17Cr-4Ni-4Cu Precipitation Hardening Stainless Steel
(The Second Report)

The Effect of Additional Alloying Element (Ti, Mo, Al) on The Properties of The Cast Material*

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The effect of additional alloying element such as Ti, Mo and Al on the reaction to heat-treatment of a cast 17-4PH Type stainless steel was studied mainly through hardness tests, and the following results were obtained. (1) The hardness of 17%Cr-4%Ni-4%Cu base composition steel decreases remarkably in the solution-treatment above 900°C, but in the case of Ti added steel, it increases gradually as solution-treatment temperature rises up to about 1200°C. The effect of Ti content on the as-solution-treated hardness of the alloy is divided into two groups, i. e., up to about 0.15% (low) Ti content and about 0.25~0.5% (high) Ti content, where low Ti alloy is harder than high Ti alloy in the solution-treated condition. The higher the Ti content is, the more noticeable age-hardening and the latter over-aging (softening) is acquired. (2) Hardness with relation to solution-treatment temperature and aging period of the Mo added alloy is similar to that of the base composition steel, though the hardness decreases with the increase of Mo content. Again the solution-treatment temperature range, which leads to low hardness, falls as Mo content increases. (3) Hardness of the Al added alloy, after the solution-treatment, is higher than that of the base composition steel, and the more Al is added the harder the alloy becomes in the experimented range of Al%. The solution-treatment temperature, which begins to lead to low hardness, goes to higher temperature according as the Al content increases. The drop of hardness decreases with the increase of Al content. The effect of added Al on age-hardening is remarkable, but the increasing of hardness due to aging reaches a maximum by about 2% Al. Moreover in the case of alloy steel containing more than 2% Al, the softening by over-aging occurs more rapidly. (4) The above-mentioned phenomena are interpreted as follows; as a result of carbide formation of alloying element, firstly the change of carbon content occurs in austenite, which induces the shift of Ms point. Secondly the hardness of martensite itself changes. (5) Tensile strength at room temperature increases with the addition of Ti. The addition of Mo increases tensile strength at high temperature and ductility, but the addition of Al raises brittleness. (6) Corrosion resistance against 5% HCl, 5% H_2SO_4 and 5% HNO_3 solution grows with the addition of any element such as Ti, Mo and Al, especially the effect is remarkable in the alloy steel containing Mo or Ti.

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Introduction

Previously we have reported on the effects of heat-treatments on the properties of the cast 17%Cr-4%Ni-4%Cu base composition steel(1). In this report the effects of the different alloying element such as Ti, Mo and Al on the properties of 17-4PH Type stainless steel and the effects of heat-treatments on that alloy steel were studied. The three alloying elements Ti, Mo and Al were selected for the following reasons: Ti is a representative element which contributes to precipitation hardening, Mo is a typical ferrite-forming element and Al is an extremely powerful ferrite-forming element and has perhaps the strongest secondary hardening effect.

Materials and Procedures

A process of preparation and dimensions of the samples used in this experiments, for the most part, are the same with those in the first report(1), and for tensile tests JIS No.4 Type test-pieces were used. The materials used in the experiments are 17-4PH Type Steels (17%Cr-4%Ni-4%Cu base composition) with 0.15~0.5%Ti, 0.3~3%Mo or 0.5~3.5%Al respectively, and their chemical compositions are given in the next tables (Table I, II, III and IV). Experimental procedures and accuracy of measurements are the same with those in previous work(1). All samples were homogenized for 2 hrs. at 1100°C prior to projected heat-treatments.

Table I Chemical Analyses of Base Composition 17-4PH Steel (%)

C	Si	Mn	Cr	Ni	Cu
0.06	0.80	0.77	17.37	4.51	4.04

Table II Chemical Analyses of Ti-Containing 17-4PH Steel (%)

Heat No.	C	Si	Mn	Cr	Ni	Cu	Ti
T- 16	0.07	0.85	0.63	16.63	4.71	3.84	0.16
T- 25	0.06	0.72	0.43	17.81	5.21	4.29	0.25
T- 36	0.05	0.63	0.45	17.93	4.57	4.43	0.36
T- 49	0.07	0.95	0.64	16.82	4.52	4.15	0.49

Table III Chemical Analyses of Mo-Containing 17-4PH Steel (%)

Heat No.	C	Si	Mn	Cr	Ni	Cu	Mo
M- 53	0.07	0.84	0.56	16.95	4.44	3.64	0.53
M-107	0.07	0.82	0.57	17.04	4.31	3.64	1.07
M-208	0.07	0.69	0.57	17.57	4.28	3.59	2.08
M-299	0.07	0.75	0.57	17.53	4.44	3.69	2.99

Table IV Chemical Analyses of Al-Containing 17-4PH Steel (%)

Heat No.	C	Si	Mn	Cr	Ni	Cu	Al
A- 40	0.07	0.82	0.55	16.91	4.44	4.00	0.40
A- 70	0.05	0.81	0.58	17.04	4.33	3.95	0.70
A-165	0.07	0.85	0.59	17.22	4.44	4.05	1.65
A-319	0.07	0.84	0.61	17.04	4.36	4.15	3.19
A-366	0.07	0.82	0.59	17.04	4.33	3.90	3.66

Effect of Ti on Hardness of Water-quenched 17-4 PH Steel.

