Precipitation Strengthening Caused by the Combined Addition of Elements of IVa or Va Family with VIa Family of Periodic Table*

By Shogo KANAZAWA,** Akira NAKASHIMA,** Kentaro OKAMOTO,** and Tokio SUZUKI**

Synopsis

It is investigated, besides the combined addition of 0.03%Nb and 0.55%Mo to steel that has shown, when properly heat treated, a great strength increase that cannot be accounted for by mere arithmetic addition of individual effects, whether there are any other combination effects between elements of IVa or Va family and elements of VIa family of the periodic table, as in the case of niobium and molybdenum.

(1) It is found that the addition of Nb–Mo has the largest combination effect, Ti–Mo, Zr–Mo, and Nb–Cr have a slight effect, and Ti–Cr, Zr–Cr, and Nb–W have none.

(2) It is found that, in the cases of the great combination effects, a large number of cubic duplex carbide particles of IVa or Va element containing VIa element precipitate in the course of tempering in a great quantity. The great combination effect appears to be associated with this precipitation.

(3) The extraction method of Nb precipitates from steels is investigated, and it is found that the best is the (1+1) HCl aqueous extraction method.

I. Introduction

In an 80 kg/mm² grade high strength steel, which contains suitable amount of niobium and molybdenum and is used in quenched and tempered state,¹⁾ commercialized under a trade name of WEL-TEN 80P, a remarkable strength increase, which cannot be explained from the arithmetic addition of strengthening by niobium (Va family) and molybdenum (VIa family) alone was observed.²⁾ (Hereafter this strength increase will be called the combination effect.)

In this paper, results of investigation of whether there are other effective combinations between IVa or Va and VIa elements which cause similar combination effect are discussed.

Also this report includes studies on the behavior of the precipitates which are inferred to be the cause of the large combination effects; it also contains the investigation on the extraction method of precipitates from the steel.

II. Material and Experimental Method

The steels used in the experiments were melted in a 100 kg high frequency induction furnace in air except a few that were melted in vacuum. They were forged into 25 mm thick plates.

The steel used as the base was an aluminium killed steel containing 0.12 to 0.18%C, 0.2 to 0.5%Si, 1.2 to 1.6%Mn, ca. 0.35%Cu and ca. 0.003%B, to which an element (0.025 to 0.040%) of IVa (Ti, Zr) or Va (Nb) family and an element of VIa family (Cr, W (0.5 or 1.0%), Mo (0.3 or 0.55%)) were added. In all 30 combinations were tested.

The steel plates were austenitized at 950°C for 60 min, quenched in the water containing 0.5% cutting oil, tempered at 600°, 625°, and 650°C for 50 min and water cooled. Tensile test specimens (JIS No. 4) and Charpy test specimens (JIS No. 4) were made from them. All the test procedures were in accordance with JIS.

For the examination of the precipitates, those steel plates were cut into plates of 10 mm thick, austenitized for 60 min, quenched into 10% NaOH aqueous solution, tempered for 60 min, and cooled in 10% NaOH aqueous solution. Chips were then made from them

Table 1. Chemical compositions of steels and their properties

C	Si	Mn	Cu	Cr	Mo	W	Ti	Zr	Nb	Al	N	B	σ_B	$\sigma_{0.2}$	vTrs
0.155	0.42	1.44	0.37	—	—	—	—	—	—	0.041	0.0090	0.0034	61.9	48.7	—74
0.143	0.33	1.40	0.10	—	—	—	0.042	—	—	0.024	0.0048	0.0038	58.7	56.7	—22
0.139	0.31	1.44	0.11	—	—	—	—	0.030	—	0.028	0.0058	0.0036	56.3	42.7	—35
0.155	0.38	1.40	0.33	—	—	—	—	—	0.036	0.034	0.0092	0.0043	60.8	48.7	—52
0.145	0.31	1.46	0.06	1.12	—	—	—	—	—	0.020	0.0129	0.0031	62.4	49.5	—32
0.150	0.31	1.43	0.07	1.06	—	—	0.046	—	—	0.028	0.0087	0.0052	65.7	53.3	—22
0.145	0.37	1.44	0.36	1.10	—	—	—	0.040	—	0.024	0.0123	0.0038	64.5	52.2	—18
0.163	0.41	1.39	0.36	0.99	—	—	—	—	0.037	0.036	0.0109	0.0034	76.3	67.1	—49
0.156	0.31	1.40	0.06	—	0.57	—	—	—	—	0.021	0.0078	0.0043	67.8	57.0	—60
0.138	0.34	1.43	0.10	—	0.51	—	0.030	—	—	0.026	0.0105	0.0043	74.5	67.3	—50
0.138	0.33	1.40	0.07	—	0.57	—	—	0.036	—	0.028	0.0101	0.0042	72.7	63.1	<—70
0.130	0.29	1.42	0.10	—	0.56	—	—	—	0.029	0.031	0.0046	0.0057	82.5	80.0	<—70
0.135	0.34	1.43	0.07	—	—	0.93	—	—	—	0.022	0.0111	0.0033	62.0	51.9	—54
0.140	0.31	1.43	0.08	—	—	0.93	—	—	0.038	0.017	0.0115	0.0039	63.5	54.0	—40

