17Cr-4Ni-4Cu Precipitation Hardening Stainless Steel

(The First Report)

The Effect of Heat Treatments on The Properties of The Casted Material*

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(Recieved October 10, 1965)

The effect of heat treatments on the casted 17-4PH Type stainless steel has been studied by means of hardness testing, dilatometric, magnetic, X-ray, corrosion proof and metallographic methods. The results were as follows: (1) Solution treatment (S. T.) temperature gives remarkable effects on the Ms-point, hence on as-quenched structure and hardness. If the materials were water-quenched to R. T. from the temperature $\leqq$ 880°C, 890°C~1080°C and $\geqq$ 1100°C, the structures were mainly martensite (+ferrite), martensite (+ferrite) + austenite and austenite respectively. (2) Ms-point gets down as S. T. temperature rises, and it reaches about 15°C at 1100°C S. T.. (3) The effect of refrigeration is most remarkable at -100°C, and for -100°C × 5Hrs the hardness reaches about 340 V.P.N. with undetectable retained austenite (γ_R). (4) If the temperature rises from desired degree for a moment during S. T., a long time is required to recover this influence. (5) When a specimen containing a large amount of γ_R is aged, a part of γ_R is transformed into martensite in cooling process. (6) The structure of as-solution-treated specimen contains always some δ-ferrite, and its quantity decreases with increasing S. T. temperature.

Introduction

In recent years considerable attention has been given to Armco 17-4PH type stainless steel because of its high-strength and -hardness, excellent corrosion resistance and low temperature age-hardening process. A starting point for the development of this alloy is a 0.1%C 17%Cr-4%Ni composition, which is just on the borderline of forming δ-ferrite and has its martensite transformation range occurring just above room temperature[1]. Consequently a small difference in alloying element or heat treatment has a considerable effect on the physical property of 17-4PH steel, its component is 0.08% $\geqq$ C, 15.5~17.5%Cr, 3.0~5.0%Ni and 3.0~5.0%Cu nominally[2) 3)].

* A part of this research was presented at the Semiannual Conventions of Japan Institute of Metals, held 7 times between November, 1959 and October, 1962.

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This report deals with the fundamental studies about the effect of heat treatment on the properties of the casted 17–4PH stainless steel.

Experimental Detail

Materials Studied

The materials used were melted in 150kgr induction furnaces, and the melt was poured in air to form a 15kgr ingot. The samples were machined from this ingot as 30mm×40mm × 15mm for hardness tests, 20mmϕ × 5mm for hardness tests and X-ray analysis, 10mmϕ × 100mm for Ms-point determination, 5mmϕ × 80mm for dilatation tests and magnetic analysis, and 15mm×15mm × 5mm for corrosion proof tests. The chemical compositions of the materials which constitute the basis of this investigation are given in the Table.

Chemical Analyses (per cent by weight)

C	Si	Mn	P	S	Ni	Cr	Cu
0.07	0.51	0.60	0.018	0.011	4.55	17.18	4.27

Procedures

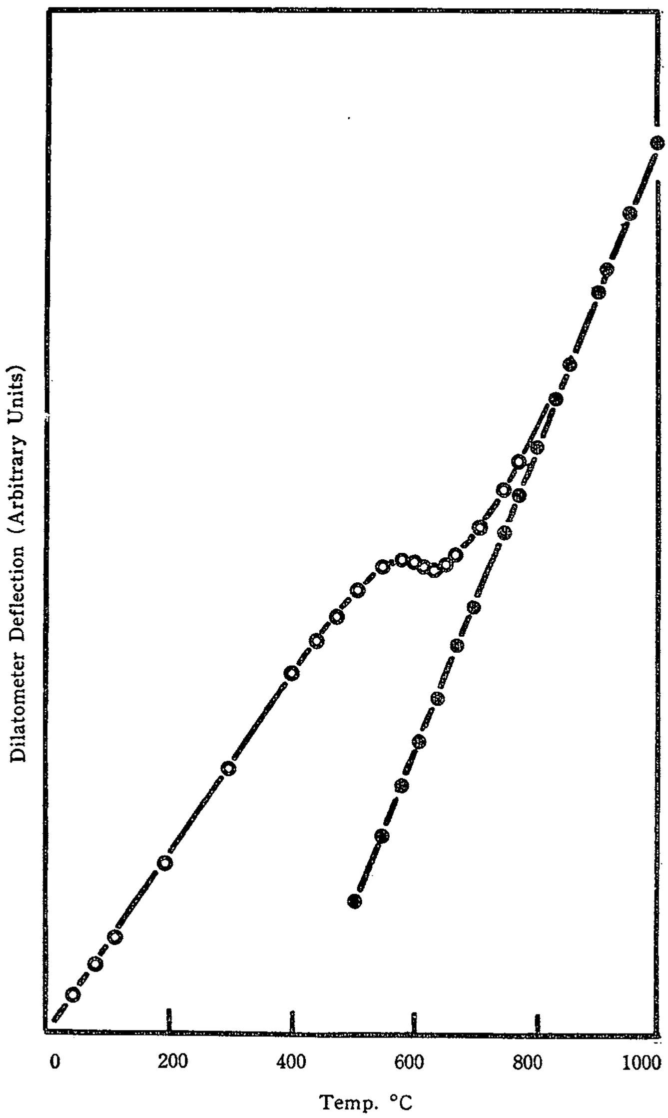
Heat treatments, except subzero-treatment, were carried on in vacuum furnace of about 5×10^{-5}mmHg. The temperature of the specimen was recorded by Chromel/Alumel couple with the accuracy of 0.5%. Temperature difference in the required part of the furnace was negligible for our experiment. For solution-treatment (S. T.) and aging, the temperature of the furnace was kept in 1°C above or below desired condition. The structural composition was analysed by X-ray diffractometer with Cr– or Co–K_α radiation. Determinations of Ms-points were made by magnetic method developed by Chapman and Jominy[4] and modified in our laboratory. Corrosion proof test was carried on under static condition at room temperature. As-machined samples were all homogenized for 2Hrs at 1100°C prior to desiered heat treatment.