(Solution-treated for 1 hour)

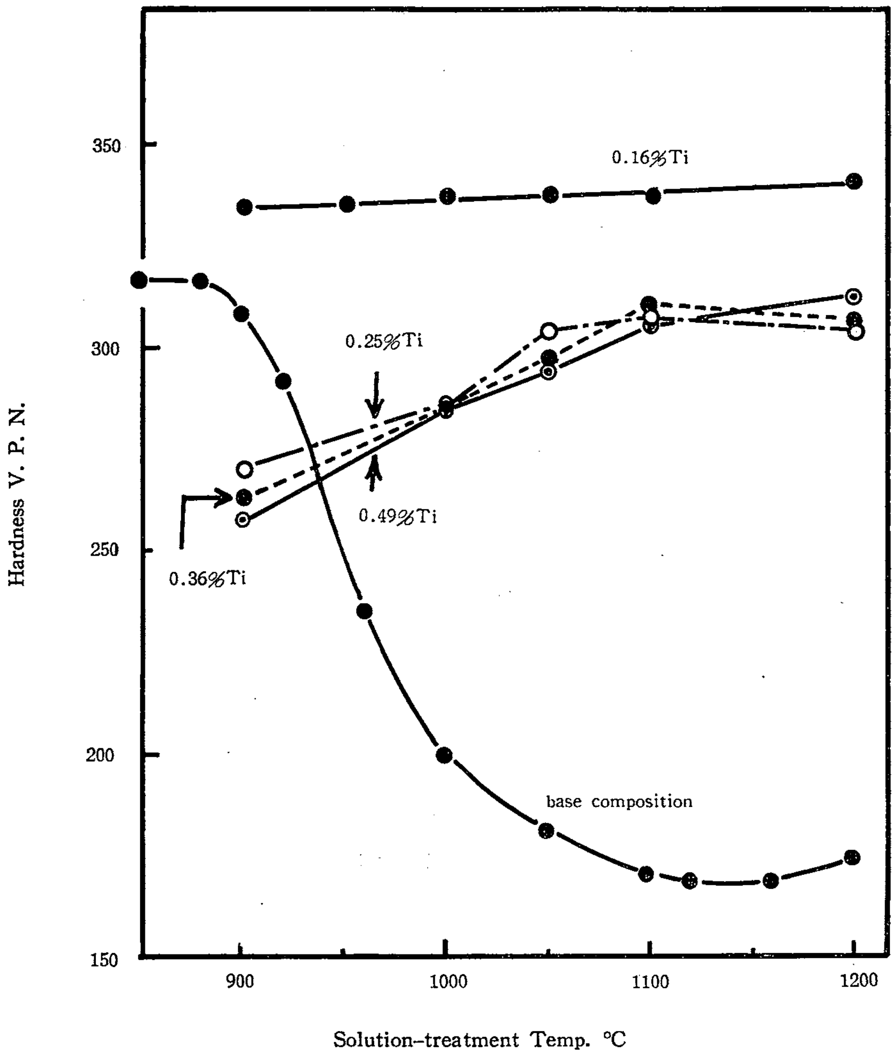

Fig. 1

Results and Discussion

Effect of Titanium

Armco 17-4PH type stainless steels alloyed with additional 0.16, 0.25, 0.36 and 0.49% Ti respectively were water-quenched from various solution-treatment (S.T.) temperatures ranging from 900~1200°C, and then their hardness were tested. The results are shown in Fig. 1. (For comparison, the same hardness curve for base composition steel is also superimposed in Fig. 1.) There is a sharp difference in the effect of Ti on as-solution-treated hardness between T-16 steel (containing 0.16%Ti) and T-25, T-36, T-49 steel group (containing 0.25, 0.36 and 0.49%Ti respectively) as is shown in Fig. 1. That is, hardness of T-16 steel differs from that of T-25 steel considerably, but T-25, T-36 and T-49 steel show nearly the same hardness. Moreover, T-16 steel shows approximately definite hardness, 335 ~ 340V. P. N., regardless of S. T. temperature experimented (ranging from 900°C to 1200°C), while as-solution-treated hardness of the alloy steel which belongs to T-25 group increases considerably as S.T. temperature rises.

As-solution-treated hardness of the base composition steel decreased rapidly as S.T. temperature rose from 890°C to 1080°C, but such a phenomenon was not recognized about any Ti-containing alloy steel at least within 1200°C. The above-mentioned results may be caused by the rise of Ms-point owing to the fixation of C in matrix by Ti. Of course to assert such a assumption more detailed researches are required, but as a result of experiment, though it was qualitively, the following fact was recognized distinctly. That is, when cooling process after the S.T. for 1 hr. at 1120°C was analyzed magnetically, magnetic permeability of base composition steel showed almost constant value while that of Ti-containing alloy steel increased gradually at about room temperature. This result may be regarded as a useful evidence supporting the above-mentioned deduction.

