

HIGH TEMPERATURE PROPERTIES AND FINE STRUCTURE
OF HIGH MANGANESE HEAT-RESISTING STEEL

H. Yoshida

K. Koike

Abstract

High manganese heat resisting steel improved in order to obtain an alloy having excellent high temperature properties, contain a large amount of manganese and nitrogen.

The reason why the alloy can contain a large amount of nitrogen, the effects of various elements and heat treatment on the high temperature properties of this type alloys and grain boundary reaction recognized in this type alloys are to be described.

H. Yoshida and K. Koike are metallurgist at National Research Institute for Metals, Tokyo, Japan.

I. Introduction

In order to improve an alloy which is not inferior to N-155 alloy ---a typical iron base heat resisting alloy---regarding the high temperature strength, and which contains expensive elements as small amount as possible, furthermore, can be easily forged, we examined the effects of austenite former such as manganese, nickel and nitrogen and those of ferrite former such as chromium, molybdenum, tungsten, niobium on the high temperature properties of the alloy eliminated cobalt from N-155 alloy.

From these experiments, an alloy which fits the purpose could be improved when 10% manganese and more than 0.6% nitrogen are contained and the proper amounts of various elements are chosen to be gamma single phase in solution treatment, though nickel content is reduced only to 6%. (1)

This high manganese, nitrogen heat resisting alloy was named 10M6N alloy (10%Mn, 6%Ni, 20%Cr, 2%Mo, 2.5%W, 1%Nb, 0.2%C, N>0.6%, balance Fe).

When small amount of boron is added to this alloy, its high temperature properties can be more improved.

In this report, four items are to be described---first; the reasons why 10M6N alloy can contain such a large amount of nitrogen as more than 0.6%, second; the effects of nitrogen, niobium and boron on the high temperature properties and structures of 10M6N alloys, third; the grain boundary reaction recognized in this type alloys, fourth; the effects of heat treatment on the high temperature properties of 10M6N type alloys.

II. Why Can a Heat Resisting 10M6N Alloy Contain a Large Amount of Nitrogen?

10M6N alloy is special in containing a large amount of manganese and nitrogen. So, we explain the reason why this alloy can contain a large amount of nitrogen. If we keep the melt of 10M6N type alloy added no nitrogen for 30min., nitrogen content of this alloy increases with the lapse of time, due to absorbing of nitrogen from the atmosphere.

On the other hand, if we keep the melt of 10M6N type alloy added 1.0% nitrogen for 10min., the nitrogen content reduces to nearly 0.6% with the lapse of time.

Nitrogen content of this type alloys are affected by the cooling velocity, the melting amount etc., even if the same amount of nitrogen is added. But, it mainly depends on the nitrogen content of the melt which is in equilibrium in the melt atmosphere.

This is recognized from the facts that the nitrogen content of the ingots coincides with the one in equilibrium in the melt of 10M6N alloy which is calculated from the activity coefficient, obtained by using the interaction coefficients of various elements. (2)

The reason why 10M6N alloy can contain a large amount of nitrogen, is considered to be due to the facts that the nitrogen solubility of the melt is large because the alloy contains a large amount of chromium and manganese.

Next, we are to describe the effects of various elements on the high temperature properties and structures of 10M6N type alloys.

III. The High Temperature Properties and Structures of High Manganese Heat Resisting 10M6N Type Alloys.

III-1 Effects of nitrogen

The compositions which nitrogen is eliminated from 10M6N alloy was selected as the base compositions. Various amounts of nitrogen were added to this composition, using Fe-Cr-N (6.2%N, 43%Cr).

Nine ingots (N-0~N-8) containing nitrogen in the range of 0.084% ~0.979%, were melted in air by using high frequency induction furnace. These compositions of alloys are shown in Table 1.

These ingots were forged, water quenched after heating for 1hr. at 1200°C as solution treatment and then cooled in air after heating for 4hr. at 800°C. Then, the creep rupture testing was conducted.

Solution treated alloys' hardness increases nearly in proportion to the nitrogen content. About 22% and 6% of delta ferrite are respectively recognized in the solution treated alloys containing 0.08% and 0.38% nitrogen.

The creep rupture life and rupture elongation at the test condition of 700°C, 26kg/mm², are shown in Fig.1, from which it is recognized that the creep rupture life is remarkably short, in the range of nitrogen up to 0.38%, because delta ferrites are easily transformed into sigma phase and M₂₃C₆ by heating, but in the range of nitrogen content more than 0.38% where the alloys' matrix becomes gamma single phase without containing delta ferrite, the creep rupture life increases in proportion to nitrogen content, and is improved to 400hr. at 0.98% nitrogen. That is to say, the increase of 0.6% nitrogen from 0.38% to 0.98%, cause the rupture life to improve about as long as twenty five times.

Photos. 1 (a)~(d) show the electron microscopic structures of alloys aged for 1000hr. at 700°C. From photo.1(a) of N-0 alloy containing 0.084% nitrogen, delta ferrite is recognized to be transformed into M₂₃C₆ and sigma phase, and M₂₃C₆ is found to be precipitated in the matrix. M₂₃C₆ and Cr₂N precipitate with Nb(C,N) as undissolved phase, in the alloy containing 0.615% nitrogen, 0.754% nitrogen, 0.979% nitrogen. (Photos. 1(b)~(d))

Further, from the comparison of photo.1(b) and photo.1(c),~(d), these precipitates are found to be more finely distributed with the increase of nitrogen from 0.615% to 0.754% and 0.979%.

From these results, the increase of nitrogen content of this type alloys may be concluded to contribute to the improvement of the high temperature properties, because the matrix become to be gamma single phase and to be strengthened, furthermore, the precipitates are more finely distributed with the increase of nitrogen content.

III-2 Effects of niobium

The alloy having composition which is eliminated niobium from 10M6N alloy was melted and the half was cast. Then, 1% niobium was added to the rest of the melt and was cast. The former was named Nb0 alloy, the latter Nb1 alloy.

As shown in Table 1, S.N. decrease and I.N. increase from the comparison of these two alloys by niobium addition.

Table 2 shows the grain size and the hardness of Nb0 and Nb1

alloys solution treated at various temperatures. At the same solution temperature, the hardness is higher and the grain size is smaller in Nb1 alloy than in Nb0 alloy.

Fig. 2 shows the age hardening properties of the two alloys solution treated at 1200°C. Nb1 alloy is yet in the hardening process after 250hr. at all heating temperatures and the hardness increase obtained by aging is about 30~40 in V.H.N. and the hardening process is not different so much at all temperatures. But, Nb0 alloy's hardness increases obtained by 250hr. heating are about 40 in V.H.N. at 650°C, and about 100~110 in V.H.N. at 700°C and 750°C. Nb0 alloy hardens more than Nb1 alloy at all aging temperatures and its tendency is more remarkable at 700°C and 750°C.