Results and Discussion

Effect of Solution-treatment Temperature

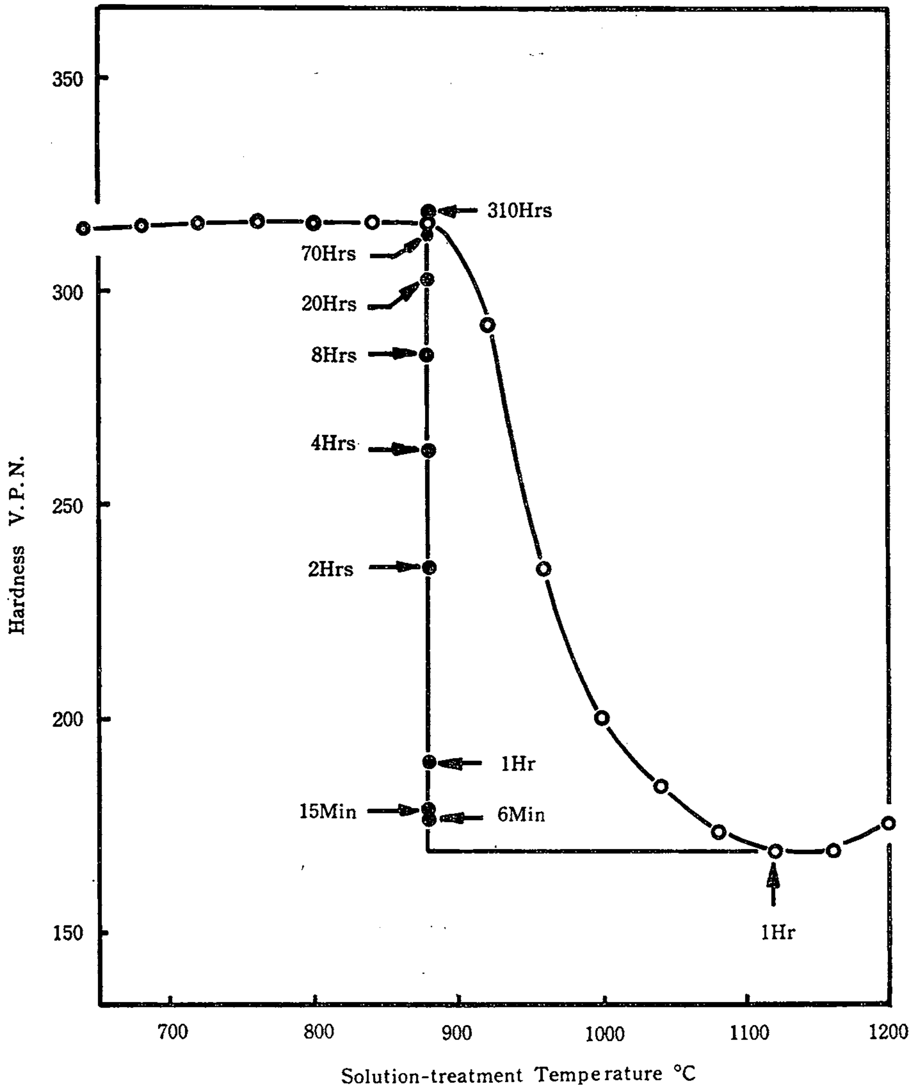
Fig. 1 shows the typical dilation curve of this material. Heating or cooling velocity was 5°C/min, and the Ac_3 point in this steel was found to be about 570～580°C. So, the specimen was solution-treated for 1Hr at various temperatures higher than 620°C and the hardness of as-water-quenched

Fig. 1 : Dilation Curves on Continuous Heating and Cooling of As-quenched 17-4PH Steel.



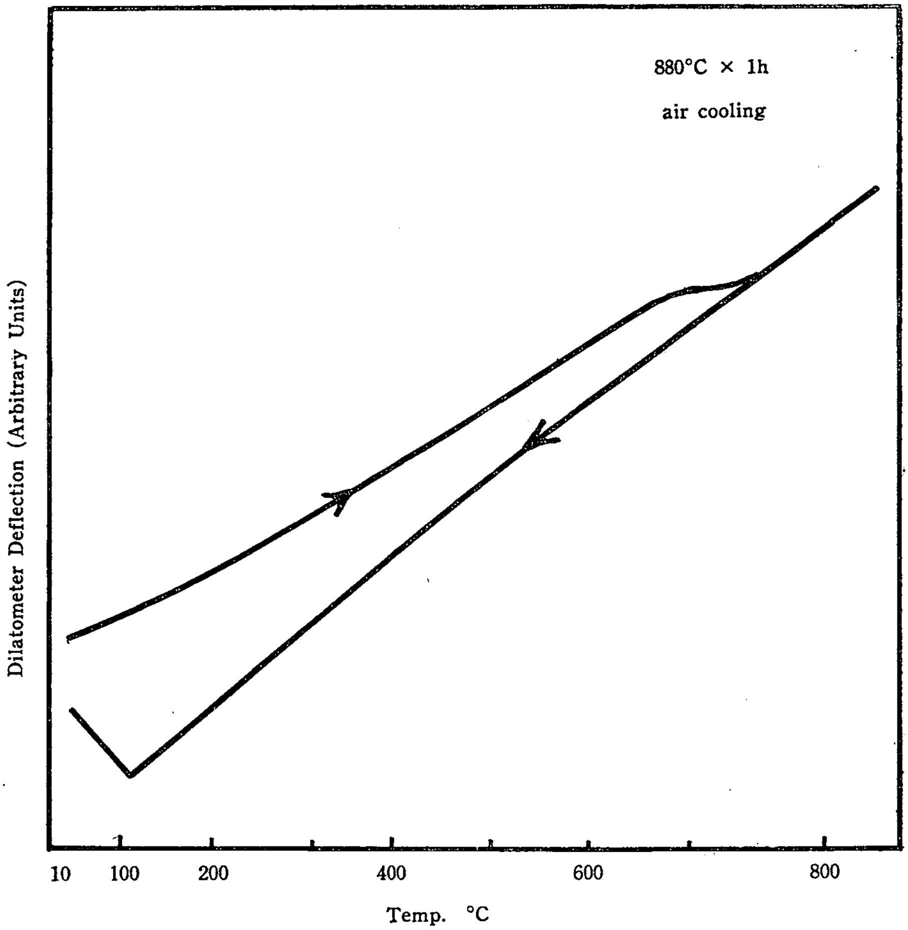
material was analysed through Vickers hardness tester. The relation between S. T. temperature and hardness is given in Fig. 2. This figure shows distinctly that the hardness curve consists of following 3 parts. (1) S. T. temperature lower than 880° C——Hardness is about 317 V.P.N., nearly constant. (2) S. T. temperature between 890° C and 1080° C——Hardness decreases rapidly from V.P.N. 317 to V.P.N. 160 as S.T. temperature rises from 890° C to 1080° C. (3) S. T. temperature higher than 1100° C——

Fig. 2 : Effect of Solution-treatment Temperature on Hardness in 17-4PH Steel. (Water-quenched to 20°C. Heating Time=1 hour, except where indicated.)



Hardness reaches again nearly constant value. Siginificance of this as-quenched hardness curve may be recognized putting the result together with the succeeding research on the Ms-point. Fig. 3 and Fig. 4 show typical quenching curve obtained using Honda-Sato type quenching dilatometer and Chapman and Jominy type magnetic analyser respectively. The remarkable dilation at 107°C appearing in the rapid cooling curve given in Fig. 3 corresponds to the notable increase of magnetic permeability at the same temperature shown in Fig. 4, and denotes the Ms-point. Fig. 5 shows the re-

Fig. 3 : Quenching Curve of 17-4PH Steel.



lationship between S. T. temperature and Ms-temperature obtained through the above methods. The rapid increase of magnetic permeability at higher temperature denoted in Fig. 4 occurs at almost constant temperature, about 570° C, irrespective of S. T. temperature. When the specimen is solution-treated at the temperature ranging from 760° C to 1100° C, the increase of magnetic permeability is remarkable as S. T. temperature gets down. Judging by Fig. 3, we can recognize that this magnetic transformation is not accompanied by structural change and shows the Curie point of ferrite. And the above-mentioned interpretation is consist with the metallographic observation as shown in the Photographs from No. 1 to No. 15. Deducing from Ms-temperatures given in Fig. 5, S.T. temperature/as-quenched hardness relationship, shown in Fig. 2, may be interpreted as follows. When S. T. temperature rises higher than 1010 °C Ms-temperature gets down lower than 15° C, and the hardened structure of the specimen water-quenched to

Fig. 4 : Magnetic Permeability vs Temperature for 17-4PH Steel. Water-quenched from 840°C to Room Temperature.