Again the hardness of as-water-quenched T-16 steel shows nearly the same value as the highest hardness, about 340V.P.N., of base composition steel refrigerated adequately. As is reported previously[(1)], in such a base composition steel martensite transformation must have been completed. Considering the above-mentioned results together, it seems reasonable that the structure of as-solution-treated T-16 steel is mainly composed of martensite. Accordingly, the fact that the alloy steel containing about 0.15%Ti shows almost fixed hardness value irrespective of S.T. temperature ranging from 900°C to 1200°C may be reasonably attributed to completion of austenite→martensite transformation at R.T., which is caused by the rise of Ms-and Mf-point owing to the decrease of C in austenite as a result of carbide-formation of Ti with C in matrix phase.

On the other hand, hardness values of as-solution-treated T-25, T-36 and T-49 steel containing much Ti are lower than those of T-16 steel containing less Ti, and these results may be interpreted as follows; in the case of high Ti alloy, the greater part of carbon in matrix transforms into titanium carbide, so that the quantity of free carbon in matrix decreases and hardness of martensite itself decreases. Moreover it may be concluded that the former as-solution-treated hardness increases as S.T. temperature rises, because a part of carbide dissolves, the quantity of C in matrix increases a little, and, as a result, hardness of martensite itself increases.

Effect of Ti on Hardness of Aged 17-4 PH Steel
(Solution Treatment=900°C×1hr., Aging Temp.=500°C)

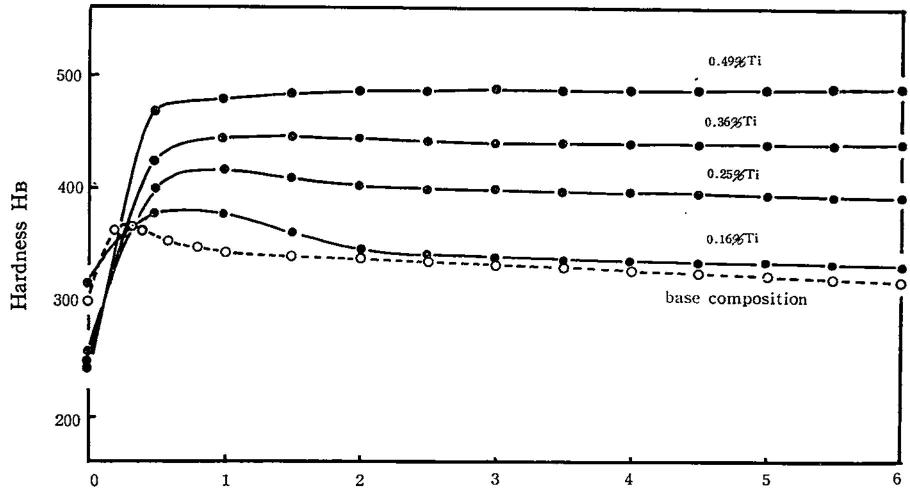

Fig. 2

Fig. 2 shows the relation between aging-time and hardness in these alloy steels after aging for 0.5~6 hours at 500°C. Solution-treatment was performed at 900°C for 2 hours. Increase of hardness caused by aging was remarkable, and hardness reached maximum after the aging for 0.5~1 hour. The more the material contains Ti, the more hardness increases. Maximum hardness in T-49 steel reaches about 488H_B=530V.P.N.. Softening, caused by over-aging, reduces with increasing Ti concentration, and is not yet observed after aging for 6 hours in the case of T-49 steel. Concluding from above-mentioned results, Ti may be regarded as an excellent precipitation-hardening alloying element for 17-4PH Type stainless steel.

Effect of Molybdenum

Fig. 3 shows the hardness of M-53, M-208, and M-299 specimen water-quenched to R. T. from various S.T. temperatures ranging from 800°C to 1200°C. These alloy steels contain 0.53%, 2.08% and 2.99% Mo beside base composition respectively. (Furthermore, S. T. temperature / hardness relationship for M-107 steel, containing 1.07%Mo, was studied. The hardness curve for this steel locates

Effect of Mo on Hardness of Water-quenched 17-4 PH Steel
(Solution-treated for 1 hour)

