1 hr.	1.5 hr.
401.....	0.04	18.27	8.36	I	I	I	I	I	I	I	I	I	I	I.
402.....	0.58	17.98	8.01	I	I	I	I	I	I	I	I	I	I	II.
411.....	0.07	18.16	12.11	I	I	I	I	I	I	I	I	I	I	I.
412.....	0.78	18.03	12.28	I	I	I	I	I	I	I	I	I	II	II.
421.....	0.05	20.33	15.27	I	I	I	I	I	I	I	I	I	I	I.
422.....	0.62	19.85	15.53	I	I	I	I	II	II	II	III	III	III	III.
431.....	0.08	25.32	19.99	I	I	I	I	I	I	I	I	I	I	I.
432.....	0.14	24.69	20.38	I	I	I	I	I	I	I	II	II	III	III.
433.....	0.20	25.04	19.57	I	I	I	I	II	II	III	III	III	III	III.
434.....	0.43	25.82	20.41	I	I	I	II	III	III	III	III	III	III	III.
435.....	0.95	24.71	20.16	I	I	II	III	III	III	III	III	III	III	III.
436.....	1.15	25.38	20.21	I	I	II	III	III	III	III	III	III	III	III.
441.....	0.04	20.21	31.82	I	I	I	I	I	I	I	I	I	I	I.
442.....	0.13	20.16	32.05	I	I	I	II	II	III	III	III	III	III	III.
443.....	0.28	19.94	32.33	I	I	I	II	III	III	III	III	III	III	III.
444.....	0.57	20.01	32.17	I	I	II	III	III	III	III	III	III	III	III.
451.....	0.04	25.07	47.80	I	I	I	I	I	I	I	I	I	I	I.
452.....	0.17	24.85	47.52	I	I	II	II	III	III	III	III	III	III	III.
453.....	0.28	24.91	48.33	I	II	II	III	III	III	III	III	III	III	III.

Niobium may be present in amounts of below 5%. The addition of niobium is intended to permit the carbides to precipitate within the grain boundaries during the use of steels to thereby improve strength. However, if the quantity of niobium used is over 5%, the hot workability and weldability will be greatly impaired.

Titanium may be present in amounts of below 5%. Titanium tends to precipitate, during the use at an elevated temperature, as carbides or Ni₃Ti within the grain boundaries. However, with a level of over 5%, hot workability of the product will be greatly impaired.

Aluminum may be present in amounts of below 5%. Aluminum tends to precipitate as Ni₃Al during use at elevated temperatures to thereby increase the strength of the steel. However, if the quantity of aluminum used is over 5%, the hot workability and weldability will be impaired.

Nitrogen may be present in amounts of up to 0.5%. Nitrogen tends to dissolve in the matrix of the austenite to increase the strength of the steel. However, if greater than 0.5% N is present, pores can develop in the ingot, thus causing difficulties in producing good steel.

HEAT TREATMENT ACCORDING TO THIS INVENTION

Table 3 describes the structures of steels according to the present invention, which have been heated to a temperature of from 1,050° to 1,350° C. for 30 minutes, subsequent to the forging, and then have been slowly cooled to 950° C. for one hour and then water quenched.

Sample number	Alloy element, percent			TABLE 3 Solution heat treatment temperature, ° C.						
	C	Cr	Ni	1,050	1,100	1,150	1,200	1,250	1,300	1,350
301.....	0.41	20.51	15.3	IV	IV	III	III	III	Melt....	Melt.
302.....	0.43	25.82	20.4	IV	IV	IV	IV	III	---do---	Do.
303.....	0.24	25.13	35.4	IV	IV	IV	IV	III	III.....	Do.
304.....	0.12	27.56	39.5	IV	IV	IV	IV	III	III.....	Do.

If the heating treatment is too low, part of the carbide will remain undissolved and, during the subsequent cooling, the undissolved carbide will serve as a nuclei for carbide precipitation, resulting in a structure as shown

It has been a common practice in producing forgings, such as producing in forgings of 25 Cr-20Ni type stainless steel having a carbon level of below 0.1% or in producing forgings of Incolloy 800 alloy, or the like, to use a solution heat treatment in which the forgings are water quenched immediately after the heating at a solution treatment temperature. However, as shown in Table 4, the structure (I) is obtained when subjected to conventional solution heat treatment in which the forgings are immediately water quenched from a temperature of 1,280° C. to 950° C. within a period of 1.1 seconds. In such a conventional solution heat treatment, the structure (III) cannot be achieved, even if the carbon level is increased to greater than 1%. Alternatively, when the steel is cooled by means of helium gas or cool air injection from 1,280° C. down to 950° C. in a period of 2 to 4 seconds, only the structure up to (II) can be obtained even with the steel containing high levels of C and Ni. In contrast, when cooling is carried out over a period of more than 5 seconds, the structure (III) is obtained at a carbon content of 0.9% or higher in case of 25Cr-20Ni steel, at a carbon content of 0.5% or higher in case of 20Cr-32Ni steel and at a carbon content of 0.2% or higher in case of 25 Cr-47Ni steel, respectively. Accordingly, cooling should occur over a period of more than 5 seconds.

Table 5 shows creep rupture strengths at 1,000° C. for samples as shown in Table 4. The results of the tests are also provided to show the desirability of slower cooling rates. On the other hand, if it takes over one hour to

complete the 1,208° C. to 950° C. temperature transition, it will adversely affect the strength so that it may be concluded that cooling should occur over a period of from 5 seconds to one hour.