Photos. 2(a), (b) are the microstructures of Nb0 and Nb1 alloys heated for 250hr. at 700°C. Grain boundary reaction (afterwards, denote G.B.R.) is recognized in Nb0 alloy, and the grain size of Nb1 alloy finer very much than that of Nb0 alloy. The precipitates at the grain boundary and in the grain are slightly found in Nb1 alloy. That is to say, the remarkable hardening behaviour of Nb0 alloy is to be due to the G.B.R. and the addition of niobium to this type alloy suppresses the remarkable age hardening.

Then, the niobium addition to pure iron (3), to carbon steel, to Ni-Cr, Ni-Cr-Co alloys (4) is reported to cause their recrystallization temperatures to be higher. The same phenomenon is recognized in this type alloy.

Namely, from the hardness change of Nb1, Nb0 alloys cold rolled to the degree of 60%, when heated in the temperature range of 400°C~1100°C, $T_{\frac{1}{2}}$ ---the temperature at which the average hardness of the maximum one and the minimum one (the hardness at 1100°C where the recrystallization is completed) is shown---was measured.

From the fact that $T_{\frac{1}{2}}$ of Nb0 alloy is about 850°C and the one of Nb1 alloy is about 875°C, the niobium addition to this type alloy can be concluded to cause the recrystallization temperature to be higher.

The tensile strength of Nb0 alloy at 700°C is 54.6kg/mm, whereas that of Nb1 alloy is 58.3kg/mm --- the latter is clearly more excellent.

Then, it is reported that the creep rate and the recrystallization temperature are to a certain degree related in 15Cr-13Ni steel. (5) So, the high temperature properties of this type alloy is supposed to be improved by niobium addition.

Fig. 3 shows the creep rupture properties of Nb0 and Nb1 alloys solution treated at 1200°C and the numerical values written in the figure are the creep rupture elongation. The creep rupture stress and the creep rupture elongation of Nb1 alloy are more excellent than those of Nb0 alloy.

From these facts, the improvement of creep rupture properties of 10M6N type alloy by addition of niobium, is explained to be due to the increase of solution treated hardness, the suppression of age hardening properties brought about by the G.B.R., the grain size refinement and the rise of the recrystallization temperature etc.

III-3 Effects of boron

The creep rupture lives of the ferritic and austenitic heat resisting steels, nickel base and cobalt base heat resisting alloys

are improved by addition of boron.

Then, in order to examine of boron addition to 10M6N alloy, about 20kg of 10M6N alloy was melted and the half of the melt was cast and then 0.01% boron was added to the rest and was cast. Thus, MN alloy (the former), MB alloy (the latter) were obtained. From the comparison of these two alloys, the boron addition to 10M6N alloy is recognized to be effective in the improvement of the high temperature properties. But, as boron addition more than a certain content is thought to be undesirable to the forgeability. So, in order to determine proper amount of boron to the alloy, in considering of various properties such as the forgeability, the oxidation resistance and the impact value, four kinds of alloys---50A(10M6N alloy), 50B (0.01% boron addition), 50D(0.05% boron addition), 50F (0.15% boron addition)---were melted by addition of boron one after another to the same melt by the same manner as the one by which MN and MB alloys were melted.

The chemical compositions of these alloys are shown in Table 1. By addition of boron, the increase of soluble nitrogen, the decrease of insoluble nitrogen are found.

Table 3 shows the undissolved phases of 50A, 50B, 50D, 50F alloys solution treated in the temperature range of 1150°C ~1250°C. The mark of A, B and C in this table respectively mean that is recognized clearly, a little, not any.

By addition of boron, $M_{23}C_6$ tends to remain in the solution treated state as the undissolved phase. This is due to the fact that carbon solubility decreases by addition of boron, as reported by V.V. Levitin. (6) That is to say, addition of boron bring about the decrease of soluble nitrogen, the increase of insoluble nitrogen and also decrease of carbon solubility in the matrix.

The Z phase in Table 3 is reported to be Fe-Cr-Nb found in the creep specimen of 18Cr-12Ni-1Nb steel tested at 850°C by H. Hugh (7), but this phase was recognized in not only Ni-Cr steel but also in Essete 1250---Ni-Cr-Mn steel, and were become clear to be Cr-Nb nitride. (8)

Next, from the comparison of aging hardness of MN and MB alloys at 700°C, addition of boron to 10M6N alloy is found to be operative in the suppression of the age hardening properties of this type alloy.

Photos. 3 (a), (b) show the microstructures of MN and MB alloys heated for 1.5hr. at 700°C. In MN alloy, precipitates of $M_{23}C_6$ are found in the matrix and at the grain boundary, but in MB alloy, only undissolved phases of Nb(C,N) and Z phase are found, and the precipitates are not recognized. Namely, addition of boron is effective in suppression of the precipitation at the grain boundary and in the grain.

The microstructures of MN and MB alloys aged for 6hr. at 700°C are shown in Photos. (c), (d) in which the precipitate from the grain boundary to the undissolved phase and the one between the undissolved phases are found in the state of string.

Photos. 3 (e), (f) show the microstructures of MN, MB alloys heated for 1.5hr. at 800°C. G.B.R. is found in MN alloy, but not in MB alloy. Namely, boron is recognized to be operative in suppression of diffusion of various elements to the grain boundary and in retarding of G.B.R.

Then, the hardness change of MN, MB alloys cold rolled to the

degree of 50%, when heated in the temperature range of 500°C~1000°C was measured. The behaviour of the hardness change between two alloys is scarcely different.

The solutioned hardness of the two alloys and their hardness cold rolled to the degree of 50% are almost same, and the age hardening is suppressed to some extent by addition of boron, and furthermore there is little difference between two alloys in the hardness change of cold rolled specimens when heated in the temperature range of 500°C~1000°C.

From these facts, addition of 0.01% boron to 10M6N alloy may be concluded to be scarcely effective to the solution hardening, as pointed by Kawabe etc. (9) regarding the effect of addition of boron to 18Cr-12Ni-0.2%C steel.

The short time tensile test of the two alloys was carried out at 0.72mm/min. The rupture elongation of MN alloy was 22.5%, and that of MB alloy was 29.2%. Namely, boron is effective in the improvement of the high temperature ductility.

Fig. 4 shows the creep rupture properties of MN, MB alloys heat treated---water quenched after heating for 1hr. at 1200°C(MN), at 1150°C(MB) and then air cooled after heating for 4hr. at 800°C. The numerical values written in the figure mean the creep rupture elongation. It is recognized that the creep rupture life and elongation are both improved remarkably by addition of boron.

From measuring of the elongation between the pull rods, addition of boron was found to alter scarcely the minimum creep rate and to improve the creep rupture life, chiefly due to that it delays the shifting from the second stage to the 3rd stage in the creep process.

The improvement of high temperature ductility by addition of boron, is reported by R.F.Decker (10) to be due to that boron cause the precipitates at the grain boundary to be finer and to suppress their coagulation.

In this type alloy, addition of boron suppress the diffusion of various elements to the grain boundary and formation of G.B.R. These effects are thought to cause the high temperature ductility of this type alloy to improve.

Next, proper amount of boron in this type alloy is to be related.