* Originally published in *Tetsu-to-Hagane*, **56** (1970), 266, in Japanese. English version received February 1, 1971.

** Products Research and Development Laboratories, Nippon Steel Corp., Sagamihara 229.

for the analysis of the precipitates. The structures and precipitates were examined with an electron microscope.

III. Experimental Results and Discussion

1. Compositions and the Combination Effect

The data of the compositions and mechanical properties of the steels used in this study are too numerous to be all shown here. Table 1 contains, therefore, chemical compositions and mechanical properties after tempering at 650°C of only representative examples from each combination.

As shown in this table, the strength increase was not recognized with the addition of titanium and zirconium to chromium steels; however, the addition of niobium to the chromium steel achieved a tensile strength of 76 kg/mm², though its toughness was not good. Molybdenum steel with titanium and zirconium achieved little strength increase, but an addition of niobium to molybdenum steel gave rise to a tensile strength of about 82 kg/mm², and its toughness was very good. The niobium addition to tungsten steel did not increase the strength, and the toughness was not especially good.

In those cases above, however, the contents of carbon, silicon, manganese, etc. differed slightly, so that the combination effect cannot be discussed accurately from Table 1 alone. The effects were calculated using Eq. (1) which relates the chemical compositions of the heat-treated high strength steels to the tensile strengths,³⁾ where the chromium term was corrected according to the present results, and the tungsten term was newly added.

$$\sigma_{Be} = 94 \sqrt{C} + 17 \sqrt{Si} + 2 \sqrt{Mn} + \sqrt{Ni} + 7.2 \sqrt{Cr} \\ + 15 \sqrt{Mo} + 7 \sqrt{W} + 10 \sqrt{Cu} + 1.3 \sqrt{N} / Al_s - 4.2 \\ \times 10^{-4} / Al_s^2 + 3 \sqrt{Al} + 47 \sqrt{V} + 70 \sqrt{B} - 7.0 \dots (1)$$

As Eq. (1) does not include titanium, zirconium, and niobium terms, the effect of these elements can be examined in Eq. (1) conversely. The increase (A) of tensile strength by niobium, titanium and zirconium was calculated as $A = \sigma_{Bm}$ (observed value) $-\sigma_{Be}$

Fig. 1. Increase of tensile strength by addition of Ti, Zr, or Nb

(value due to Eq. (1)) and plotted in Fig. 1. The increase in niobium content does not increase the strength. The strength increase by addition of zirconium is within the error range of this equation until 0.05%, but is evident above 0.08%. A similar result is obtained with titanium. From Eq. (1) and A , all the individual effects of the elements can be calculated.

Fig. 2. Increase of tensile strength by combined effect

Fig. 3. Increase of tensile strength by combined effect

Fig. 4. Increase of tensile strength by combined effect

The combination effect ($\Delta\sigma_B$) of alloying was calculated from Eq. (2).

$$\Delta\sigma_B = \sigma_{Bm} - (\sigma_{Be} + A) \dots\dots\dots(2)$$

The results are shown in Figs. 2, 3, and 4. Figure 2 shows the results of Cr, Ti-Cr, Zr-Cr, and Nb-Cr steels. Addition of titanium and zirconium does not show any combination effect, but niobium addition shows a small effect (5 kg/mm²) when chromium is 1%.

Next, Fig. 3 shows the results on W and Nb-W steels. Nb-W combination does not show the combination effect until 1%W.

Figure 4 shows the case of addition of titanium, zirconium, or niobium to molybdenum steel. The co-existence of zirconium or titanium with molybdenum shows a small combination effect (4 to 7 kg/mm²), whereas with the Nb-Mo (0.5%) combination effect is about 15 kg/mm².