TABLE 5

Test sample number	Alloy element, percent		Cooling time from 1,280° C. down to 950° C.			
	C	Cr	Ni	1.1 sec.		1.5 hr.
				Struc- ture	Strength* (kg./mm. ²)	
402	0.53	17.98	8.01	I	0.65	I
411	0.07	18.16	12.11	I	0.75	I
412	0.78	18.03	12.28	I	0.80	I
422	0.62	19.85	15.53	I	0.90	I
431	0.08	25.32	19.99	I	1.00	I
432	0.14	24.69	20.38	I	1.00	I
434	0.43	25.82	20.41	I	1.05	I
435	0.95	24.71	20.16	I	1.05	I
443	0.28	19.94	32.33	I	1.10	I
452	0.17	24.85	47.52	I	1.10	I
402	0.60	0.65	0.65	I	0.65	I
411	0.75	0.75	0.75	I	0.75	I
412	0.80	0.80	0.80	I	0.80	I
422	0.90	0.90	0.90	I	0.90	I
431	1.00	1.00	1.00	I	1.00	I
432	1.00	1.00	1.00	I	1.00	I
434	1.05	1.05	1.05	I	1.05	I
435	1.05	1.05	1.05	I	1.05	I
443	1.10	1.10	1.10	I	1.10	I
452	1.10	1.10	1.10	I	1.10	I
402	0.60	0.65	0.65	I	0.65	I
411	0.75	0.75	0.75	I	0.75	I
412	0.80	0.80	0.80	I	0.80	I
422	0.90	0.90	0.90	I	0.90	I
431	1.00	1.00	1.00	I	1.00	I
432	1.00	1.00	1.00	I	1.00	I
434	1.05	1.05	1.05	I	1.05	I
435	1.05	1.05	1.05	I	1.05	I
443	1.10	1.10	1.10	I	1.10	I
452	1.10	1.10	1.10	I	1.10	I

*1,000 hr. creep rupture strength at 1,000° C.

**Structure.

The lower the temperature at which the cooling procedure terminates, the greater will be the amount of carbide occurring on the grain boundaries, but the smaller will be the amount of carbide forming elements contained as solid solution in the grains, which will be available to precipitate within the grains during creep conditions. For this reason, the lower the temperature at which the slow cooling procedure terminates, the higher will be the creep rupture strength. On the other hand, the creep rupture strength will reach a maximum at a certain temperature. If, however, the range of the slow cooling procedure extends below a certain minimum temperature, the creep rupture strength will be lowered. Table 6 shows the effect of the terminating temperature of the cooling procedure on the structure of the steel and on the attainable creep rupture strength. In this test, the heat treatment was conducted at 1,280° C. for 30 minutes, followed by slow cooling to a temperature between 1,265° C. and 850° C. for one hour. The heat treated material was then quenched in water.

As can be seen from Table 6, good results are attained if the terminal cooling point is no lower than 950° C. At lower temperatures, creep rupture strength begins to be adversely affected. If the terminating temperature is around 1,265° C., structure (III) is not obtained. In fact, unless cooling treatment extends down to 1,250° C., structure (III) will not be obtained. For these reasons, the terminal point of the cooling treatment should be within the range of from 950° C. to 1,250° C.

Table 7 indicates the creep rupture strength of 0.4C-25Cr-20 Ni steels which have been subjected, in turn, to forging, heating to 1,280° C., slow cooling from the above temperature down to 1,050° C. for one hour and then water quenching, or air cooling (rapid cooling) or furnace cooling.

TABLE 7

Alloy element, percent	Creep rupture strength (kg./mm. ²)*		
	Cr	Ni	W.Q.
C	0.43	20.41	2.10
0.43	25.83	20.41	1.90

* 1,000 hr. creep rupture strength at 1,000° C.

The structures thus obtained are unexceptionally the structure (III). However, the creep rupture strength of steels subjected to water quenching and air cooling exhibit higher values, whereas that of the steels subjected to furnace cooling show extremely lower values, suggesting that no substantial improvement occurs as compared to steels which have been subjected to conventional solution heat treatment involving the water quenching immediately after the heating at 1,280° C. It is theorized that this effect is due to the precipitation of the carbides during the furnace cooling with a resultant precipitation on the grain boundaries together with a decrease in the amount of carbide forming elements contained as solid solution in the matrix. This results in a decrease in the amount of carbides which will precipitate in the matrix during creep, so that the effect of the carbides precipitation on the grain boundaries is offset. Preferably, after the slow cooling has terminated at a temperature in the range from 950° C. to 1,250° C., water quenching or air cooling to room temperature can be used to accelerate the cooling rate.

Although the description has been given with reference to the forging materials, the same can apply to the casting materials.

Having now generally described the invention, a further understanding can be attained by reference to certain specific Examples which are presented herein for purposes of

TABLE 6

Slow cooling terminating temperature (° C.)	0.41C-20.51Cr-15.30Ni		0.43C-25.83Cr-20.41Ni		0.37C-25.18Cr-45.40Ni	
	Struc- ture	Creep rupture strength (kg./mm. ²)*	Struc- ture	Creep rupture strength (kg./mm. ²)*	Struc- ture	Creep rupture strength (kg./mm. ²)*
1,265	I	0.80	I	0.90	II	1.00
1,250	I	0.75	I	0.95	III	1.75
1,200	I	0.70	II	1.05	III	1.90
1,150	II	0.85	III	1.85	III	2.00
1,100	II	0.90	III	1.90	III	2.10
1,050	II	0.95	III	2.10	III	2.05
1,000	III	1.75	III	2.00	III	1.95
950	III	1.85	III	1.95	III	1.85
900	III	1.50	III	1.65	III	1.60
850	III	1.35	III	1.45	III	1.40

*1,000 hr. creep rupture strength at 1,000° C.

illustration only and are not intended to be limiting in any manner unless otherwise specified.

EXAMPLE 1

Table 8 shows the results of tests using steel containing 25% Cr and 15% Ni. The conventional forging material, i.e., Sample No. 81, has an extremely low strength than high carbon casting material, i.e., sample No. 80. Samples Nos. 82 and 84 which have been subjected to the normal

heated to a temperature of 1,280° C. for 30 minutes and immediately thereafter placed in another furnace maintained at 1,100° C. where it was held for 20 minutes, then followed by the water quenching. Sample No. 97 was heated to a temperature of 1,280° C. for 30 minutes and furnace cooled to a temperature of 1,100° C. for 10 minutes, followed by being held for 10 minutes and then water quenched. Both samples Nos. 96 and 97 show the same degree of strength as that of sample No. 90.