The forging of 50B alloy is as easy as 50A alloy, but that of 50D alloy becomes difficult to some extent, and further, that of 50F alloy becomes more difficult in comparison to 50D alloy.

As the result of the oxidation test, at the test condition of heating for 100hr. at 800°C, 900°C and 1000°C, it is recognized that the oxidation resistance of 50B alloy is nearly equal to that 50A alloy, but that of 50F alloy become to be considerably poor. From these results, addition of boron to this type alloy is desirable to be less than 0.01%.

An alloy added a small amount of boron to 10M6N alloy is named 10M6NB alloy.

IV. Grain Boundary Reaction

We already described that the precipitation of 10M6N type alloy consists of two types---one is general precipitation, the other G.B.R. and that latter was suppressed by addition of niobium or boron.

Then, G.B.R. has been hitherto mainly investigated regarding non-ferrous alloys, but recently G.B.R. is reported to be recognized in various kinds of ferrous alloys (11) and to be regarded as important to

the mechanical properties.

So in this chapter, the informations obtained regarding G.B.R. of this type alloy, is to be described.

IV-1 Microstructures

Photo 4 (a) shows the microstructures of NbO alloy heated for 4hr. at 800°C after solution treatment at 1200°C. From this photo., it is recognized that G.B.R. tends to occur at the triple points of grain boundaries. Photos. 4 (b), (c) respectively show G.B.R. from grain boundary having knick, and that from the regions where the twin and the grain boundary meet each other. Photo. 4 (d) shows G.B.R. at the front of the twin, and the G.B.R. is considered to occur from the region where two twins meet each other.

From these photos., G.B.R. in this type alloy is recognized to tend to occur from the regions where the lattice is disordered.

IV-2 Effect of stress on G.B.R.

Fig. 5 show the effect of stress and heating time on the amount of G.B.R. in the test condition that load is applied at the same time when the temperature of the specimen is reached to 750°C, using of the creep rupture specimens of B alloy eliminated niobium from 10M6N alloy. It is recognized that the amount of G.B.R. increases with increase of stress and farther the effect of stress becomes to disappear with the increase of heating time.

Then the same experiment was tested, using 50S alloy which has almost similar compositions as B alloy and contains niobium. In this case, the amount of G.B.R. was also recognized to be increased by stress.

The contents of S.N. in B alloy and in 50S alloy, are nearly equal, but the amount of G.B.R. is less in 50S alloy than in B alloy at the same test condition. Namely, also when the contents of S.N. are nearly equal in 10M6N type alloys, niobium is recognized to be effective in the suppression of G.B.R.

Photo. 4 (e) shows the microstructure of alloys heated for 20 min. at 900°C, after hardness measuring by Vickers Hardness Tester. In this photo., G.B.R. is found to occur remarkably around the trace of indenter.

That G.B.R. is accelated by stress, is reported regarding 25%Cr austenitic steel, Al-Ag, and Al-Zn alloys. R. Blower(12) reports that G.B.R. of 15Cr-20Ni-3Ti steel is not recognized by heating after small amount of working, but recognized after large amount of working.

G.B.R. tends to occur from the regions where the lattice is disordered and G.B.R. of austenitic steel, non ferrous alloys are all accelated by cold working. So, G.B.R. can be generally concluded to be accelated by stress.

IV-3 Effect of forging ratio on G.B.R.

Photos. 5 (a), (b), (c) are respectively the microstructures of 10M6N alloy which are respectively forged to the degree of about 1.5, 4 and 9, and then heated for 1hr. at 900°C after water quenching from 1250°C.

As the forging ratio becomes larger, G.B.R. and the undissolved phase become to distribute parallel to the forging direction.

So, G.B.R. in this type alloy is considered to be related to Nb(C,N) of the undissolved phase at the grain boundary. Therefore, we examined it true or not by electron microscope. Such behaviour could scarcely be recognized.

Photo. 5 (c) shows that the grain size tends to become smaller in the regions where Nb(C,N) exists.

So, the fact that G.B.R. tends to distribute parallel to the forging direction with increase of the forging ratio, is thought to be partly due to the existence of Nb(C,N), but chiefly due to that the grain size does not become coarse owing to Nb(C,N) and that fine grain has larger grain boundary energy than the coarse one.

IV-4 Effect of solution temperature on the amount of G.B.R.

Fig. 6 shows the effect of solution temperatures on the amount of G.B.R. occurred at test conditions of heating for 4hr. at 800°C and for 1.5hr. at 900°C.

When solution temperature is 1200°C, the amounts of G.B.R. become maximum in all test conditions. In this type alloy, as the solution temperature becomes higher, S.N. increase and G.B.R. tends to easily occur as nitrogen content increases.

So, the reason why the amounts of G.B.R. increases when the solution temperatures become higher from 1150°C to 1200°C, is considered to be due to the increase of S.N., on the contrary, the reason why the amount of G.B.R. decrease as the solution temperatures become from 1200°C to 1250°C, 1300°C is considered to be due to the enlargement of grain size, because G.B.R. tends to occur easily in the fine grain than in the coarse grain.

That is to say, the reason why the amount of G.B.R. show maximum in the above mentioned test condition when the solution temperature is 1200°C, is considered to be due to the balance of the opposite factors as the solution temperature becomes higher, regarding the amount of G. B.R.

Thus, the behaviour of G.B.R. found in this type alloys depend on the stress, forging ratio and solution temperature etc. at the condition of the same heating time and temperature. As already described, addition of niobium and boron to this type alloys suppress the G.B.R. and improve the creep rupture elongation and the creep rupture life.

V. Effects of Heat Treatment on the High Temperature Properties of High Manganese Heat Resisting 10M6N and 10M6NB alloys

In this chapter, the effects of heat treatment on the high temperature properties of this type alloys and the factors governing the high temperature strength, are to be described.

10M6N, 10M6NB alloys were melted by the same manner as that of MN and MB alloys.

As solution treatment, four temperatures---1150°C, 1200°C, 1250°C and 1300°C---were selected and the alloys were water quenched after heating for 1hr. at each temperatures. As preaging treatment, three

conditions---air cooling after heating for 4hr. at 750°C, heating for 4hr. at 800°C and heating for 20hr. at 800°C---were adopted.

As solutioned and preaging after solution treatment were suitably selected as heat treatment.

Creep rupture test was carried out chiefly at the test condition of 700°C, 26kg/mm² and 700°C, 20kg/mm². Furthermore, in order to consider the relation between the creep rupture properties and the heat treatment, the age hardening properties, short time tensile properties and hardness at 700°C were tested. The analysis of the electrically extracted residue and the examination of the structures were carried out.

V-1 Age hardening properties

Fig. 7 shows the effects of heat treatment on the hardness change of 10M6N alloy heated at 700°C. As the solution temperatures become higher, hardness of solution treated alloys falls, because such phases as $M_{23}C_6$ and Z phase become to solute into the matrix.