2. The Origin of the Combination Effect

Some combinations between an element of IVa or Va family and an element of VIa family showed the combination effect, while some did not. As examination on all the combinations has not been completed, however, Nb-Mo group and Nb-Cr group are compared: the former represents the case where the combination effect is large, while the latter represents the case where the effect is nil.

Niobium was chosen among IVa and Va elements because the method of chemical analysis of precipitates has been well established. (See Appendix.) Molybdenum and chromium were chosen from VIa family because tungsten hydrolyzes easily and hence it is relatively difficult to analyse its precipitates.

The following factors will affect the combination effect:

- (a) Hardenability of the steels;
- (b) Microstructures in the matrix of tempered martensite; and
- (c) Precipitates formed during the tempering.

Table 2 shows the chemical compositions of the steels used for the study and their mechanical properties when tempered at 650°C.

These steels were heated at 950°C for 1 hr, and the hardenability was examined by Jominy test. Figure 5 shows the results with Nb-Mo and Nb-Cr steels. As shown in the figure, the difference in the hardenability is not large.

Cementite precipitation during the tempering was examined in an electron microscope with carbon extraction replica,^{4),5)} while fine structure of the tem-

pered martensite was examined by thin foil technique.^{4),5)} No difference was detected on the behavior of cementite precipitation between molybdenum steel and Nb-Mo steel. Photographs 1 and 2 are the transmission electron-micrographs of them. The materials for Photos. 1 and 2 were melted in vacuum, deoxidized by carbon, and forged. The compositions are also shown. Photograph 1 is the electron-micrographs in the as quenched condition: steels were held at 1 000°C for 1 hr and quenched in 10% NaOH aqueous solution. According to the electron metallography addition of niobium does not cause any change to both chromium and molybdenum steel. Photograph 2 shows the microstructure of quenched and tempered steels, in which tempering was performed at 625°C and then cooled quickly in 10% NaOH aqueous solution. Regardless of the niobium content, chromium steel shows more advanced recovery than the molybdenum steel. Addition of niobium does not change the recovery rate of chromium steel nor of molybdenum steel. The combination effect, therefore, cannot be attributed to the change in the matrix during the tempering.

Next, precipitation during tempering was examined. To do this, the quantity of the undissolved precipitate phase in the quenched specimen should be known first. Chips were taken out from the sample firstly after quenching from 900°C and secondly after tempering at 625°C. The contents of compounds of niobium and molybdenum in molybdenum steel and Nb-Mo steels were analyzed. Well known (1+1) HCl aqueous solution⁶⁾ was used to extract niobium compound, while molybdenum compound was analyzed by newly developed duplex method,⁷⁾ which uses both (1+3) H₂SO₄ aqueous solution and (1+1) HCl-CH₃OH.

Fig. 5. Jominy curves of Nb-Cr and Nb-Mo steels

Table 2. Chemical compositions of steels and their properties

No.	C	Si	Mn	B	Al	Nb	Mo	Cr	σ_B	$\sigma_{0.2}$
A	0.14	0.35	1.41	0.003	0.022	—	—	—	58.5	49.5
B	0.14	0.32	1.43	0.005	0.024	0.040	—	—	60.1	53.0
C	0.12	0.21	1.31	0.003	0.020	—	0.54	—	62.5	57.0
D	0.13	0.29	1.42	0.004	0.031	0.029	0.56	—	82.5	80.0
N	0.15	0.42	1.35	0.003	0.038	—	—	0.93	68.5	55.8
O	0.16	0.41	1.39	0.003	0.036	0.037	—	0.99	76.3	67.1

Photo. 1.

Electron-micrographs of steels as quenched from
1 000°C in 10% NaOH aqueous solution
($\times 20\,000$) (2/3)

- (a) 0.136% C–0.86% Cr
(b) 0.140% C–0.86% Cr–0.023% Nb
(c) 0.108% C–0.63% Mo
(d) 0.112% C–0.65% Mo–0.031% Nb

Photo. 2.