TABLE 9 (EXAMPLE 2)

No.	Alloy element, percent					Type of working	Heat treatment	Creep rupture strength* (kg./mm. ²)				Remarks
	C	Si	Mn	Cr	Ni			800° C.	900° C.	1,000° C.	1,050° C.	
90.....	0.40	1.32	1.06	24.91	19.92	Casting	6.20	3.80	1.90	1.30	Comparative steel.
91.....	0.04	0.32	1.53	25.12	20.37	Forging	1,100° C., 1 hr., W.Q.	3.75	2.05	0.80	0.70	Conventional steel.
92.....	0.43	0.37	1.24	25.82	20.41	do	1,280° C., 30 min., W.Q.	4.50	2.55	0.95	1.00	Comparative steel.
93.....	0.43	0.37	1.24	25.82	20.41	do	1,280° C., 30 min.-(10 min.)-1,050° C., W.Q.	6.60	3.85	2.00	1.25	Steel of the present invention.
94.....	0.82	0.45	1.04	25.45	19.74	do	1,280° C., 30 min., W.Q.	0.90	Comparative steel.
95.....	0.82	0.45	1.04	25.45	19.74	do	1,280° C., 30 min.-(10 min.)-1,050° C., W.Q.	1.80	Steel of the present invention.
96.....	0.31	0.52	0.97	25.46	20.59	do	1,280° C., 30 min.-1,100° C. 20 min. W.Q.	1.85	Do.
97.....	0.31	0.52	0.97	25.46	20.59	do	1,280° C., 30 min.-(10 min.)-1,100° C., 15 min., W.Q.	1.80	Do.

*Creep rupture strength in 1,000 hours.

solution heat treatment show higher strength than the low carbon sample No. 81, but they are extremely inferior in strength to the casting material of Sample No. 80.

In contrast to this, samples Nos. 83 and 85 show extremely high strengths as compared to samples Nos. 81, 82 and 84, presenting substantially the same strength as that of the casting material sample No. 80.

TABLE 8 (EXAMPLE 1)

No.	Alloy element, percent					Type of working	Heat treatment	Creep rupture strength* (kg./mm. ²)		Remarks
	C	Si	Mn	Cr	Ni			900° C.	1,000° C.	
80.....	0.55	1.24	1.13	25.72	15.10	Casting	2.40	1.50	Comparative steel.
81.....	0.06	0.38	1.58	25.53	15.58	Forging	1,100° C., 1 hr. W.Q.	1.10	0.75	Conventional steel.
82.....	0.54	0.42	1.33	25.35	15.74	do	1,280° C., 30 min., W.Q.	1.70	1.10	Comparative steel.
83.....	0.54	0.42	1.33	25.35	15.74	do	1,280° C., 30 min. (30 min.)-1,050° C., W.Q.	2.40	1.60	Steel of the present invention.
84.....	0.94	0.61	1.01	24.93	15.01	do	1,280° C., 30 min., W.Q.	1.80	1.15	Comparative steel.
85.....	0.94	0.61	1.01	24.93	15.01	do	1,280° C., 30 min.-(30 min.)-1,050° C., W.Q.	2.50	1.65	Steel of the present invention.

*Creep rupture strength in 1,000 hours.

EXAMPLE 2

Table 9 shows test results using steels containing 25% Cr and 20% Ni. Samples Nos. 92 and 94, which are high carbon steels, have been subjected to conventional solution heat treatment after forging. The conventional low carbon forging steel, sample No. 91, are all lower in strength than the high carbon cast steel of sample No. 90.

TABLE 10 (EXAMPLE 3)

No.	Alloy element, percent					Type of working	Heat treatment	Creep rupture strength* (kg./mm. ²)	Remarks
	C	Si	Mn	Cr	Ni				
1,100.....	0.43	1.34	1.23	14.95	35.18	Casting	2.20	Comparative steel.
1,101.....	0.05	0.35	1.65	15.18	36.03	Forging	1,150° C., 1 hr., W.Q.	0.70	Conventional steel.
1,102.....	0.19	0.68	1.01	15.26	35.72	do	1,280° C., 1 hr., W.Q.	0.95	Comparative steel.
1,103.....	0.19	0.68	1.01	15.26	35.72	do	1,280° C., 1 hr.-(5 min.)-1,050° C., W.Q.	2.15	Steel of the present invention.
1,104.....	0.41	0.35	1.11	15.47	35.50	do	1,280° C., 1 hr., W.Q.	0.90	Comparative steel.
1,105.....	0.41	0.35	1.11	15.47	35.50	do	1,280° C., 1 hr.-(5 min.)-1,050° C., W.Q.	2.10	Steel of the present invention.

*1,000 hr. creep rupture strength at 1,000° C.

TABLE 11 (EXAMPLE 3)

No.	Alloy element, percent					Type of working	Heat treatment	Creep rupture strength* (kg./mm. ²)	Remarks
	C	Si	Mn	Cr	Ni				
1,200.....	0.41	1.48	1.25	18.62	40.73	Casting	1.80	Comparative steel.
1,201.....	0.05	0.28	0.86	19.23	41.30	Forging	1,150° C., 1 hr., W.Q.	0.65	Do.
1,202.....	0.15	0.20	0.65	18.92	40.68	do	1,280° C., 1 hr., W.Q.	0.75	Do.
1,203.....	0.15	0.20	0.65	18.92	40.68	do	1,280° C., 1 hr.-(15 min.)-1,050° C., W.Q.	1.85	Steel of the present invention.
1,204.....	0.30	0.22	0.93	19.75	41.73	do	1,280° C., 1 hr., W.Q.	0.80	Comparative steel.
1,205.....	0.30	0.22	0.93	19.75	41.73	do	1,280° C., 1 hr.-(5 min.)-1,050° C., W.Q.	1.80	Steel of the present invention.

*1,000 hr. creep rupture strength at 1,000° C.

In contrast to this, samples Nos. 93 and 95 present the same degree of strength as that of a high carbon steel No. 90. Samples Nos. 96 and 97 are shown as special examples of the present invention. Sample No. 96 was

EXAMPLE 4

This invention has been essentially described by reference to C-high Cr-high Ni type stainless steel in Examples 1 to 3. Example 4 illustrates the test results of a

stainless steel containing, additionally, at least one of Co, W, Mo, Nb, Ti, Al or N.