The differences between the hardness as solution treatment and the one obtained by 1000hr. heating, are respectively 52, 52, 89 and 105 when the solution temperatures are 1150°C, 1200°C, 1250°C and 1300°C. Namely, as the solution temperatures become higher, the hardness differences increase. Especially, the hardness of the alloy solution treated at 1300°C, increases remarkably after 3hr. Further, the hardness of the alloy heated for 4hr. at 800°C after solution treatment at 1200°C scarcely increases by heating for 1000hr.

Similar phenomenon is also recognized in 10M6NB alloy and the hardening property is poorer in 10M6NB alloy than in 10M6N alloy from comparison of two alloys heat treated at the same condition.

Photos. 6 (a), (b) and (c) show respectively the microstructures of 10M6N alloys aged for 1000hr. at 700°C, after solution treatment at 1150°C, 1200°C and 1300°C.

Photo. 6 (d) shows the microstructure of 10M6N alloy which is solution treated at 1200°C, then heated for 4hr. at 800°C as preaging and afterwards aged for 1000hr. at 700°C. From this photo, the precipitates clearly grow and coagulate. The reason why the age hardening becomes more intense with the increase of solution temperature, can be recognized to be due to the fact that the precipitates of $M_{23}C_6$ and Cr_2N tend to distribute more finely.

Photo. 6 (e), (f) show respectively the microstructures of 10M6NB alloys which is solution treated at 1150°C, 1300°C and heated for 1000hr. at 700°C. As the solution temperature becomes higher, the precipitates become to distribute finer as in 10M6N alloy. Furthermore, the precipitates of the alloys solution treated at 1300°C, tend to be less amount in 10M6NB alloy than in 10M6N alloy.

V-2 High temperature short time tensile properties

Fig. 8 shows the short time tensile properties at 700°C, regarding 10M6NB alloys which were aged for 20hr. at 700°C, after solution treatment in the intervals of 50°C in the temperature range of 1150°C ~ 1300°C.

As the solution temperature becomes higher, the tensile strength tends to increase only a little, but 0.2% yield stress clearly

increases and this tendency is remarkable in the alloy solution treated at 1300°C. On the other hand, the rupture elongation and reduction of area decrease.

Hardness of 10M6NB alloys at 700°C is higher than that of 10M6N alloy heat treated at same condition. Hardness of 10M6NB alloy at 700°C when it is solution treated at 1300°C and aged for 20hr. at 700°C, is about 220 in V.H.N., but that of the other test pieces of two alloys at various conditions is less than 200 in V.H.N.

Photos. 7 (a)~(c) show the microstructures of 10M6NB alloys ruptured at 700°C. With the increase of the solution temperatures, the precipitates distribute more finely and this behaviour is considered to be due to the increase of yield stress. The fine precipitates found in photo. 7 (c) are thought to be $M_{23}C_6$.

V-3 Creep rupture properties

Fig. 9, 10 respectively show the effects of solution temperatures on the creep rupture properties of 10M6N and 10M6NB alloys. It is recognized that the creep rupture lives are improved and the rupture elongations become poorer as the solution temperatures become higher.

The creep rupture elongations of 10M6N alloys solution treated at 1300°C, are both less than 7% at the test condition of 700°C, 26kg/mm² and 20kg/mm²; but the creep rupture life of 10M6NB alloy solution treated at 1300°C is about 2200hr. which is about five times as long as 433hr. of 10M6N alloy solution treated at 1150°C and the rupture elongation is 17.7% at the test condition of 700°C, 26kg/mm². Further, the creep rupture life of 10M6NB alloy solution treated at 1300°C is about 9800hr. and the creep rupture elongation is about 26.4% at the test condition of 700°C, 20kg/mm². That is to say, 10000hr creep rupture strength of 10M6NB alloy at 700°C is about 20kg/mm² and shows fairly ductility. This rupture strength is thought to belong to the strongest group in the austenitic heat resisting steels.

Yamazaki(13) reports that the minimum creep rates of 18Cr-12Ni steel containing various amount of carbon are improved as the solution temperatures become higher, on the other hand, failure tends to occur due to the enlargement of grain size, and that the optimum solution temperature regarding creep rupture life, is recognized due to the balance of these two opposite factors.

Then, the relation between the creep rupture elongation and solution temperature in 10M6N type alloy is as same as that in above-mentioned 18Cr-12Ni steel. But, though 10M6N type alloy is solution treated at 1300°C, its grain size number is in the range of 3~5 in A.S.T.M. No., due to Nb(C,N) of undissolved phase. So it is remarkably smaller than that of the above-mentioned 18Cr-12Ni steel heat treated at the same condition. This is considered to be the reason why the creep rupture lives of 10M6N type alloys are improved with increasing of solution temperature in the temperature range of up to 1300°C. The creep rupture elongation of 10M6NB alloy is longer than that of 10M6N alloy solution treated at the same temperature. This may be thought to be due to that G.B.R. is suppressed by addition of boron.

Then, the minimum creep rate of 10M6NB alloy is more excellent than that of 10M6N alloy when they are only solution treated at same temperature. This may be due to the strengthening effect obtained by

retardation of precipitation process due to addition of boron. The reasons why the creep rupture life and elongation are both more excellent in LOM6NB alloy than in LOM6N alloy, is thought to be due to the above-mentioned two factors.

The notch creep rupture test was carried out at the test condition of 700°C, 26kg/mm², using the test piece of $d_0/d_n=3.7$. These results are shown in Table 4. The values in the parenthesis are the creep rupture life and elongation of the plain specimen. Except LOM6N alloy solution treated at 1300°C, the notched specimens show longer creep rupture life than the plain specimens. Namely, in this type alloy, strengthening by notch can be concluded to be obtained when the creep rupture elongation of the plain test piece shows more than 7%.

Fig. 11 shows the effects of aging on the creep rupture properties of LOM6NB alloy. As heating temperature becomes higher at constant heating time, and as the heating time becomes longer at constant heating temperature,---namely, as aging process is preceded--- the creep rupture life become inferior. This is considered to be due to the inforation of the solution strengthening owing to the decrease of the amount of carbon and nitrogen soluted in the matrix, and also to be due to the inforation of precipitation strengthening owing to rapid growth of the precipitates. This behaviour is also so in LOM6N alloy. Accordingly, preaging treatment of heating for long time at higher temperature than testing temperature, is not hopeful.

Further, the higher the solution temperature in the range of up to 1300°C, the longer the creep rupture life, in this type alloy. But as solution temperature, about 1200°C is suitable in LOM6N alloy in point of view of creep rupture ductility. But, in LOM6NB alloy, it is hopeful that the solution temperature is as high as possible in the temperature range of up to 1300°C, because it has excellent creep rupture ductility.

VI. Conclusion

The process how the high manganese heat resisting LOM6N type alloys were improved, was to be described. The reason why this type alloys can contain a large amount of nitrogen; the effects of various elements and heat treatment on the high temperature properties; and G.B.R. recognized in this type alloy were examined.

Results obtained are as follows.

1. This type alloy contains a large amount of manganese and nitrogen, and the proper amount of molybdenum, tungsten and niobium were selected so that the matrix consists of gammer single phase when the alloy was solution treated. The reason why this type alloys contain such a large amount of nitrogen more than 0.6%, is due to that they contain a large amount of manganese and chromium.