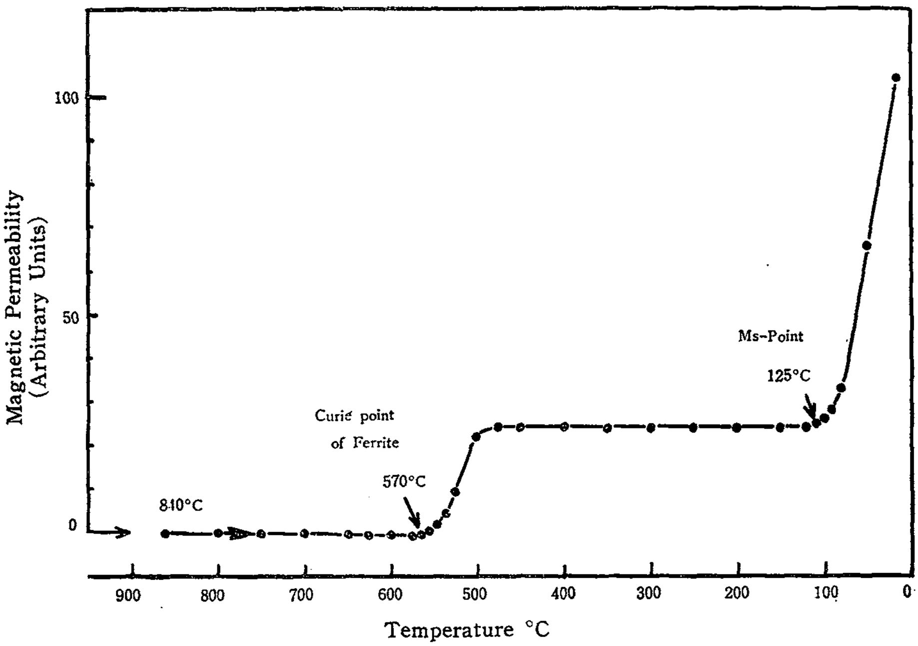
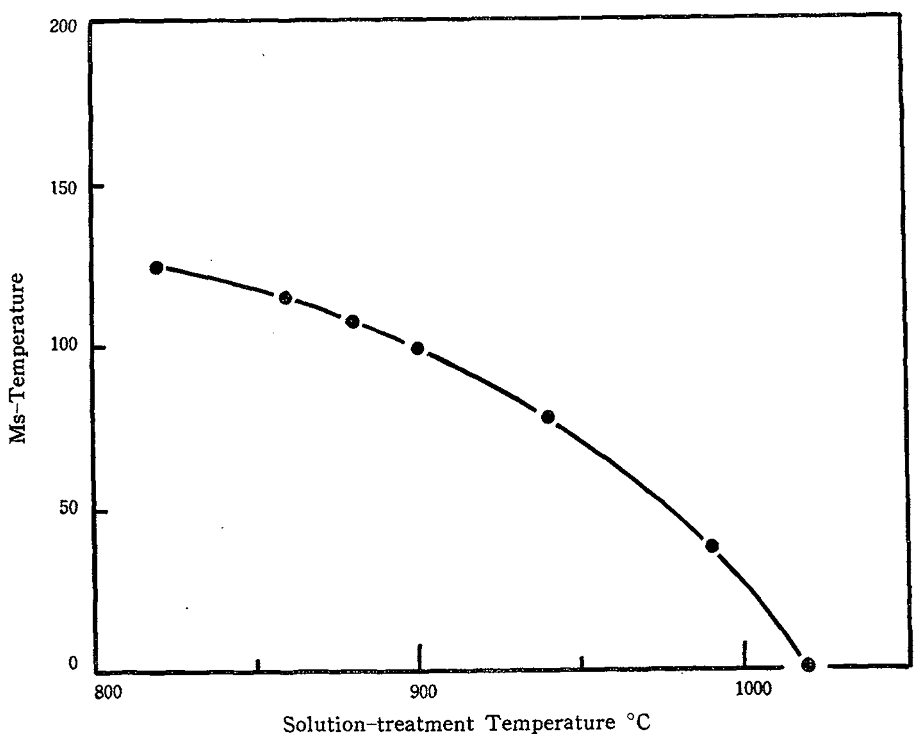
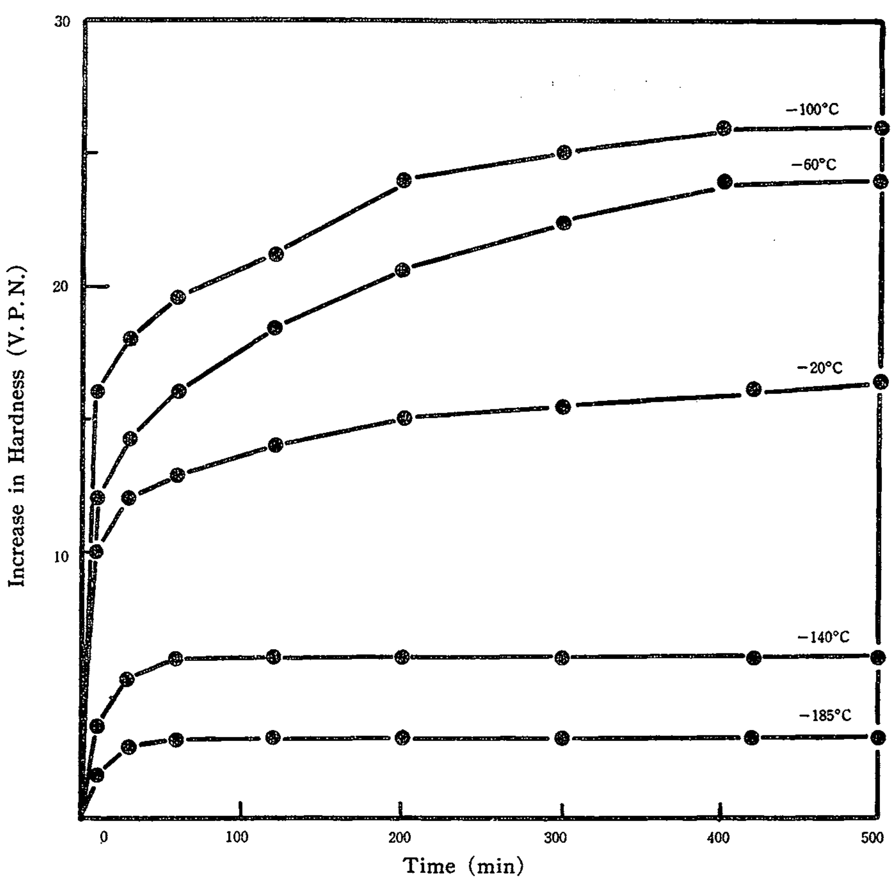


Fig. 5 : (Ms-Temperature)-(Solution-treatment Temperature) 17-4PH Steel.