Table 12 shows the test results of the steels containing 27% Cr and 33% Ni, which further contain each of Co,

W, Mo, Nb, Ti, Al and N, separately. Table 13 shows the test results of the steels containing 27% Cr and 33% Ni, which steels further contain at least two elements of the elements enumerated above.

TABLE 14 (EXAMPLE 7)

No.	Alloy element, percent						Type of working	Heat treatment	Creep rupture strength* (hr.)	Remarks
	C	Si	Mn	Cr	Ni	Others				
140.....	0.29	0.47	1.12	26.75	33.02	-----	Forging	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	102.3	Steel of the present invention.
1,400.....	0.26	0.28	1.16	25.04	33.17	Co 15.45	Casting	-----	160.4	Comparative steel.
1,401.....	0.06	0.67	1.51	25.27	33.38	Co 15.49	Forging	1,150° C., 1 hr., W.Q.	25.7	Do.
1,402.....	0.26	0.28	1.16	25.04	33.17	Co 15.45	Extrusion	1,280° C., 30 min., W.Q.	53.8	Do.
1,403.....	0.26	0.28	1.16	25.04	33.17	Co 15.45	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	158.0	Steel of the present invention.
1,405.....	0.24	0.39	1.10	27.14	32.75	Co 26.19	Casting	-----	200.4	Comparative steel.
1,406.....	0.24	0.39	1.10	27.14	32.75	Co 26.19	Extrusion	1,280° C., 10 min., W.Q.	65.2	Do.
1,407.....	0.24	0.39	1.10	27.14	32.75	Co 26.19	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	241.9	Steel of the present invention.
1,410.....	0.31	0.61	1.04	26.53	33.10	W 5.32	Casting	-----	190.2	Comparative steel.
1,411.....	0.06	0.41	1.53	27.04	31.22	W 5.24	Forging	1,150° C., 1 hr., W.Q.	35.9	Comparative steel.
1,412.....	0.31	0.61	1.04	26.53	33.10	W 5.32	Extrusion	1,280° C., 30 min., W.Q.	43.0	Do.
1,413.....	0.31	0.61	1.04	26.53	33.10	W 5.32	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	193.4	Steel of the present invention.
1,420.....	0.24	0.51	1.63	25.85	31.82	Nb 3.23	Casting	-----	221.5	Comparative steel.
1,421.....	0.07	0.85	0.82	26.15	32.41	Nb 3.57	Forging	1,150° C., 1 hr., W.Q.	32.1	Do.
1,422.....	0.24	0.51	1.63	25.85	31.82	Nb 3.23	Extrusion	1,280° C., 30 min., W.Q.	47.3	Comparative steel.
1,423.....	0.24	0.51	1.63	25.85	31.82	Nb 3.23	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	215.2	Steel of the present invention.
1,430.....	0.28	0.32	1.35	26.21	32.53	Mo 4.96	Casting	-----	144.8	Comparative steel.
1,431.....	0.28	0.32	1.35	26.21	32.53	Mo 4.96	Extrusion	1,280° C., 30 min., W.Q.	35.2	Do.
1,432.....	0.28	0.32	1.35	26.21	32.53	Mo 4.96	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	123.5	Steel of the present invention.
1,440.....	0.31	0.28	1.32	25.85	33.28	Ti 2.62	Casting	-----	138.1	Comparative steel.
1,441.....	0.31	0.28	1.32	25.85	33.28	Ti 2.62	Extrusion	1,280° C., 30 min., W.Q.	35.3	Do.
1,442.....	0.31	0.28	1.32	25.85	33.28	Ti 2.62	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	141.2	Steel of the present invention.
1,450.....	0.30	0.76	1.43	26.60	33.44	Al 2.53	Casting	-----	140.6	Comparative steel.
1,451.....	0.30	0.76	1.43	26.60	33.44	Al 2.53	Extrusion	1,280° C., 30 min., W.Q.	35.3	Comparative steel.
1,452.....	0.30	0.76	1.43	26.60	33.44	Al 2.53	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	158.0	Steel of the present invention.
1,480.....	0.28	0.65	1.44	27.07	33.93	N 0.32	Casting	-----	138.5	Comparative steel.
1,481.....	0.28	0.65	1.44	27.07	33.93	N 0.32	Extrusion	1,280° C., 1 hr., W.Q.	36.8	Do.
1,482.....	0.28	0.65	1.44	27.07	33.93	N 0.32	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	121.7	Steel of the present invention.

*1,050° C., 25 kg./mm.².

TABLE 15 (EXAMPLE 8)