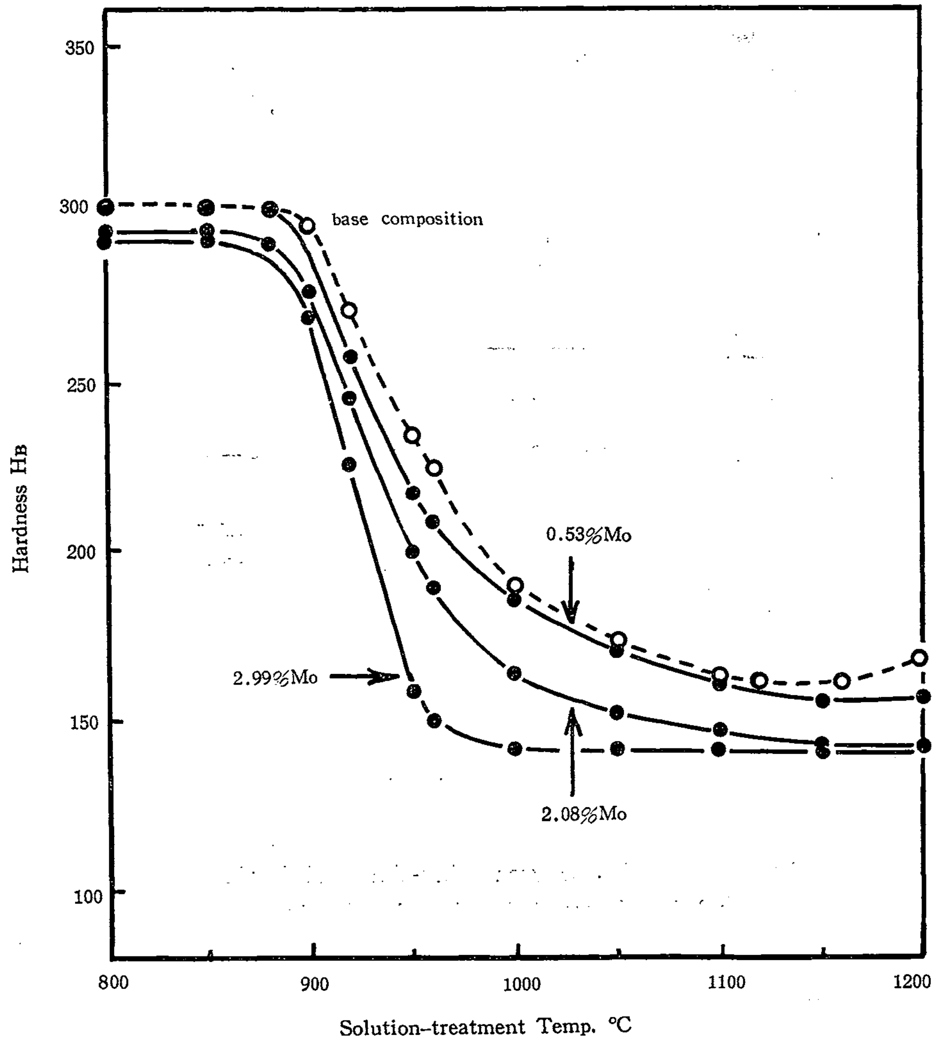

Fig. 3

between that of M-53 and that of M-208, and it is placed closely to the curve for M-53 steel.) As is shown in this figure, hardness of these materials decreases gradually as the content of Mo increases, but the shapes of S.T. temperature/hardness curves for these alloys are similar to that of base composition steel. Namely, hardness of as-water-quenched material remains nearly constant till a certain S.T. temperature is reached, and above this S.T. temperature it drops rapidly, and when S.T. temperature rises more, hardness reaches again nearly a constant value. This behaviour may be interpreted in the similar way as in the case of base composition steel(1). Consequently, the structure of Mo-containing alloy steel, which is water-quenched from about 1100°C to R.T., may be, for the most part, composed of austenite, regardless of Mo content. As Mo is added, the upper plateau in the hardness curve ends at lower temperature. Moreover, the lower plateau in hardness curve appears at lower temperature, and its starting point becomes more definite with increasing Mo content. It may be considered that hardness of Mo-containing alloy decreases with increase of Mo content, because, like the effect of Ti, Mo formes carbide with C in matrix, the content of C in matrix reduces, and as a result the hardness of martensite itself decreases.

Effect of Mo on Hardness of Aged 17-4 PH Steel

(Solution Treatment=850°C×1hr., Aging Temp.=500°C)

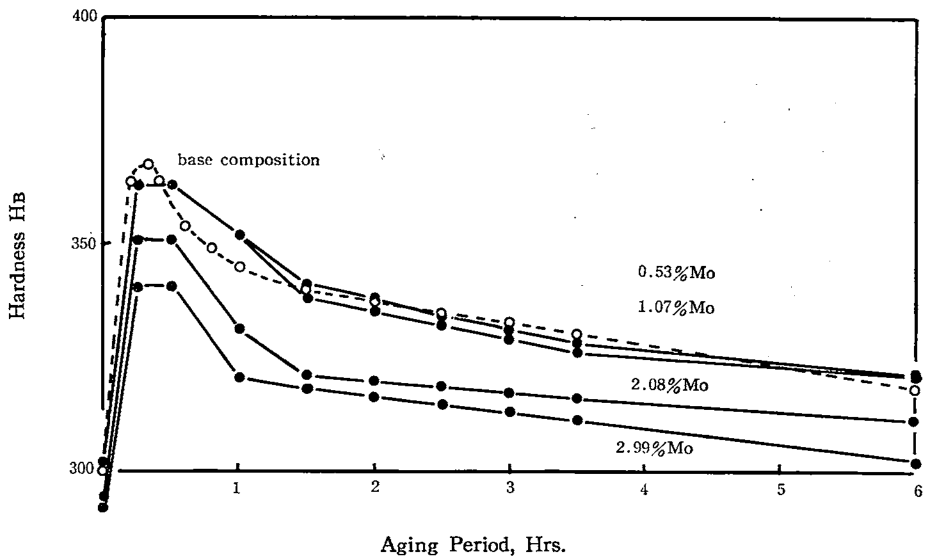

Fig. 4

Fig. 4 shows the relation between aging-time and aged-hardness in these materials after aging for 0.5~6 hours at 500°C. Solution-treatments were always performed at 850°C for 2 hours. The precipitation-hardening curves for M-53 and M-107 steels, which contain a little Mo, nearly coincide with that for base composition steel, but the aged-hardness begins to decrease with increase of Mo addition. Like the base composition steel, aged-hardness in any Mo-containing steel reaches maximum after aging for shorter than 20 min. at 500°C. Softening began already after aging for 30 min.. Generally it may be said that, Mo actes rather as a anti-precipitation-hardening element but, if the Mo concentration is smaller than about 1%, Mo scarcely has a harmful effect on age-hardening of 17-4PH Type stainless steel.