2. With increase of nitrogen, the matrix becomes to consist of only gammer single phase, and the precipitates of $M_{23}C_6$ and Cr_3N become to distribute more finely when heated for 1000hr. at 700°C. These effects cause the creep rupture strength to increase with strengthening of the matrix. By addition of niobium to this type alloy, the solutioned hardness increases, the grain size becomes finer, and G.B.R., the age hardening properties are suppressed.

Further, by addition of boron to this type alloy, G.B.R. is suppressed and the high temperature ductility is improved and also

effective precipitation strengthening in high temperature strength is considered to be obtained. These are thought to be the reason why the creep rupture life and elongation are improved by addition of boron.

3. G.B.R. recognized in this type alloy, tends to occur at such a region where the lattice is disordered as the triple point region of the grain boundaries, and the region where twin and grain boundary meet each other.

4. Preaging is not hopeful from the point of view of high temperature strength. As the solution temperature becomes higher, the creep rupture life is improved, on the contrary, creep rupture elongation decreases. So, solution temperature of about 1200°C is suitable in 10M6N alloy regarding creep rupture ductility. But, 10M6NB alloy solution treated at 1300°C show the excellent creep rupture ductility and also show about 20kg/mm² of the creep rupture strength at 700°C, 10000hr. So, it is desirable that the solution temperature is as high as possible in the temperature range of up to 1300°C in 10M6NB alloy. The excellent high temperature strength of this type alloys is considered to be due to the solution hardening by molybdenum, tungsten and nitrogen; increase of solutioned hardness and refinement of grain size by niobium; improvement of creep rupture ductility due to suppression of G.B.R. by boron and niobium; fine distribution of such precipitates as M₂₃C₆, Cr₃N, etc., and so on.

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Table 1. Chemical compositions of alloys (* charged composition)

Alloy	C	Mn	Cr	Ni	Mo	W	Nb	S.N.	I.N.	B
N-0	0.20	10.23	19.82	6.59	1.96	2.45	0.54	0.0654	0.0187	-
N-1	0.23	10.18	19.98	6.03	1.83	2.38	0.74	0.2975	0.0825	-
N-2	0.23	10.33	20.44	6.48	2.03	2.15	0.56	0.5096	0.1050	-
N-3	0.23	10.48	20.36	5.92	2.21	2.72	0.77	0.5348	0.1204	-
N-4	0.22	9.48	20.24	5.98	1.87	2.63	0.66	0.5495	0.1149	-
N-5	0.22	10.13	19.87	5.88	1.92	2.24	0.75	0.6013	0.1531	-
N-6	0.25	9.68	19.27	6.42	1.87	2.37	0.98	0.8017	0.1230	-
N-7	0.25	9.72	20.63	6.04	2.13	2.21	0.84	0.7701	0.1631	-
N-8	0.23	10.31	19.25	5.87	1.97	2.45	0.78	0.8749	0.1040	-
Nb0	0.26	9.85	19.45	5.88	2.0*	2.39	-	0.588	0.022	-
Nb1	0.27	10.0*	20.0*	6.0*	2.0*	2.5*	1.0*	0.455	0.115	-
MN	0.17	10.21	19.16	5.82	1.90	2.34	0.61	0.434	0.102	-
MB	0.17	10.26	19.04	5.90	1.88	2.33	0.62	0.377	0.129	0.02
50A	0.26	10.0*	22.0*	6.0*	2.0*	2.5*	1.0*	0.50	0.11	-
50C	0.25	9.41	21.67	5.72	1.90	2.43	0.65	0.482	0.123	0.009
50D	0.245	9.40	21.64	5.67	1.92	2.42	0.62	0.447	0.144	0.04
50E	0.24	10.0*	22.0*	6.0*	2.0*	2.5*	1.0*	0.27	0.20	0.11
B	0.24	8.51	19.50	5.92	2.08	2.24	-	0.602	0.023	-
10M6N	0.20	10.0*	20.0*	5.95	2.0	2.5*	1.1	0.571	0.169	-
10M6NB	0.21	10.0*	20.0*	6.0*	2.0*	2.5*	1.0*	0.497	0.187	0.0083

Table 2. Effect of niobium on the relation between the solution temperature and the grain size, hardness

Sol. temp.	Grain Size Hardness	Alloy	
		Nb 0	Nb 1
1100°C	G. S.	5~6	>8
	H.	258	305
1150°C	G. S.	4~5	>8
	H.	247	299
1200°C	G. S.	4	7~8
	H.	242	294
1250°C	G. S.	2~3	6~7
	H.	236	269
1300°C	G. S.	2	3~4
	H.	233	263

Table 3. X-ray analysis of undissolved phase of 50A, 50C, 50D and 50F alloys solution treated at 1150°C, 1200°C and 1250°C

note: A, detected clearly
 B, detected a little
 C, detected not any

Sol. temp.	Alloy	Nb(C,N)	BN	M C	Z
1150°C	50A	A	C	C	A
	50C	A	C	A	A
	50D	A	A	A	A
	50F	A	A	A	A
1200°C	50A	A	C	C	A
	50C	A	C	C	A
	50D	A	A	A	A
	50F	A	A	A	B
1250°C	50A	A	C	C	B
	50C	A	C	C	B
	50D	A	C	A	B
	50F	A	C	A	C

Table 4. Creep rupture properties of 10M6N, 10M6NB alloys of notched specimens at 700°C, 26 kg/mm²

note: $d_t=3.7$ R.A. : reduction of area
 numerical numbers in parenthesis mean creep rupture life and elongation of plain specimen

Alloy	Sol. temp(C°)	Creep rupture life (hr)	R. A.(%)
10M6N	1200	1119.8 (547.3hr, 30.6%)	7.0
	1300	75.4 (649.9hr, 7.0%)	1.9
10M6NB	1150	3786.2 (751.2 hr, 41.6%)	12.4
	1300	8985.3 (2200.4hr, 17.7%)	4.4

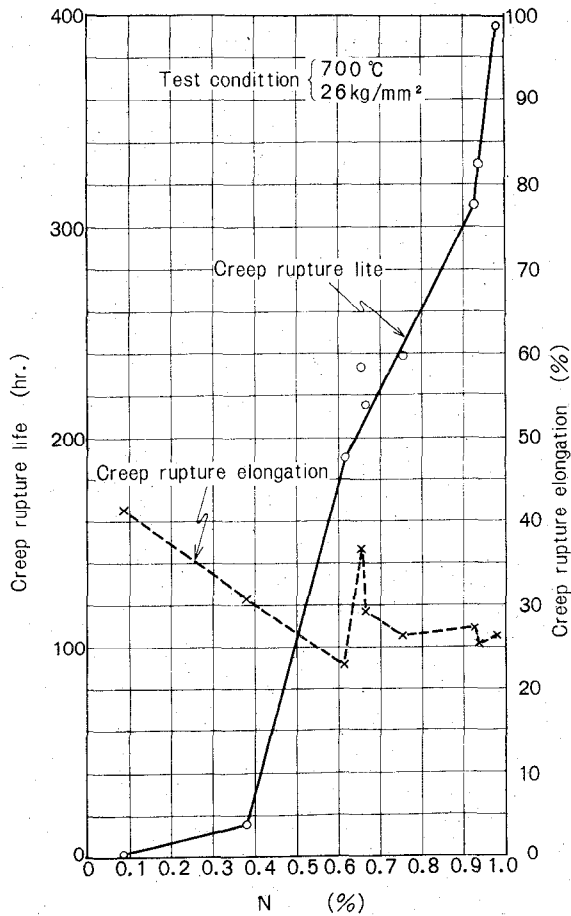


Fig. 1. Effect of nitrogen on the creep rupture life and the creep rupture elongation of 10M6N type alloys.