R.T. contains unnoticeable small martensite. This may be also distinctly observed from the magnetic transformation curve. Moreover, the magnetic curve shows that the quantity of δ-ferrite is small as S.T. temperature is high. Consequently, the structural composition which contributes to lower plateau (V.P.N. ≒ 160) shown in Fig. 2, is mainly austenite. On the other hand, when S.T. temperature gets down lower than 900° C, Ms-temperature rises higher than 100° C and the greater part of austenite transforms into martensite. The hardened structure which gives higher plateau (V.P.N. ≒ 317) shown in Fig. 2, is mainly composed of martensite with additional small quantity of δ-ferrite and retained austenite (γ_R). When the specimen is solution-treated at the temperature ranging from 900°C to 1010°C, hardened structure is composed of martensite + austenite + δ-ferrite, while their ratio changes remarkably according to chemical composition and S.T. temperature, and the marked change in hardness is caused. Again the right end of upper plateau in the hardness curve shifts slightly as the chemical composition changes. Concluding from above-mentioned results, in order

Fig. 6 : Effect of Subzero-treatment.

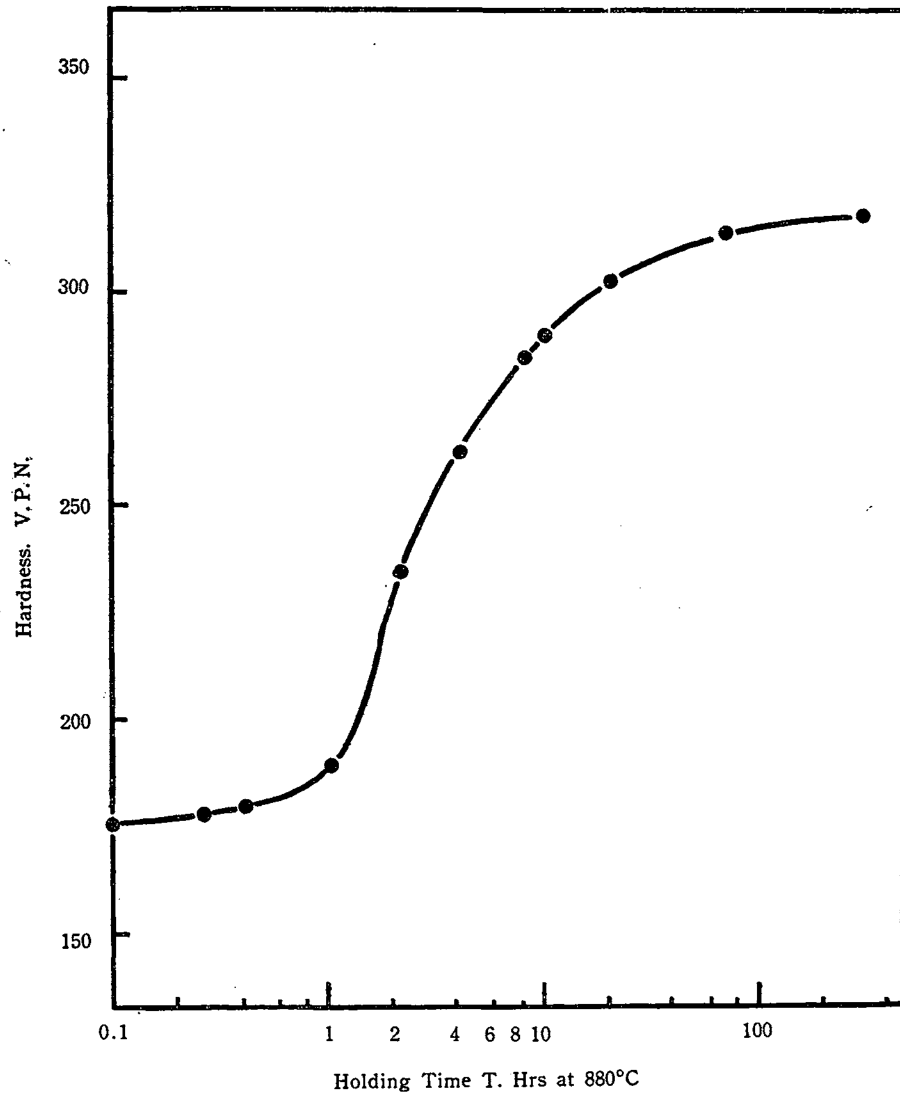


to get a definite hardness after the solution-treatment, irrespective of small differences in chemical composition and S. T. temperature, it may be desirable to keep S. T. temperature at about 880° C.

Effect of Subzero-treatment

Fig. 6 shows the effect of subzero-treatment on hardness. Before refrigeration each specimen was homogenized for 2 Hrs at 1100° C, cooled to R. T. in air, solution-treated for 1 Hr at 880° C, water-quenched to R.T. and aged about 1 Hr at R.T.. As is shown in the diagram, when the specimen is subzero-treated at the temperature higher than -100°C the effect of refrig-

Fig. 7 : Effect of Solution-treatment Temperature and Time on Hardness in 17-4PH Steel. 1120°C×1 hr→880°C×T Hrs→W.Q. to R.T.

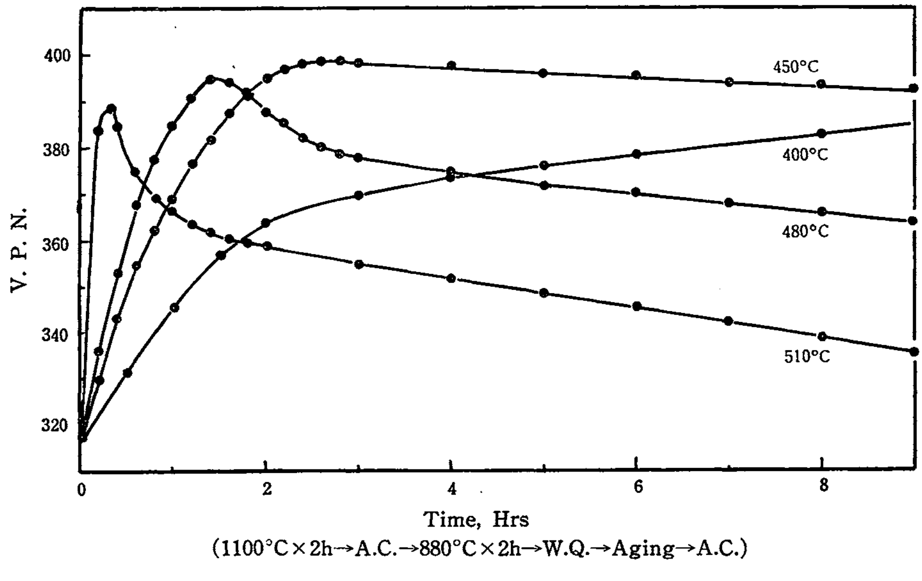


eration increases gradually as the temperature gets down, and at the temperature lower than -100°C this relation is reversed. Namely, the effect of refrigeration is maximum at about -100°C. Though the X-ray diffraction pattern of the as-water-quenched specimen contains the (111) line of γ_R, it was not recognized after -100°C×5 Hrs subzero-treatment. Consequently it may be concluded that if the specimen, water-quenched from 880°C to R.T., is refrigerated at -100°C for more than 5 Hrs, almost all austenite transforms into martensite reaching 340 V.P.N. hardness.