Effect of Aluminum

Fig. 5 shows the as-water-quenched hardness of the Al added alloy steel. The content of Al in each alloy was 0.40, 0.70, 1.65, 3.19 and 3.66% respectively, and the S.T. temperature ranged from 850°C to 1200°C. Hardness of these alloys after S. T. is higher than that of base composition steel in general and increases as the amount of Al added increases. Every Heat, after solution-treatment, shows a nearly constant hardness untill S.T. temperature reaches a definite

Effect of Al on Hardness of Water-quenched 17-4 PH Steel

(Solution-treated for 1 hour)

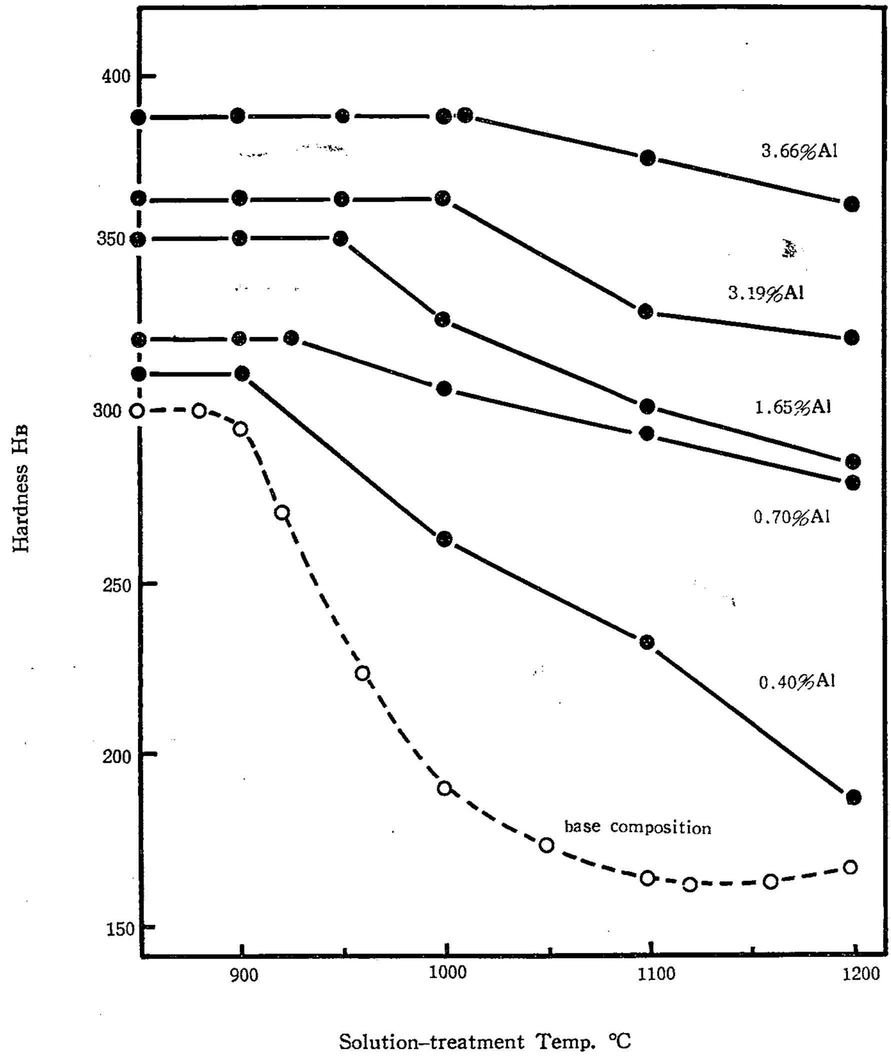

Fig. 5

degree respectively. This critical temperature rises as Al content increases. When S.T. temperature goes over this point, the hardness after S.T. begins to decrease, but the drop of hardness reduces as the content of Al increases. To get the precise information, the more study may be needed, but it seems that these results are caused by differences in quantity of martensite and in hardness of martensite itself in any case.

Again these alloys were solution-treated at 900°C for 2 hrs. were water-quenched to R.T., and then were aged for 0.5~6 hours at 500°C. The relationships between aging-time and hardness after aging for these steels are given in Fig. 6. Up to about 0.5% Al content, there was not so many difference in age-hardening

Effect of Al on Hardness of Aged 17-4 PH Steel
(Solution Treatment=900°C×1hr., Aging Temp.=500°C)