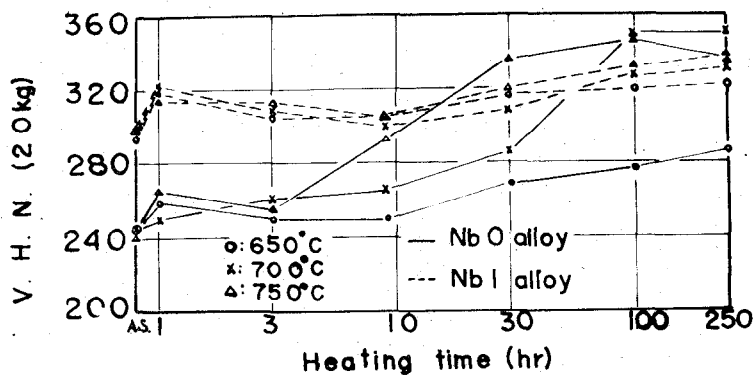


Fig. 2. Effect of niobium on the age hardness of 10M6N type alloy

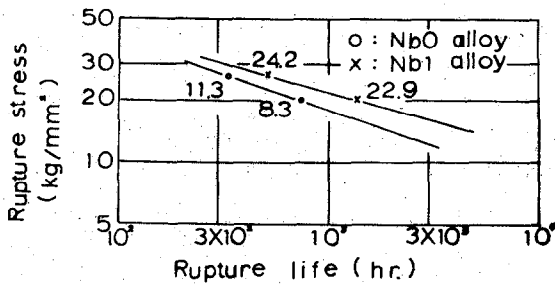


Fig. 3. Effect of niobium on the creep rupture properties of 10M6N type alloys at 700°C

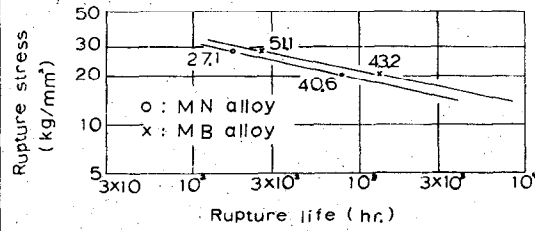


Fig. 4. Effect of boron on the creep rupture properties of 10M6N type alloys at 700°C

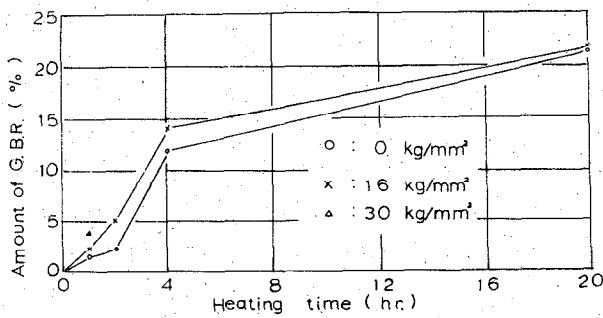


Fig. 5. Effect of stress on the amount of G.B.R. of B alloy at 750°C

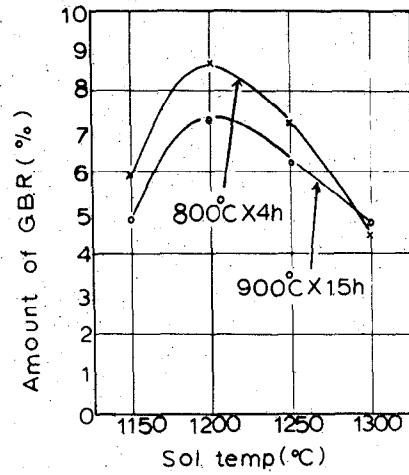


Fig. 6. Effect of solution temp on amount of G.B.R.

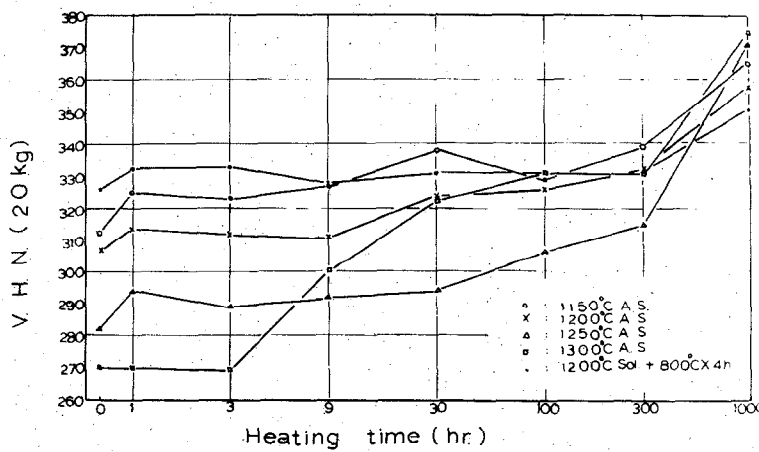


Fig. 7. Effect of heat treatment on age hardening properties of 10M6N alloy

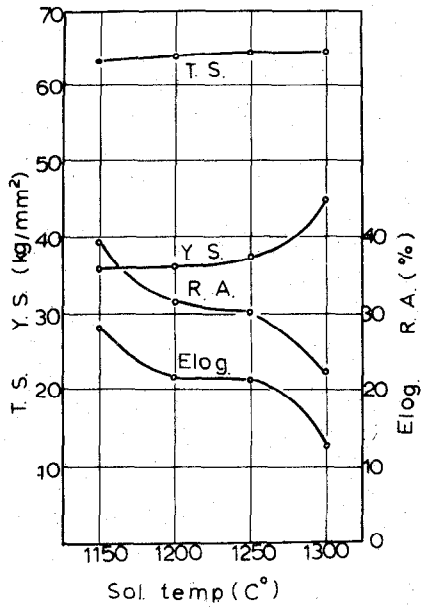


Fig. 8. Effect of sol temp on short time tensile properties of 10M6NB alloy

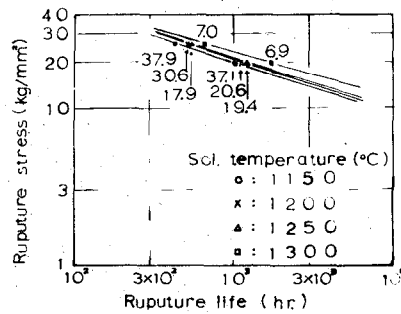


Fig. 9. Effect of solution temperatures on the creep rupture properties of 10M6NB alloys