Effect of Temperature Variation during The Solution Treatment

Even if the temperature lowers from desired degree for a short time during S.T., Ms-temperature is not affected at all. While, if the temperature rises from desired degree for a moment during S.T., Ms-point undergoes a remarkable influence. One extreme example in the latter case is given in Fig. 7, which shows the relation between the as-water-quenched hardness and holding time at 880°C; in this experiment the specimen was first solution-treated at 1120°C for 1 Hr, then cooled to 880°C and held for various time at that temperature, and then water-quenched to R.T.. This relation is also superimposed on S.T. temperature/hardness curve in Fig. 2. From these results we can recognize that if the S.T. temperature rises from desired degree for a time, a long time is required to recover this influence. M. Cohen[5] attributes the similar phenomenon in 1.1%C-5.4%Ni-steel to "*statistical concentration distribution*", and the above-mentioned result may be caused by the same reason.

Fig. 8 : Vickers Hardness of 17-4PH Steel after Aging for Various Hours at Indicated Temperatures.

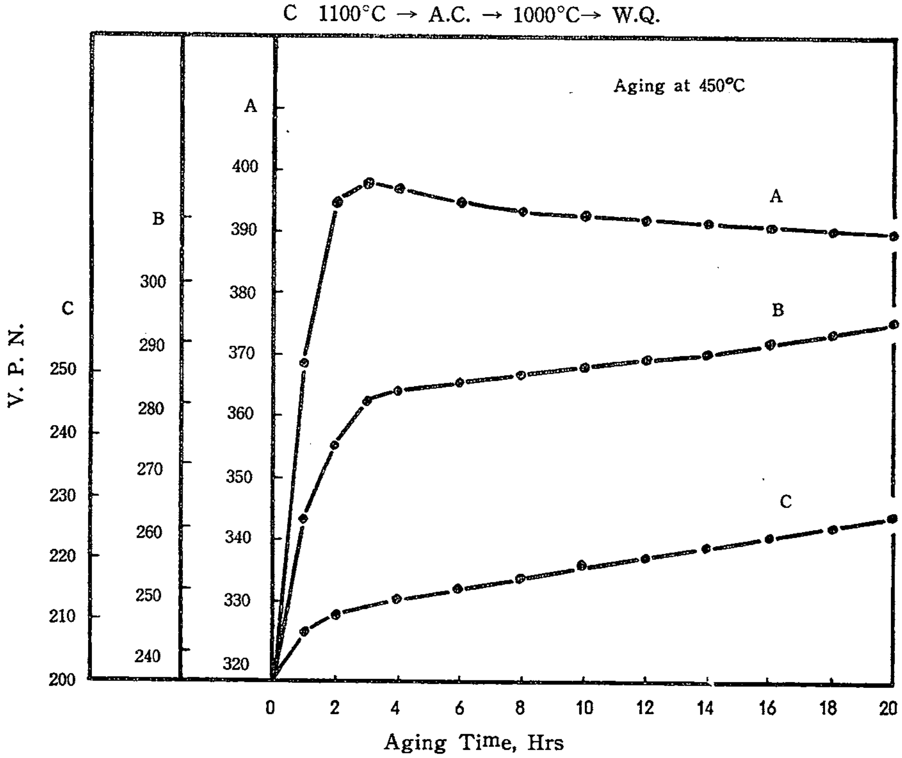


Effect of Aging

Fig. 8 denotes the results of the hardness tests after the aging for 1~10 hours at 400°C, 450°C, 480°C and 510°C. Solution-treatments were always performed at 880°C × 2Hrs. Maximum hardness after aging reached about 385~400 V.P.N., and at above-mentioned aging temperature range, the material was more rapidly over-aged as aging temperature rose. That is, according as the aging temperature rises the following tendencies were observed; maximum aged-hardness gets down, softening begins in the earlier period of aging and progresses more rapidly. Concluding from above-mentioned results, it may be desirable to age the material at 450°C ~ 480°C.

Fig. 9 shows the hardness/aging-period curves at 450°C, and denotes the relation between the increment of hardness caused by aging and the quantity of martensite in as-quenched condition. A, B and C series gives the aged hardness curves of materials water-quenched from 880°C, 960°C and 1000°C respectively. Structural compositions of the as-quenched materials are as follows: A = almost all martensite (+ferrite), B = martensite (+ferrite)+austenite (nearly the same quantity). C=almost all austenite and little martensite (+ferrite). As is shown in Fig. 9, the more mar-

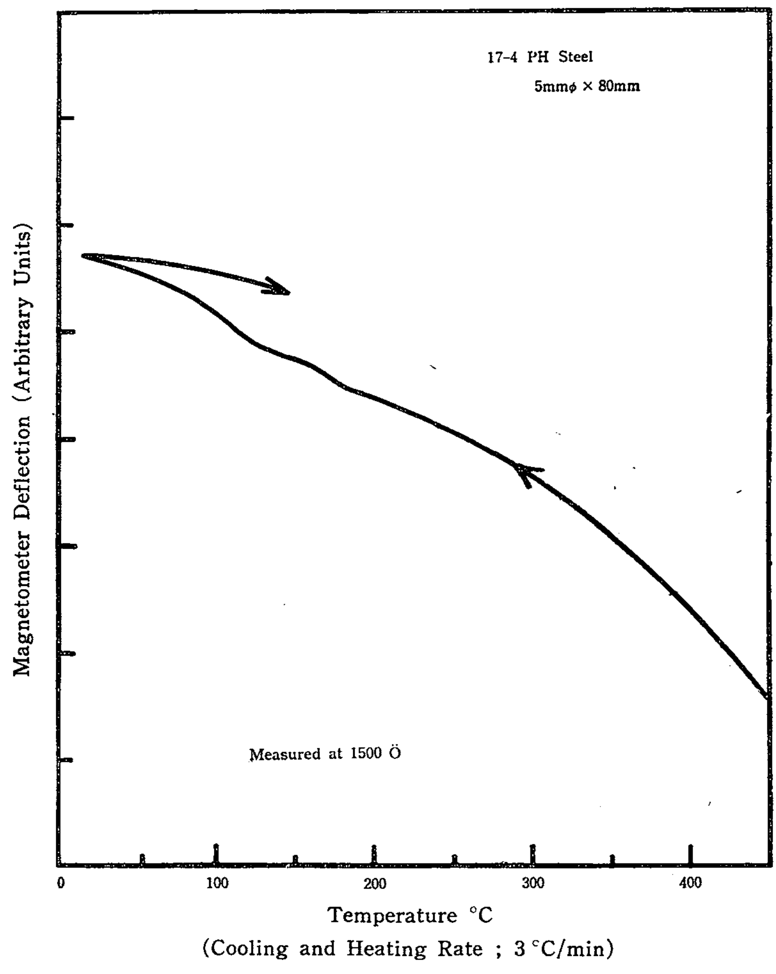
Fig. 9 :
A 1100°C → A.C. → 880°C → W.Q.
B 1100°C → A.C. → 960°C → W.Q.
C 1100°C → A.C. → 1000°C→ W.Q.



tensite is contained the more aging effect is remarkable. Regardless of the series A, B, C, aged-hardness increases rapidly with time in the early period of aging. However softening begins gradually after 2 Hrs (maximum hardness=V.P.N. 400) in the case of A series which contains much martensite, while a slight increase of hardness goes on at least for 20 Hrs in the case of B and C series which contains less martensite.