No.	Alloy element, percent						Type of working	Heat treatment	Creep rupture strength* (hr.)	Remarks
	C	Si	Mn	Cr	Ni	Others				
1,500.....	0.37	0.34	0.82	27.09	32.93	17.69 Co, 5.69 W	Forging	-----	613.6	Comparative steel.
1,501.....	0.05	0.50	1.59	26.82	33.64	16.36 Co, 6.02 W	do	1,150° C., 1 hr., W.Q.	40.3	Do.
1,502.....	0.37	0.34	0.82	27.09	32.93	17.69 Co, 5.69 W	Extrusion	1,280° C., 30 min., W.Q.	52.3	Do.
1,503.....	0.37	0.34	0.82	27.09	32.93	17.69 Co, 5.69 W	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	603.7	Steel of the present invention.
1,510.....	0.32	0.56	1.61	25.96	31.65	3.26 W, 1.56 Nb	Casting	-----	309.6	Comparative steel.
1,511.....	0.32	0.56	1.61	25.96	31.65	3.26 W, 1.56 Nb	Extrusion	1,280° C., 30 min., W.Q.	46.5	Do.
1,512.....	0.32	0.56	1.61	25.96	31.65	3.26 W, 1.56 Nb	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	323.5	Steel of the present invention.
1,520.....	0.29	0.63	1.18	26.24	33.27	2.29 W, 2.27 Mo	Casting	-----	350.8	Comparative steel.
1,521.....	0.29	0.63	1.18	26.24	33.27	2.29 W, 2.27 Mo	Extrusion	1,280° C., 30 min., W.Q.	40.5	Do.
1,522.....	0.29	0.63	1.18	26.24	33.27	2.29 W, 2.27 Mo	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	456.8	Steel of the present invention.
1,530.....	0.31	0.56	1.23	27.77	35.90	2.45 Al, 1.97 Ti	Casting	-----	392.1	Comparative steel.
1,531.....	0.31	0.56	1.23	27.77	35.90	2.45 Al, 1.97 Ti	Extrusion	1,280° C., 30 min., W.Q.	39.5	Do.
1,532.....	0.31	0.56	1.23	27.77	35.90	2.45 Al, 1.97 Ti	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	398.5	Steel of the present invention.
1,540.....	0.28	0.25	1.69	27.83	34.75	5.38 Mo, 0.45 N	Casting	-----	285.7	Comparative steel.
1,541.....	0.28	0.25	1.69	27.83	34.75	5.38 Mo, 0.45 N	Extrusion	1,280° C., 30 min., W.Q.	45.3	Do.
1,542.....	0.28	0.25	1.69	27.83	34.75	5.38 Mo, 0.45 N	do	1,280° C., 30 min.- (10 min.)-1,050° C., W.Q.	370.3	Steel of the present invention.
1,550.....	0.38	0.18	0.73	27.40	33.32	17.08 Co, 7.27 W, 2.33 Mo	Casting	-----	704.4	Comparative steel.
1,551.....	0.38	0.18	0.73	27.40	33.32	17.08 Co, 7.27 W, 2.33 Mo	Extrusion	1,280° C., 30 min., W.Q.	43.8	Do.
1,552.....	0.38	0.18	0.73	27.40	33.32	17.08 Co, 2.27 W, 2.33 Mo	do	1,280° C., 30 min.- (15 min.)-1,050° C., W.Q.	689.9	Steel of the present invention.
1,560.....	0.30	0.23	1.52	26.94	33.04	15.35 Co, 5.35 W, 0.94 Nb	Casting	-----	765.4	Comparative steel.
1,561.....	0.30	0.23	1.52	26.94	33.04	15.35 Co, 5.35 W, 0.94 Nb	Extrusion	1,280° C., 30 min., W.Q.	47.3	Do.
1,562.....	0.30	0.23	1.52	26.94	33.04	15.35 Co, 5.35 W, 0.94 Nb	do	1,280° C., 30 min.- (15 min.)-1,050° C., W.Q.	883.5	Steel of the present invention.
1,570.....	0.27	0.27	1.38	26.79	32.63	5.22 W, 2.32 Mo, 1.02 Nb	Casting	-----	388.1	Comparative steel.
1,571.....	0.27	0.27	1.38	26.79	32.63	5.22 W, 2.32 Mo, 1.02 Nb	Extrusion	1,280° C., 30 min., W.Q.	42.0	Do.
1,572.....	0.27	0.27	1.38	26.79	32.63	5.22 W, 2.32 Mo, 1.02 Nb	do	1,280° C., 30 min.- (15 min.)-1,050° C., W.Q.	392.6	Steel of the present invention.
1,580.....	0.37	0.35	1.40	27.68	32.81	15.03 Co, 4.55 W, 2.79 Mo, 0.95 Nb	Casting	-----	867.2	Comparative steel.
1,581.....	0.37	0.35	1.40	27.68	32.81	15.03 Co, 4.55 W, 2.79 Mo, 0.95 Nb	Extrusion	1,250° C., 1 hr., W.Q.	50.6	Do.
1,582.....	0.37	0.35	1.40	27.68	32.81	15.03 Co, 4.55 W, 2.79 Mo, 0.95 Nb	do	1,250° C., 1 hr.- (15 min.)	910.3	Steel of the present invention.
1,590.....	0.32	0.54	1.69	26.80	33.75	16.89 Co, 5.39 W, 2.32 Mo, 0.12 N	Casting	-----	656.8	Comparative steel.
1,591.....	0.32	0.54	1.69	26.80	33.75	16.89 Co, 5.39 W, 2.32 Mo, 0.12 N	Extrusion	1,250° C., 1 hr., W.Q.	45.6	Do.
1,592.....	0.32	0.54	1.69	26.80	33.75	16.89 Co, 5.39 S, 2.32 Mo, 0.12 N	do	1,250° C., 1 hr.- (15 min.)-1,050° C., W.Q.	594.3	Steel of the present invention.

*1,050° C., 2.5 kg./mm.².

The test results are illustrative of the superb characteristics of high creep rupture strength obtainable with the alloy of the present invention. Accordingly, it may readily be appreciated that the heat resistant steels of the present invention will find application in producing reformer tubes and cracking tubes, as well as forming heat exchanger tubes, wherein high strength is required at temperatures as high as 850° C., or higher, which cannot be achieved by the conventional 0.01 C-25Cr-20 Ni stainless steel or Incolloy 800 alloys. These achievements can be attributed both to the elevated temperature strength of steels of the present invention, and of their capabilities of providing thinner wall thicknesses as required in such reformer and cracking tubes and in heat exchanger tubes.

In addition, it is to be understood that the steels of the present invention exhibit excellent characteristics in the application to forgings, rollings and extrusions. These characteristics permit the production of tubes having outer diameters of 10 mm. and yet wall thickness of even below 1 mm., which is particularly suited for use as heat exchanger tubes, and they further permit the production of tubes having a length of over 10 m., thus minimizing the number of welding joints which tend to cause trouble during the use of the tubes.

It can still further be recognized that the steel of the present invention provides good, sound layers on the inner surface of the tube, thus permitting the use of a tube having a thinner wall thickness with resulting good heat capability, while eliminating the likelihood of rapid carburization of the reducing gas due to imperfections in the tube surfaces.

In addition, the methods of the present invention permit the production of sheet form steel by ordinary rolling processes.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific examples of the invention described herein.

What is claimed and intended to be covered by Letters Patent is:

1. An austenite type heat resistant steel article characterized by high strength properties at elevated temperature consisting essentially of from 0.1 to 1% by weight carbon, from 0.01 to 3% by weight silicon, from 0.01 to 10% by weight manganese, from 13 to 35% by weight chromium, from 15 to 50% by weight nickel, and the balance essentially impurities and iron, wherein a continuous carbide precipitation formed by heat treatment at a temperature of greater than 950° C. is present on the grain boundaries.