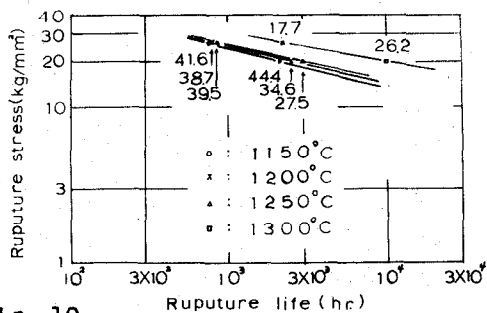


Fig. 10. Effect of solution temperatures on the creep rupture properties of 10M6NB alloys

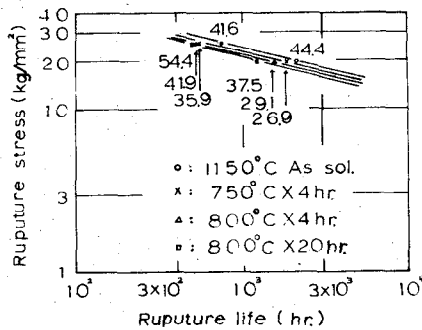
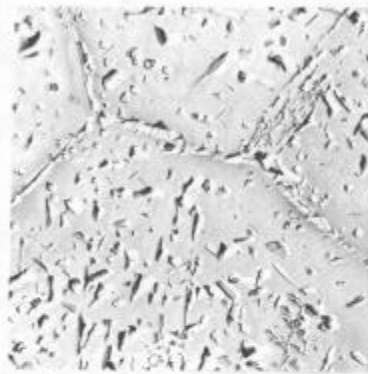


Fig. 11. Effect of aging on the creep rupture properties of 10M6NB alloys solution treated at 1150°C



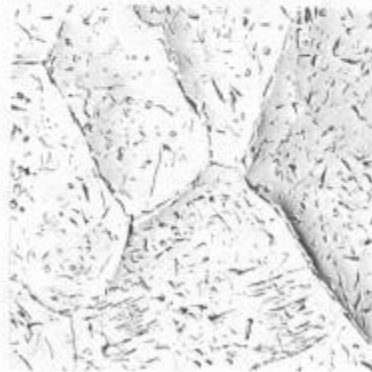
(a) N-0 (0.084%)



(b) N-2 (0.615%)



(c) N-5 (0.754%N)

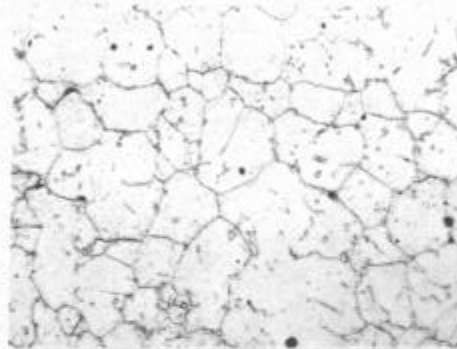


(d) N-8 (0.979%N)

Photo. 1 Microstructures of alloys aged for 1000hr. at 700°C. (X 3000)



(a) Nb0

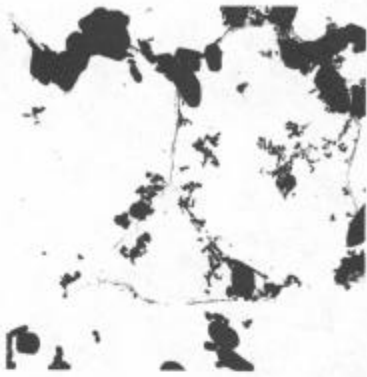


(b) Nb1

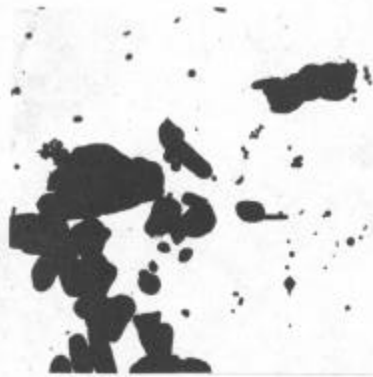
Photo. 2 Microstructures of Nb0, Nb1 alloys aged for 250hr. at 700°C. (X 400)

H-72226

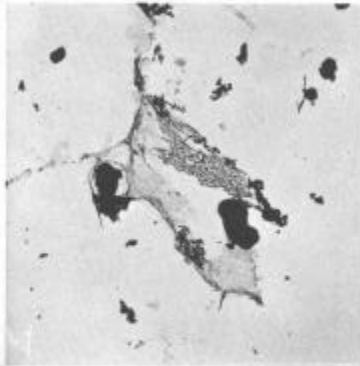
H-72226



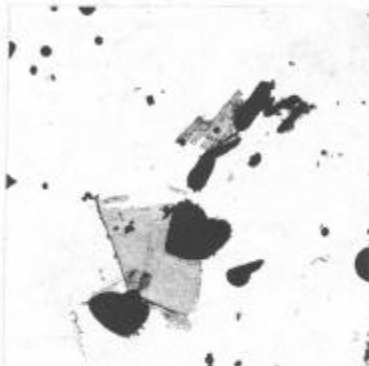
(a) MN 700°C 1.5hr.



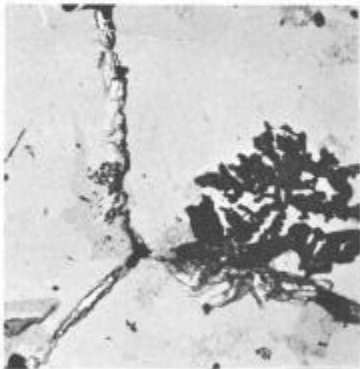
(b) MB 700°C 1.5hr.



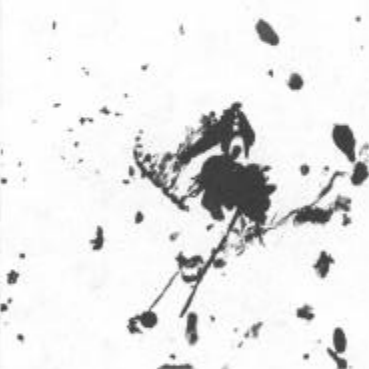
(c) MN 700°C 6hr.



(d) MB 700°C 6hr.

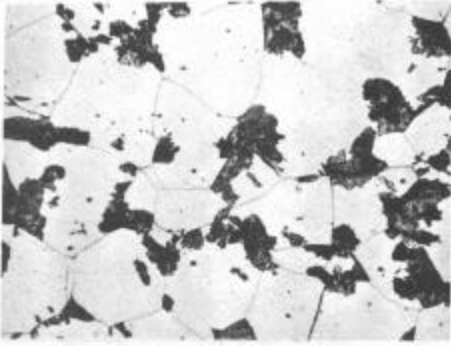


(e) MN 800°C 1.5hr.