Age-hardening of 17-4PH type steel may be mainly attributed to the precipitation of Cu solid solution in martensite as is reported in references [1),2),6),7),8)] and our result for A series also coincided their conclusion. However also in C series, which is chiefly composed of austenite and contains almost negligible martensite, considerable aging was recognized and this is a very interesting problem. If the specimens, belonged to C series, are aged at 450°C and then their cooling processes are analysed with dilatometric or

Fig. 10 : Thermomagnetic Curve of 17-4PH Steel following 450°C Aging



magnetic method, the irreversible dilation or increase of magnetic intensity on the cooling process are recognized as is shown in Fig 10. Consequently it may be concluded that the increase of hardness in C series may be attributed to the next two; (1) a little precipitation of Cu-rich phase in austenite during the aging, (2) martensite transformation of partial γ_R on the cooling process, caused by the unstability of γ_R originated in the carbide precipitation during the aging.

Fig. 11 : Corrosion of 17-4PH Steel Aged at 450°C, Dipped in 5% H_2SO_4 for 50 Hrs.

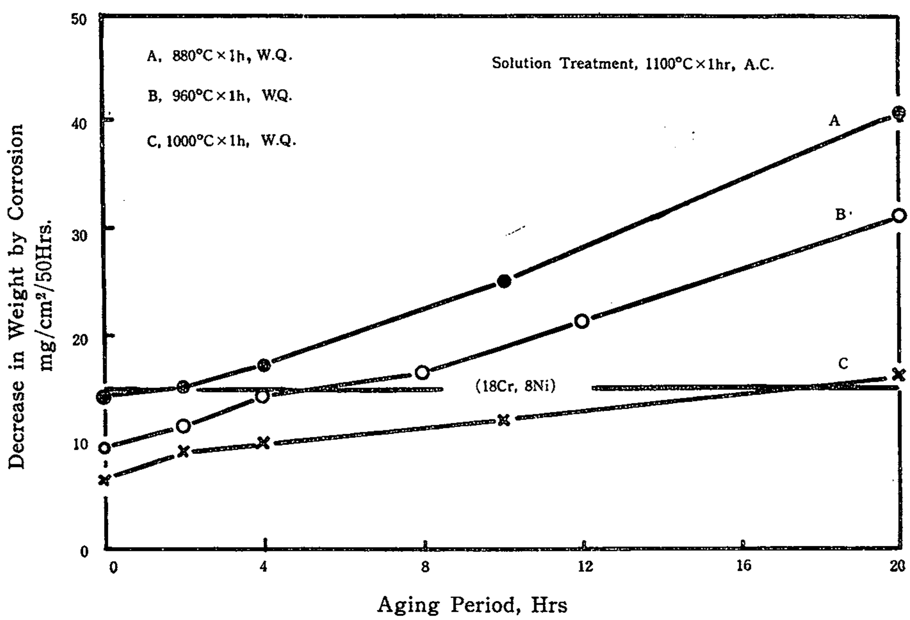
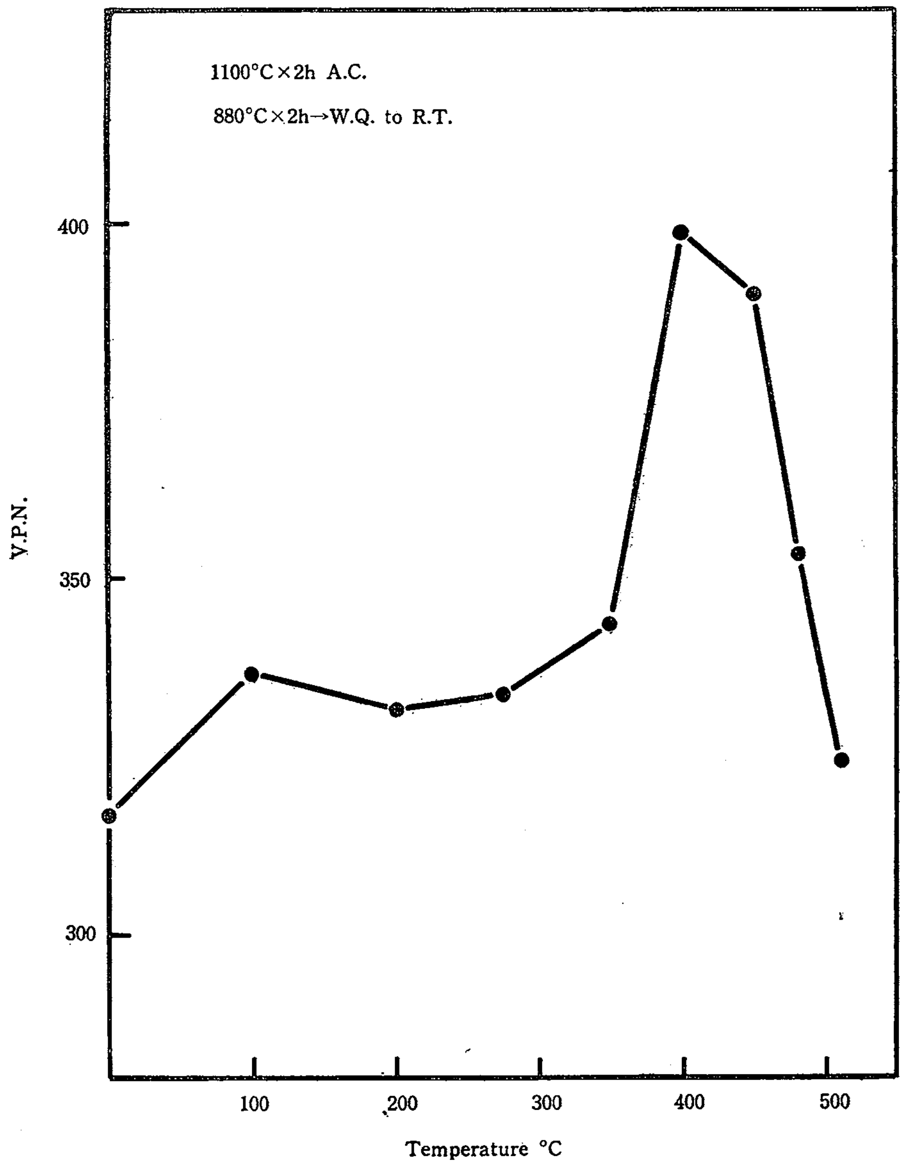


Fig. 11 shows the corrosion rate of the material after the aging at 450°C for various times. Corrosive reagent is 5 wt% H_2SO_4 solution, time needed for corrosion is 50 Hrs and the specimens were machined from the same Heat as was used in the experiment shown in Fig. 9. The heat treatments before the corrosion proof tests are also the same as in Fig, 9. For comparison, the same corrosion proof test of 18Cr—8Ni stainless steel is also superimposed in Fig. 11. The results denoted in Fig. 11 may be considered as a good evidence for the above-mentioned interpretation on Fig. 9.