Electron-micrographs of steels as tempered at
625°C ($\times 20\,000$) (2/3)

- (a) 0.136% C–0.86% Cr
(b) 0.140% C–0.86% Cr–0.023% Nb
(c) 0.108% C–0.63% Mo
(d) 0.112% C–0.65% Mo–0.031% Nb

Table 3. Precipitates of steels (extracted by (1+1) HCl aqueous solution)

Steels	900°C Q	900°C Q 625°C T
B	δ -NbC	δ -NbC
C	Unknown	Mo ₂ C
D	δ -NbC	δ -NbC Mo ₂ C*
N	—	—
O	δ -NbC	δ -NbC

* Extracted by (1+3) H₂SO₄ aq.-(1+1) HCl-CH₃OH method

The latter dissolves only cementite leaving Mo₂C.

With Cr and Nb–Cr steels the (1+1) HCl aqueous solution was used to extract the precipitates. The results of X-ray diffraction and electron diffraction of the extracts are shown in Table 3. The cementite existed in the steel but did not exist in the extracted residue. No precipitate was extracted from chromium steel both from quenched and tempered specimens. Cubic δ -NbC precipitate of NaCl structure was detected in Nb and Nb–Cr steels both before and after

tempering. With molybdenum steel some precipitates of unconfirmed structure were detected in the as quenched samples. After tempering, the existence of hexagonal Mo₂C was confirmed by both (1+1) HCl aqueous method and (1+3) H₂SO₄ aq.+(1+1) HCl-CH₃OH duplex method. With Nb–Mo steel, only NbC was detected even after repeated extraction by (1+1) HCl aqueous solution both after quenching and even after tempering. Hexagonal Mo₂C was not detected. Extraction by (1+3) H₂SO₄ aq.+(1+1) HCl-CH₃OH, however, revealed Mo₂C in addition to δ -NbC after tempering.

As shown in the table, Mo₂C precipitates are seen in Nb–Mo steel in the as tempered state, while they are not with Nb–Cr steel. The result may seem to explain the combination effect, but such reasoning is irrelevant since Mo₂C precipitates are found even in the as tempered state of molybdenum steel. Mo₂C precipitation, therefore, cannot be considered as the cause of the combination effect of tempered Nb–Mo steel.

As mentioned above, no difference was noticed in the kind of the precipitate. The amount of precipitate was then compared. The results are shown in Table 4. Nb and Nb-Cr steels (steels *B* and *O* respectively) contained the same amounts of niobium precipitate before and after tempering; little niobium precipitated during the tempering. No chromium compound was extracted from Nb-Cr steel by (1+1) HCl aqueous solution as mentioned before, while with Nb-Mo steel, 0.002% niobium precipitated during the tempering. The amount of Mo_2C was analyzed by extracting with (1+3) H_2SO_4 aqueous solution, then dissolving the cementite with (1+1) $\text{HCl}-\text{CH}_3\text{OH}$; those are identified with the * mark in Table 4. The result indicated that 0.043% Mo precipitated in the Nb-Mo steel, while 0.037% Mo precipitated in the molybdenum steel during tempering. The contribution of these Mo_2C precipitates to tensile strength is already included in the molybdenum term of Eq. (1) as shown in Fig. 4. The precipitation of Mo_2C , therefore, cannot explain the reason of large combination effect in Nb-Mo steel.

The amount of molybdenum compound in quenched and tempered Nb-Mo and Mo steels were analyzed by extraction with (1+1) HCl aqueous solution, which, as mentioned earlier, does not extract Mo_2C from tempered Nb-Mo steel. The results obtained by this solution showed that in Nb-Mo steel 0.011% Mo precipitated during tempering. However, repeated X-ray diffraction of the residue did not confirm the existence of Mo_2C . As apparent from the results of molybdenum steel, Mo_2C does not dissociate perfectly by (1+1) HCl aqueous solution. Some of the 0.011% Mo precipitated in the Nb-Mo steel during tempering may be Mo_2C , but most of molybdenum is likely to be combined with the 0.002% Nb to form cubic δ -(Nb, Mo) (C, N) duplex carbide.

Next problem is whether niobium and molybdenum can form such a duplex carbide or not. Rudy, *et al.*⁸⁾ examined Nb-Mo-C ternary system and obtained phase diagram as shown in Fig. 6. Although their results cannot be applied as it is to the case of precipitates in steel, they at least suggest that such duplex carbide can be expected to form in steel.

According to Table 4, δ -NbC in Nb-Cr steel does not seem to contain chromium, while it is almost certain that cubic δ -(Nb, Mo) (C, N) carbo-nitride has precipitated in the tempered Nb-Mo steel.