2. The austenite type heat resistant steel of Claim 1, wherein said steel additionally contains at least one element selected from a group consisting of up to 30% cobalt, up to 10% tungsten, up to 10% molybdenum, up to 5% niobium, up to 5% titanium, up to 5% aluminum and up to 0.5% nitrogen.

3. A process for producing an austenite type heat resistant steel characterized by high strength at elevated temperatures, said steel containing, in weight percent, from 0.1 to 1% carbon, from 0.01 to 3% silicon, from 0.01 to 10% manganese, from 13 to 35% chromium, from 15 to 50% nickel, and the balance essentially impurities and iron, which comprises working said steel, heating said worked steel to a temperature of from 1,150° C. to the solidus line, slow cooling said steel from said temperature down to a temperature of 950° C. or higher, over a period of from 5 seconds to one hour and thereafter rapidly cooling said steel.

4. The process for producing an austenite type heat resistant steel as defined in Claim 3, wherein said steel additionally contains at least one element selected from a group consisting of up to 30% cobalt, up to 10% tungsten, up to 10% molybdenum, up to 5% niobium, up to 5% titanium, up to 5% aluminum, and up to 0.5% nitrogen.

5. A process for producing an austenite type heat resistant steel characterized by high strength at elevated temperatures, said steel containing, in weight percent, from 0.1 to 1% carbon, from 0.01 to 3% silicon, from 0.01 to 10% manganese, from 13 to 35% chromium, from 15 to 50% nickel, and the balance essentially impurities and iron, which comprises casting said steel, heating said cast steel to a temperature of from 1,150° C. to the solidus line, slow cooling said steel from said temperature down to a temperature of 950° C. or higher, over a period of from 5 seconds to one hour and thereafter rapidly cooling said steel.

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50 WAYLAND W. STALLARD, Primary Examiner

U.S. Cl. X.R.

148—12, 12.3, 12.4, 38, 136, 142

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,826,689
DATED : July 30, 1974
INVENTOR(S) : SADA OHTA ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 1, "0.50C-25Cr20Ni" should read --0.50C-25Cr-20Ni--.

Column 3, line 6, "manganes" should read --manganese--.

Column 4, line 10, "as" should read --at--;
line 62, "provent" should read --prevent--.

Column 6, Table 4, third from the last column, "2.85 min." should read --28.5 min.--.

Column 8, fourth line after Table 7, delete "hibit" and insert --hibits--
fifth line after Table 7, delete "show" and insert --shows--.

Column 9, line 6, delete "low" and insert --lower--;
Table 10 (Example 3), in the Column labeled "No.", correct the alignment of the numbers.
line 73, after "carbon" insert --cast--.

Columns 11 and 12, Table 15 (Example 8), in the row of No. 1,581, delete "Extursion" and insert --Extrusion--;
in the row of No. 1,582,
after "1,250°C., 1Hr.-(15 min.)" insert --1050°C., W.Q.--.

The sheets of drawings appearing in the patent should be cancelled and the sheets shown on the attached sheets should be substituted therefor, but will apply to the Grant only.