Fig. 12. denotes the aging-temperature/hardness relation about the specimen aged for 20 Hrs at various temperature ranged from 100°C to 510°C. As is denoted in this diagram, though the age hardening is remarkable at the temperature higher than 400°C, over aging is caused rapidly when the aging temperature exceeds 480°C.

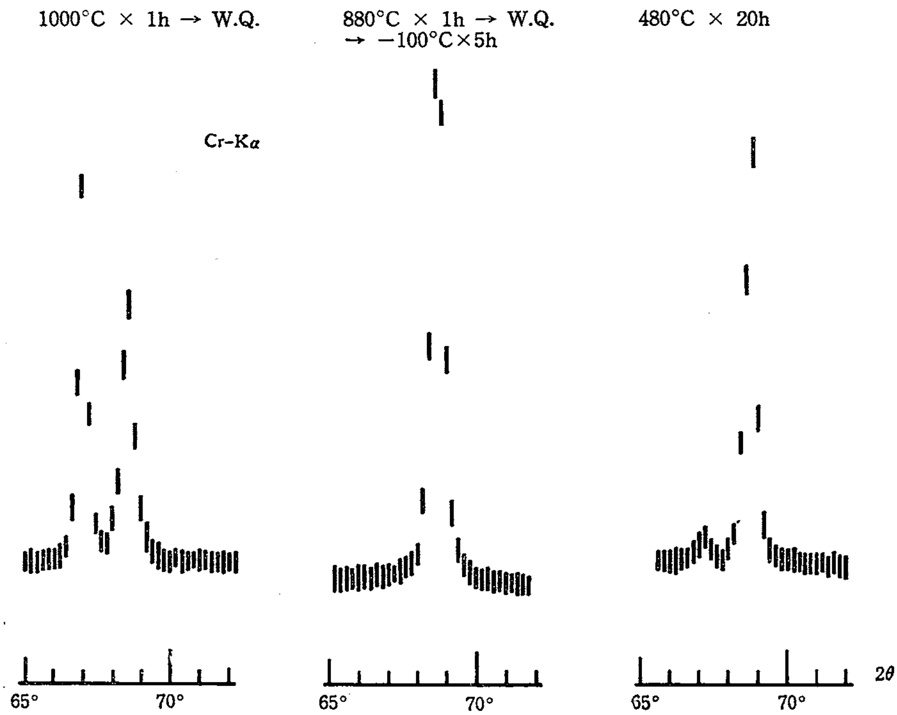
Fig. 12 : Vickers Hardness of 17-4PH Steel
After 20 Hrs Aging at Various Temp.



Results of X-ray Analysis

The structure of the alloys after heat treatments was determined by X-ray Diffractometer using Cr-K_α radiation filtered with V. The representative results are shown in Fig. 13. After the solution treatment at 1100°C for 1 Hr, the X-ray diffraction line (111) of austenite could be discerned strongly, but this diffraction line was not observed when the material was refrigerated at -100°C for 5 Hrs immediatly after the solution treatment at 880°C × 1Hr.

Fig. 13 :



Putting together this and the other results in the above-mentioned hardness tests, it may be concluded that in the material, which is solution-treated at 880°C for 1 Hr and succeeded by refrigeration −100°C×5Hrs, almost all austenite transforms to martensite. However, if the alloy, which is refrigerated as above-mentioned and causes no diffraction pattern of γ_R is aged at 480°C for 20 Hrs, a new diffraction line appears at $2\theta \fallingdotseq 67.1°$. This newly appeared diffraction line may be considered as nothing but the line of precipitated phase. But another diffraction line of precipitated phase could not be detected. Indeed it is difficult to discuss on the structure of precipitated phase by only one diffraction line, but at least following interpretation may be deduced reasonably so far as it goes. That is, as the diffraction angle of this line is $2\theta \fallingdotseq 67.1°$, the interplanar spacing of the atomic plane which caused this diffraction line is $d_{obs} \fallingdotseq \lambda / 2\sin\theta \fallingdotseq 2{,}2909\,\text{Å}/2\sin 33.55° \fallingdotseq$ 2.07Å. Now, it may be appropriate to consider that the precipitated phase is mainly composed of Cu and has face-centered cubic structure. So that, regarding this diffraction line as reflected from (111) atomic plane of F. C. C. structure, the lattice parameter of the precipitated phase is given as follows.

$$\because \quad a_{obs} = d_{obs}\sqrt{h^2+k^2+l^2} = 2.07\sqrt{3}\ \text{Å} = 3.58\ \text{KX}$$

By the way, solubility of Cr in Cu is very small, and Cu does not appear in the carbide phase and does not form intermetallic compounds with iron. On the other hand, Cu and Ni form a continuous solid solution, and its lattice spacing is 3.5823 KX at 22.99 at% Ni by Coles[10] and 3.580 KX at 26.33 at% Ni by Owen and Pickup[11]. Accordingly, though the diffraction line of precipitated phase is few as is mentioned above and the way of finding the lattice parameter is rough, it may be considered reasonably that the precipitated phase is Cu-Ni solid solution with about 25 at% Ni. Of course, in order to decide the structure of precipitated Cu-rich phase, more detailed experiments are required, and now they are in progress.

Conclusion

1. The effect of heat treatments on the properties of the casted 17-4PH Type stainless steel has been studied by means of hardness testing, dilatometric, magnetic, X-ray, corrosion-proof and metallographic methods.

2. Solution treatment temperature (S.T.T.)/Hardness or As-quenched structure relationships were as following;

S.T.T. $\leqq$ 880°C; hardness $\fallingdotseq$ 317 V.P.N.

As-water-quenched structure was mainly composed of martensite and contained some δ-ferrite and a small amount of austenite.

S.T.T. $\geqq$ 1100°C; hardness $\fallingdotseq$ 160 V.P.N.

Mainly austenite, and a small amount of δ-ferrite.

1080°C > S.T.T. > 890°C;

As S.T.T. increases, amount of austenite increases and hardness decreases.

3. Ms-point gets down as S.T.T. rises, and is about 15°C at 1100°C solution treatment.

4. The effect of refrigeration was most remarkable at -100°C. For -100°C ×5Hrs refrigeration treatment, the greater part of retained austenite (γ_R) was transformed to martensite and the hardness value reached 340 V.P.N.