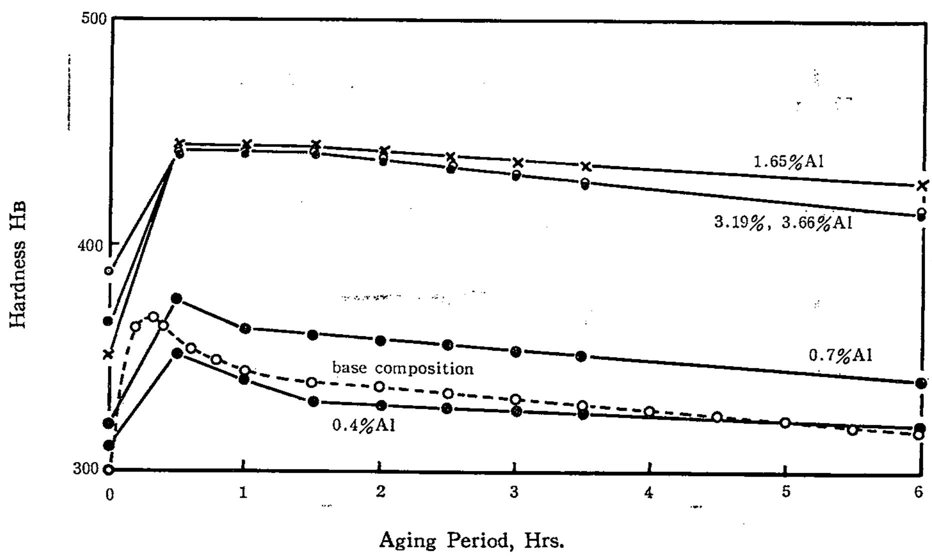

Fig. 6

curve between Al-containing alloy and base composition steel, but when the content of Al was reached about 1.5%, the hardness of aged alloy steel increased rapidly. Nevertheless, further Al addition scarcely caused discernible increase of age-hardening. Moreover, when aging period exceeds 2 hours, after aging, the hardness of A-319 and A-366 steel, which contain a large amount of Al, is lower than that of A-165 steel which contains a small amount of Al, and these are interesting problems. The maximum aged-hardness comes after 0.5 hours aging at 500°C, and when aging-time exceeds 1 hour at that temp., as a result of over-aging, the softening begins to occur irrespective of Al content. Considering the above-mentioned results, it may be said that Al has a remarkable effect on precipitation-hardening of 17-4PH steel, though its effect is not so powerful as Ti.

Comparison of the effects of different alloying elements

To get the effects of different alloying elements on age-hardening of 17-4PH Type steel clearly, alloying element content/aged-hardness relationships for 500°C×30min. and 500°C×5 hrs. aging were brought together, and these results are shown in Fig. 7 and Fig. 8 respectively. These diagrams show that Ti is the most effective alloying element for precipitation-hardening of 17-4PH Type stainless steel.

Effect of Additional Element on Hardness of Aged 17-4 PH Steel
Aging; 500°C×0.5hr.

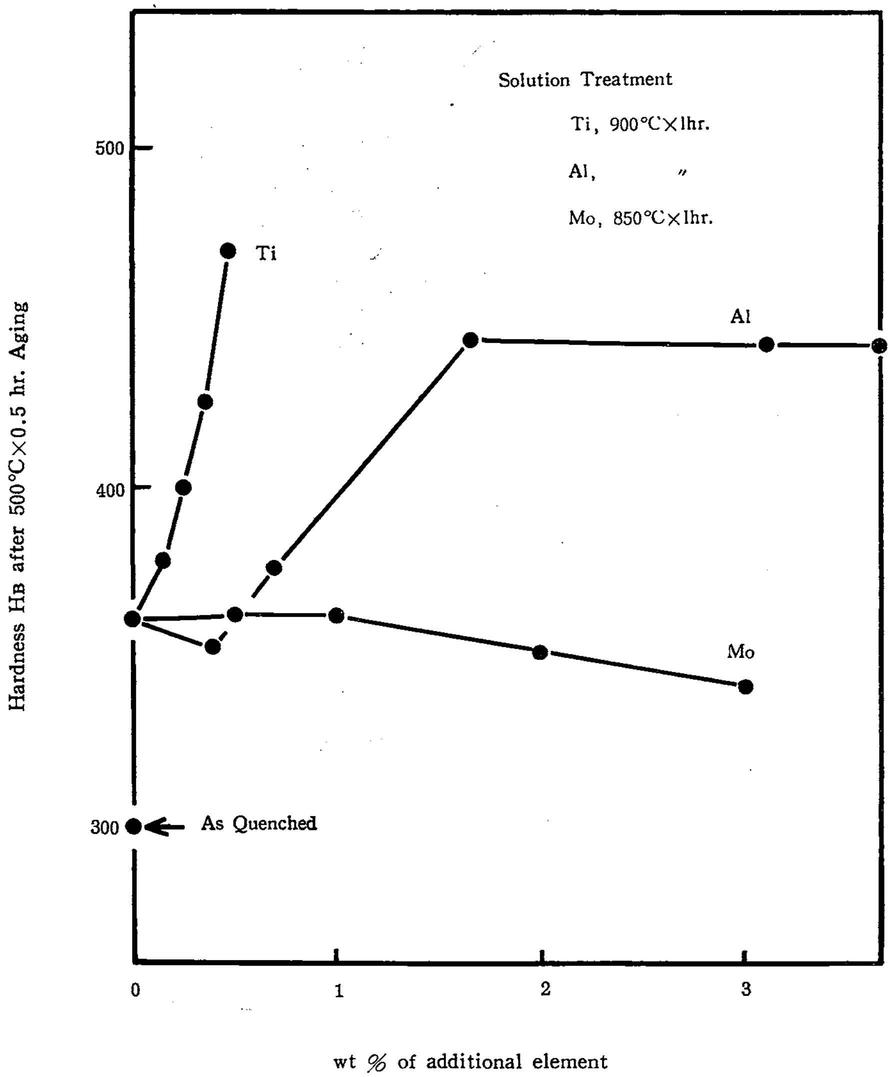

Fig. 7

Effect of Additional Element on Hardness of Aged 17-4 PH Steel.
Aging; 500°C×5 hrs.