Signed and Sealed this

fourth Day of May 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

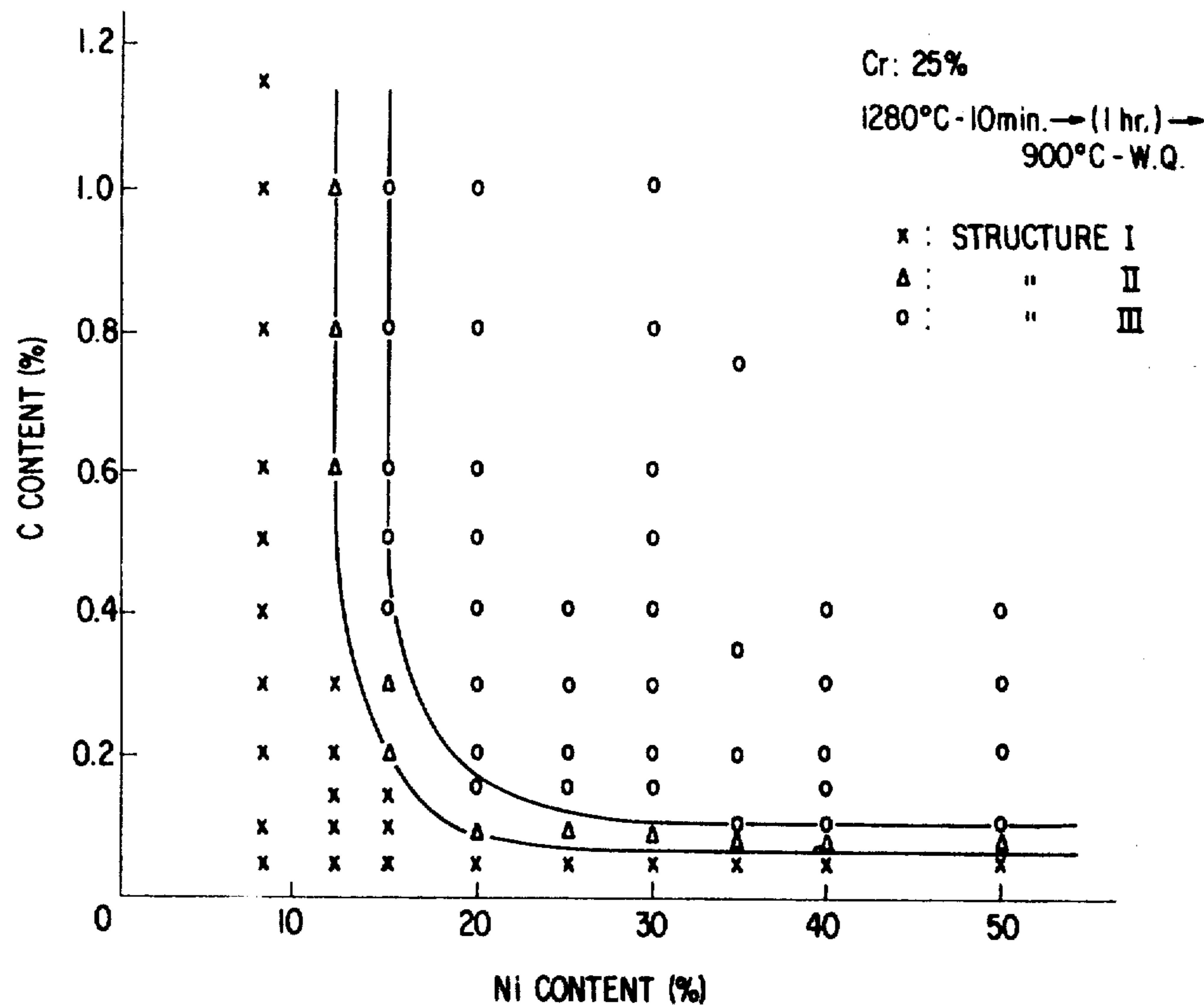


FIG. 1

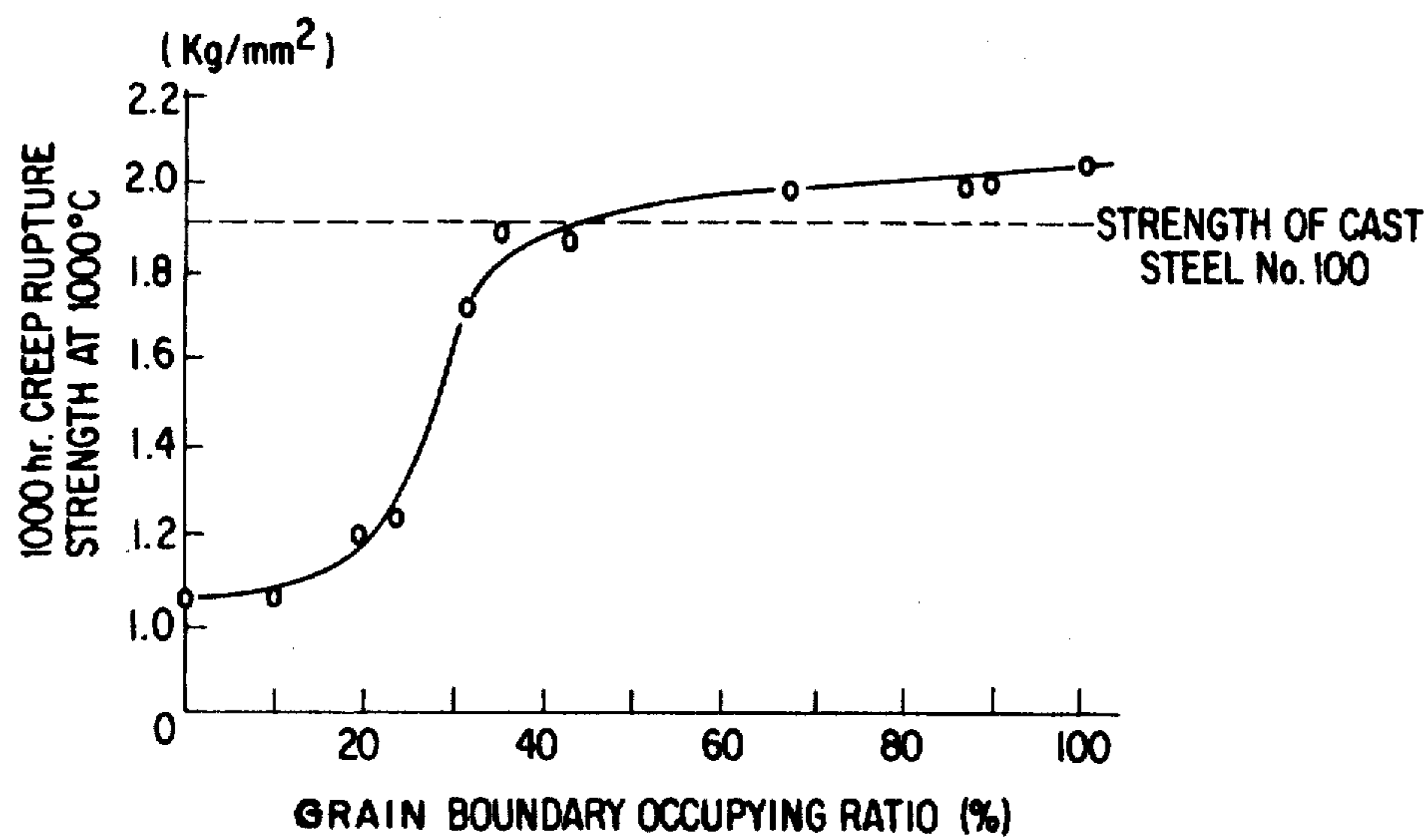


FIG. 3

FIG. 2(I)