(f) MB 800°C 1.5hr.

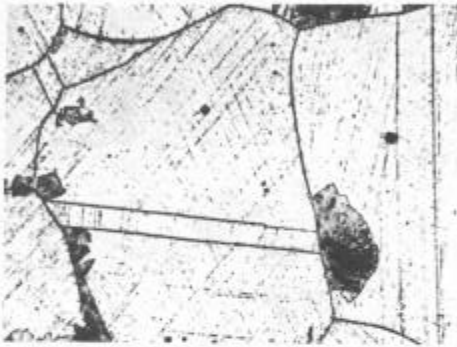
Photo. 3 Microstructures of MN, MB alloys aged at 700°C and 800°C, (X 3000)



(a) 800°C 4hr.(X 100)



(b) 800°C 4hr.(X 400)



(c) 800°C 4hr.(X 400)



(d) 800°C 4hr.(X1000)



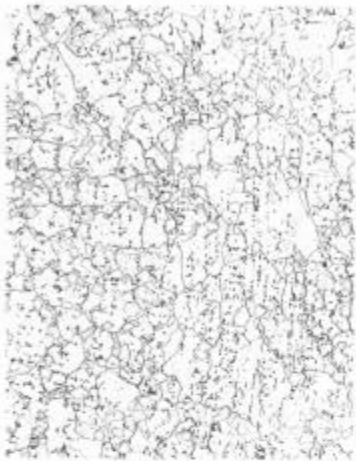
(e) 900°C 20min.(X 250)

Photo. 4 Microstructures of NbO alloy aged at 800°C and 900°C.

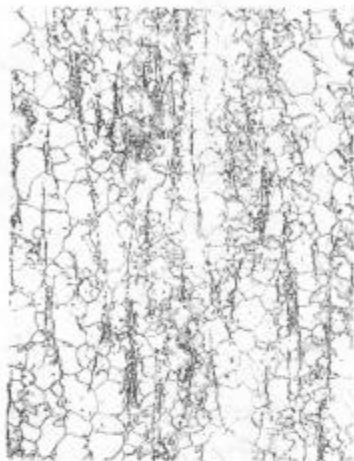
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H-72229



(a)



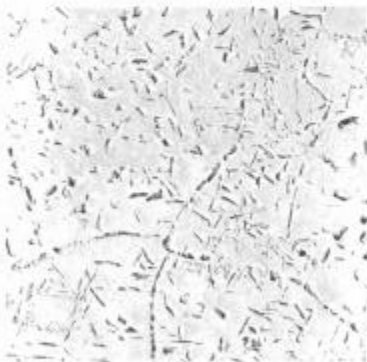
(b)



(c)

Photo. 5 Microstructures of 10M6N alloy heated for 1hr. at 900°C after solution treated at 1250°C. (X 63)

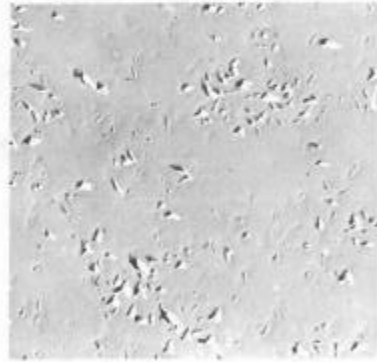
- (a) forging ratio, about 1.5
- (b) forging ratio, about 4
- (c) forging ratio, about 9



(a)
10M6N
solution treated
at 1150°C

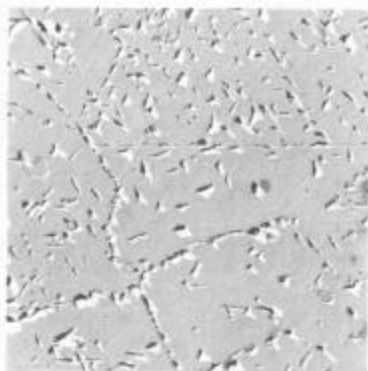


(b)
10M6N
solution treated
at 1200°C

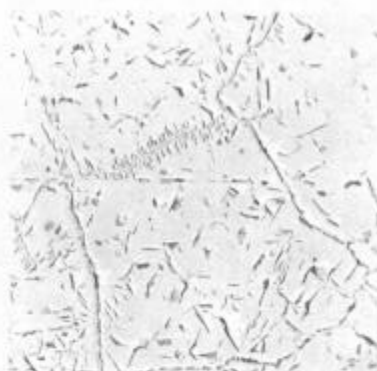


(c)
10M6N
solution treated
at 1300°C

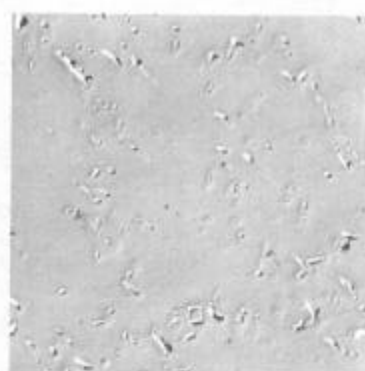
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(d)
10M6N
solution treated
at 1200°C and heated
for 4hr. at 800°C

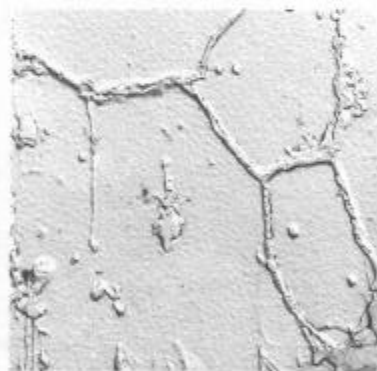


(e)
10M6NB
solution treated
at 1150°C

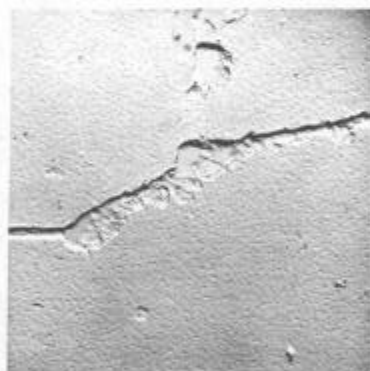


(f)
10M6NB
solution treated
at 1300°C

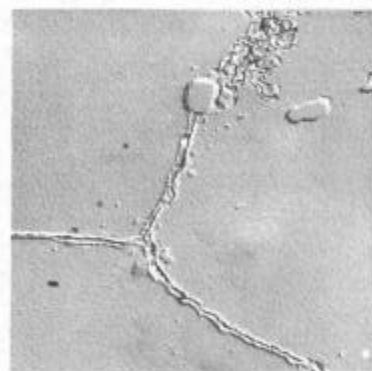
Photo. 6 Microstructures of 10M6N type alloys heated for 1000hr. at 700°C, after heat treated at various conditions. (X 3000)



(a)



(b)



(c)

Photo. 7 Microstructures of 10M6N alloy aged for 20hr. at 700°C. (X 3000)
a: solution treated at 1150°C
b: solution treated at 1250°C
c: solution treated at 1300°C