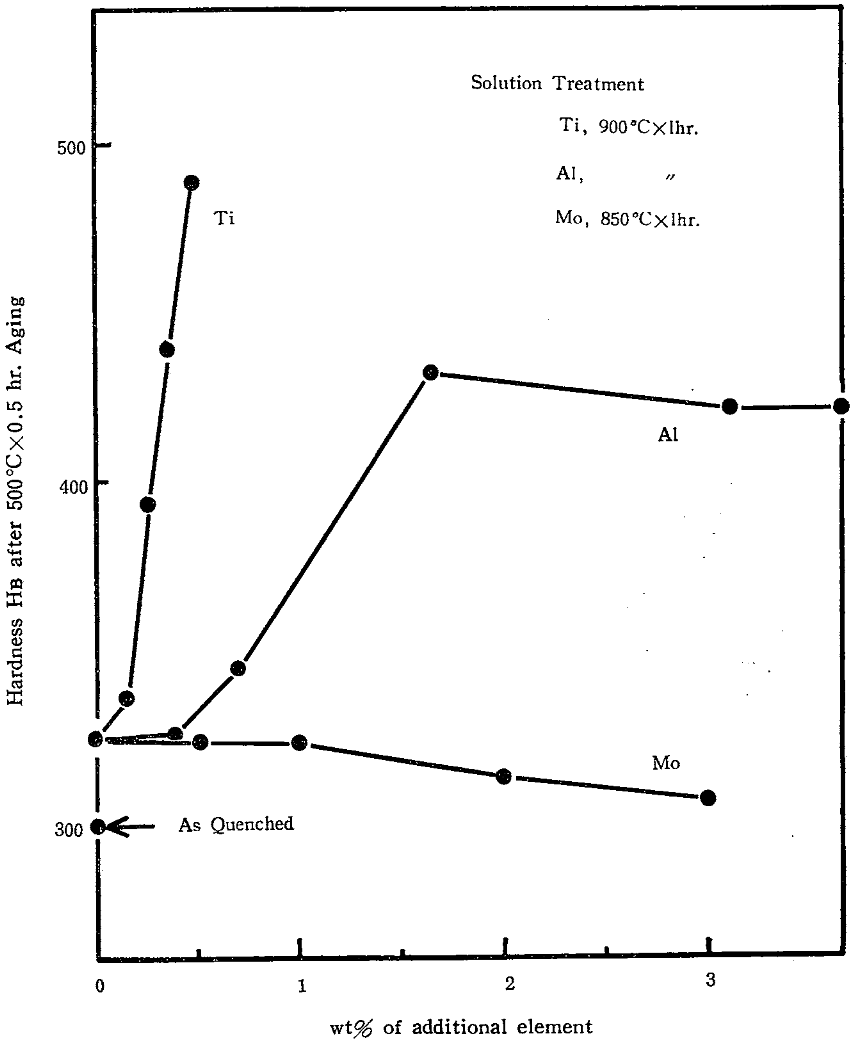

Fig. 8

Some results on Tensile Test and Others

Tensile test at room temp. was carried out for some alloy steel mentioned above. The dimension of test piece followed JIS No. 4. The results are listed in Table V together with solution-treatment and aging conditions. As is shown in the table, among Ti, Al and Mo, Ti is the only alloying element which increases tensile strength. Moreover, with increasing Ti content, though the aged-hardness is increased remarkably, the gain in tensile strength is small. Again the tensile strength of these Ti-containing alloy steels, aged for 1 hour at 500°C, can be classified into two groups, namely the group of T-16 and the group of T-25 and

Table V Tensile Strength at R. T.

Material	Solution–treatment	Aging	Tensile Strength (σ_{RT}) (Kgr/mm²)	Yield Point (Kg/mm²)	Elongation (%)	Hardness (HB)
Base Composition Steel	880°C×2hrs. →W.Q.	450°C×2hrs. →W.Q.	107	98	4	363
T- 16	900°C×2hrs. →W.Q.	500°C×1hr. →W.Q.	110	103	5	375
T- 25	〃	〃	117	108	2	415
T- 36	〃	〃	116	109	2	444
A- 70	〃	〃	97	89	2	363
A-165	〃	〃	76	63	0	444
A-319	〃	〃	57	48	0	423
M-107	850°C×2hrs. →W.Q.	500°C×0.5hr. →W.Q.	102	95	6	363
M-208	〃	〃	99	91	6	352

T-36, as in the case of the hardness after the solution-treatment, and it is an interesting problem. Mo decreases both hardness and tensile strength, increases elongation and reduces brittleness. On the other hand, Al increases hardness, reduces tensile strength, yield point and elongation and increases brittleness. Fractured surface of Al-containing alloy steel after tensile test is rather anomalous and has the appearance of a cleavage plane, and this situation clarifies with increasing Al content. Putting all the results mentioned above together, it may be concluded that Ti is the most effective alloying element to improve upon the mechanical properties of 17-4PH base composition steel.