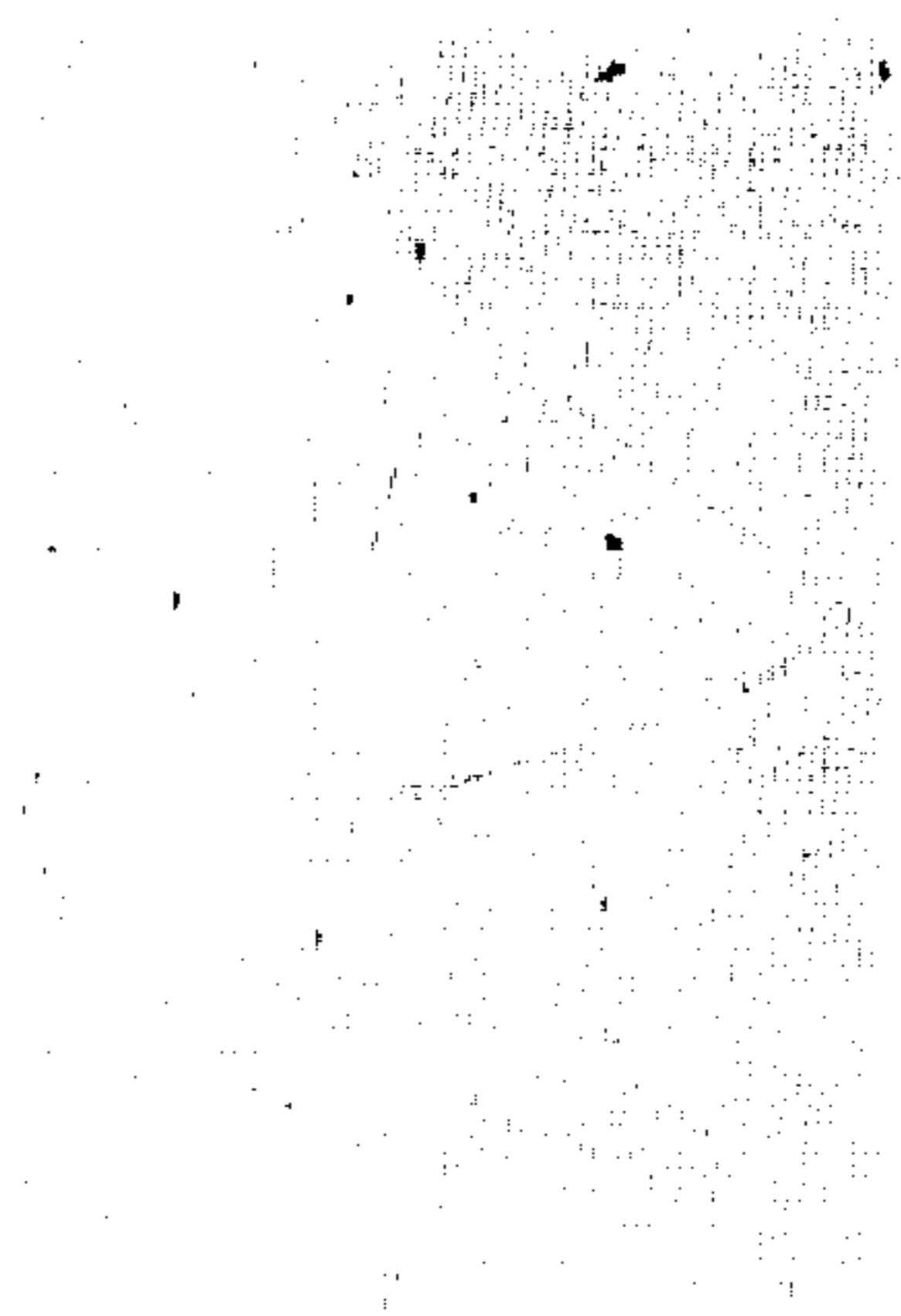


FIG. 2(II)

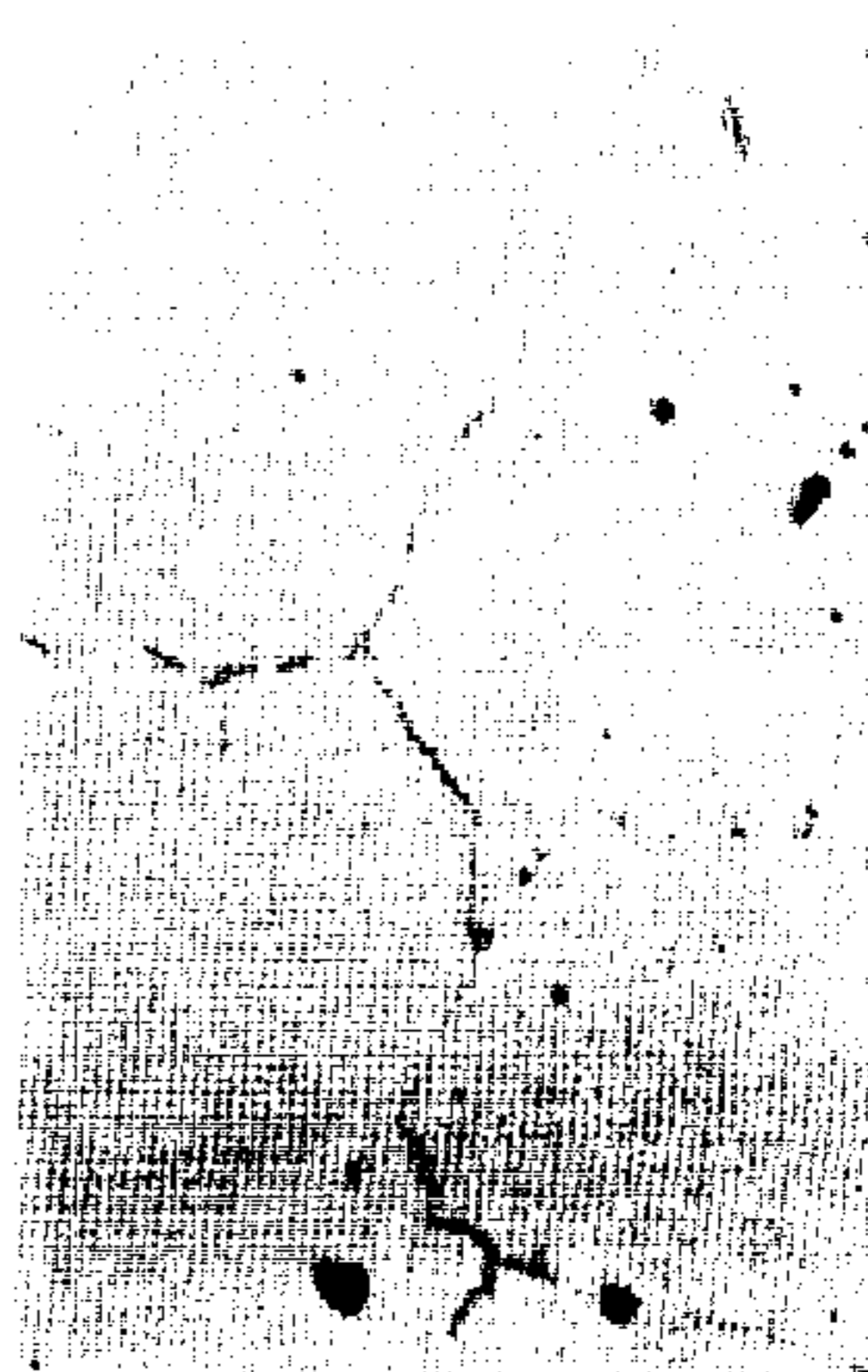


FIG. 2(III)



FIG. 2(IV)