5. When the temperature, during solution treatment, rose from desired degree for a moment, a long time was required to recover this influence.

6. The most desirable aging temperature was 450°C ~ 480°C.

7. The greater the quantity of martensite contained in the specimen on as-quenched condition is, the more remarkable the aging effect is. On the other hand corrosion resistance gets worse as the aging progresses, and this tedency is pronounced in the specimen containing much martensite on as-quenched condition. This means that the precipitation occurs mainly in martensite.

8. When the specimen containing a great quantity of γ_R is aged, a part of γ_R transforms into martensite in cooling process and a considerable in-

crease of hardness is caused.

9. As-solution-treated structure contains always some δ-ferrite, and its quantity decreases with increasing S.T.T.

10. Though it may be rather rough estimation, the precipitated phase is considered reasonably as Cu-Ni solid solution with about 25 at% Ni.

References

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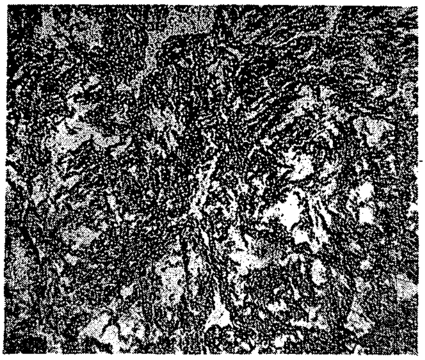
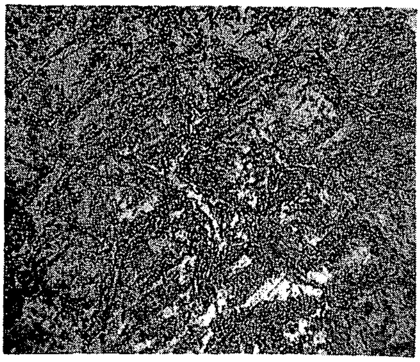
Micrograph of As-solution-treated 17-4 PH Steel (×400)



No. 1

No. 4



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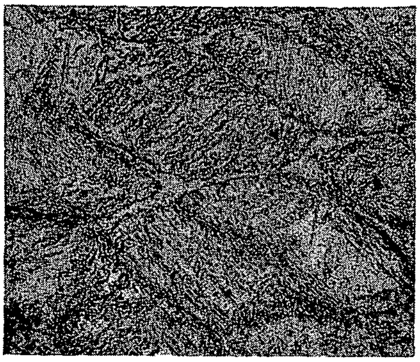


No. 5

No. 3

No. 1 640°C × 1Hr → W. Q.

No. 2 680°C × 1Hr → W. Q.

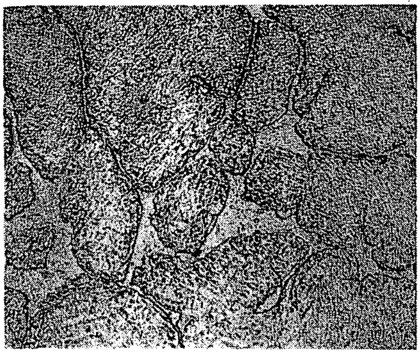
No. 3 720°C × 1Hr → W. Q.

No. 4 760°C × 1Hr → W. Q.

No. 5 800°C × 1Hr → W. Q.

Micrograph of As-solution-treated 17-4 PH steel (×400)

No. 6



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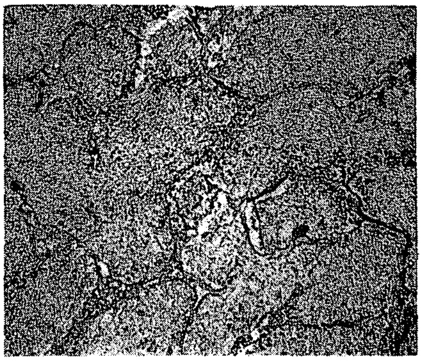

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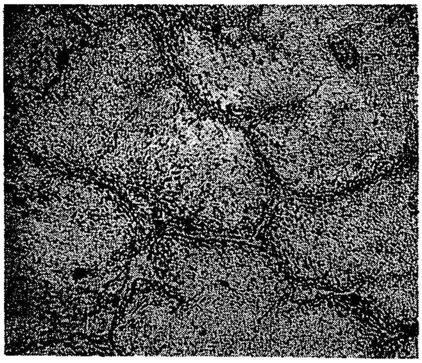


No. 8

No. 6 840°C × 1Hr → W. Q.

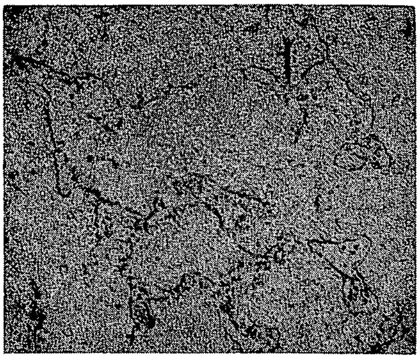
No. 7 880°C × 1Hr → W. Q.

No. 8 920°C × 1Hr → W. Q.

No. 9 960°C × 1Hr → W. Q.

No. 10 1000°C × 1Hr → W. Q.

Michrograph of As-solution-treated 17-4PH Steel (×400)



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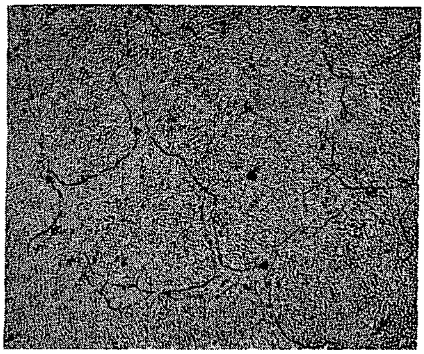

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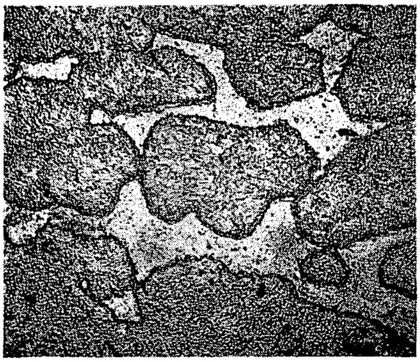

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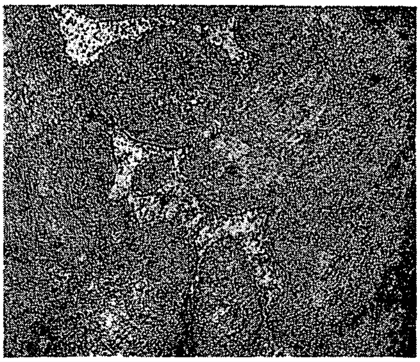

No. 15

No. 13

No. 11 1040°C × 1Hr → W. Q.

No. 12 1080°C × 1Hr → W. Q.

No. 13 1120°C × 1Hr → W. Q.

No. 14 1160°C × 1Hr → W. Q.

No. 15 1200°C × 1Hr → W. Q.