Again the tensile strength at high temperature (500°C) was studied for three representative alloy steels. Each alloy steel stands for the series of Ti-, Mo- and Al-containing 17-4PH Type stainless steel respectively, in a sense that it has the largest tensile strength in each series. The holding time of every specimen at the high temperature was 1 hour. The results are given in Table VI. Though

Table VI Tensile Strength at 500°C

Material	Tensile Strength $\sigma_{500°C}$ (Kg/mm²)	Elongation (%)	Tensile Strength Ratio $\frac{\sigma_{500°C}}{\sigma_{RT}}$ (%)
Base Composition Steel	84.4	4	79
T- 25	70.3	5	60
M-107	93.1	6	91
A- 70	67.2	2	69

Solution-Treatment and Aging Conditions are the same as Table V,
Holding Time at 500°C is 1hour,

the deta listed in Table VI is rather few, it may be considered that Mo is the most desirable alloying element for this sort of alloy steel to raise the tensile strength at high temperature, as in the case of usual alloy steel.

On some of the above-mentioned alloy steels, after the aging which gives them the maximum hardness respectively, the corrosion proof tests against 5 wt% HCl, 5 wt% H_2SO_4 or 5 wt% HNO_3 solution were studied statically at R.T. for various periods up to 95 hours. Each additional alloying element (Ti, Mo, Al) improved the corrosion resistance. Especially the effects of Mo and Ti were remarkable, and the corrosion resistance of 17-4PH Type stainless steel, which contained Mo or Ti, was greater than that of 18-8 stainless steel.

Conclusion

The effects of additional alloying element such as Ti, Mo and Al, together with that of heat-treatments, on the properties of the cast 17-4PH Type stainless steel were studied, and the following results were obtained.

(1) The hardness of the as-solution-treated base composition steel (17% Cr-4%Ni-4%Cu) decreases remarkably, when the solution-treatment (S.T.) temperature exceeds about 900°C. However, the hardness of the as-solution-treated alloy steel, which contains Ti, increases gradually as S.T. temperature rises up to about 1200°C. This behaviour may be attributed to the rise of Ms and Mf temperature caused by the addition of Ti. The effect of Ti content on the as-solution-treated hardness of the alloy steel is remarkably different in low (about 0.15%)- and high (about 0.25~0.5%)-Ti alloy group, where the former is harder than the latter in the solution-treated condition. This fact may be caused by the difference in hardness of each martensite itself. The age-hardening caused by Ti addition is noticeable and it increases with increasing Ti content. Moreover softening, which is due to over-aging, decreases with increasing Ti content. The addition of Ti causes the increase of tensile strength at R. T., where the relation between the amount of Ti added and the increment of tensile strength is classified into two groups, as is the case in as-water-quenched hardness/S.T. temperature relationship. The corrosion resistance can also be improved by the addition of Ti.

(2) The relation between S. T. temperature and hardness in alloy steel containing Mo is similar to that in base composition steel, though the hardness decreases with the increase of Mo content. Moreover the S.T. temperature range, which leads to low hardness, extends to the lower temperature region as Mo content increases. It may be concluded that, after high temperature S. T., each Mo-containing alloy steel shows a nearly constant low hardness depending on the Mo content. This is due to the fact that, after such treatment, the structure of Mo-containing alloy steel are composed of, for the most part, austenite. The decrease of as-solution-treated hardness with the increase of added Mo may be attributed

to the decrease of the hardness of martensite itself, as is the case in Ti-containing alloy. This fact is caused by the diminution of carbon concentration in matrix phase as a result of Mo-carbide formation. The aging-time/hardness relationship of Mo-containing alloy steel is similar to that of base composition alloy steel. Ductility, high temperature tensile strength and corrosion resistance of 17-4PH Type steel are improved by the addition of Mo.

(3) Hardness of the Al added alloy steel, after S. T., is higher than that of the base composition steel, and it rises with the increase of Al content in the range of our interest. The S.T. temperature, which begins to lead to low hardness, shifts to higher degree according as the Al content increases. The drop of hardness decreases with the increase of Al content. The effect of added Al on age-hardening is remarkable, but the increase of hardness due to aging reaches a maximum in about 2%Al. Moreover, in the case of alloy steel containing more than 2%Al, the softening progresses more rapidly. The corrosion resistance of 17-4PH Type stainless steel is scarcely changed by the addition of Al. It is further noted that Al may be a rather harmful alloying element for 17%Cr-4%Ni-4%Cu base composition steel, in the following sense, i. e., it reduces the tensile strength and increases the brittleness.

References

(1) M. Takemura, K. Kiuchi and I. Shinoda : Ann. Sci.. KANAZAWA Univ., 2, 21 (1965)

(2) K. J. Irvine, D. T. Llewellyn and F. B. Pickering : J. Iron and Steel Inst, 192, 218 (1959)