The large combination effect suggests that the newly precipitated niobium and molybdenum during

the tempering do not merely join the cubic δ -(Nb, Mo) (C, N) pre-existed in the as quenched state, but form fine new precipitates. The size of the cubic precipitates was measured by Scherrer's equation using the residue extracted by acid. The result is shown in Table 5. The mean size of δ precipitates in Nb-Mo steel (*D*) does not change before and after the tempering in contrast to that of niobium steel (*B*). This result implies that δ -precipitates do not grow during tempering, but new precipitates are formed at the new sites. In conclusion, it is thought that numerous fine cubic δ -(Nb, Mo) (C, N) precipitates newly during the tempering of Nb-Mo steel and can cause a large combination effect of about 15 kg/mm².

Further study has been performed to know whether this 15 kg/mm² strength increase due to combination effect can be sufficiently explained by the amount of precipitation given in Table 4. Niobium steels shown in Table 6 were heated at 900°C and 1 100°C, quenched in 10% NaOH aqueous solution, and tempered at

Fig. 6. Phase diagram of Nb-Mo-C alloy at 1 500°C (by Rudy)

Table 5. Mean size of δ -NbC type precipitate as measured by X-ray method. Extracted by (1+1) HCl aqueous solution

Steel	900°C Q	900°C Q 625°C T
<i>B</i>	150 Å	168 Å
<i>D</i>	120 Å	122 Å

Table 4. Results of chemical analyses of residues extracted by (1+1) HCl aqueous solution (%)

Steels	Total content			900°C Q				900°C Q 625°C T			
	Nb	Mo	Cr	(Nb) _T	(Mo) _T *	(Mo) _T	(Cr) _T	(Nb) _a	(Mo) _a *	(Mo) _a	(Cr) _a
<i>B</i>	0.040	—	—	0.032	—	—	—	0.032	—	—	—
<i>C</i>	—	0.54	—	—	0.005	0.010	—	—	0.042	0.017	—
<i>D</i>	0.029	0.56	—	0.026	0.014	0.014	—	0.028	0.057	0.025	—
<i>N</i>	—	—	0.93	—	—	—	0.002	—	—	—	0.002
<i>O</i>	0.037	—	0.99	0.036	—	—	0.002	0.036	—	—	0.002

* Extrated by (1+3) H_2SO_4 aqueous solution, subsequently by (1+1) $\text{HCl}-\text{CH}_3\text{OH}$

Table 6. Chemical composition of the steel

C	Si	Mn	Nb
0.16	0.36	1.35	0.036

Table 7. Analyses of the steel (insoluble Nb%)

Treatment	1 100°C Q	900°C Q
Quenched	0.028	0.030
Tempered*	0.031	0.030

* 650°C × 1 hr tempered

650°C for 1 hr. The tensile strengths, thus heat-treated, were 77.8 and 85.6 kg/mm² respectively. This means that the difference in quenching temperature resulted in the increase of 8 kg/mm² in strength. The amount of precipitates are shown in Table 7. As mentioned previously, little precipitation occurred during the tempering of a specimen quenched from 900°C, while in a specimen quenched from 1 100°C, as much as 0.003%Nb had precipitated. It is those precipitates that appear to have caused the 8 kg/mm² increase in the tensile strength. In this experiment, little difference was observed by optical microscopy in the structures of quenched and quench-tempered specimens when the austenitized temperature was 900°, 1 000°, and 1 100°C. The structure of the specimen austenitized at 1 200°C, however, was quite different. Therefore, two specimens were austenitized at either 900°C or 1 100°C, tempered at the same temperature, and compared. From this result, it is quite reasonable to think that fine cubic precipitates of about 0.01% that appeared in tempering can explain the strength increase of 15 kg/mm².

According to this hypothesis, Ti-Mo,¹⁰⁾ Zr-Mo,¹¹⁾ and Nb-W¹²⁾ combinations have a possibility to form similar duplex carbide. Titanium and zirconium in the former two steel systems, however, have stronger tendencies to form nitrides, so that they tend to exist as large inclusions of an order of microns. The inclusions do not dissolve nor reprecipitate by an ordinary quench and temper treatment. Little amount of complex carbo-nitride precipitates during tempering in these systems so that the combination effect is small in them.

The analysis of niobium precipitates compounds was done by the (1+1) HCl aqueous solution method, which has been proved in this research to be the most suitable for the purpose (see Appendix).

IV. Summary

The strength of steels when niobium and molybdenum were added in suitable amounts has been known to be raised beyond conventional comprehension. Therefore, the cause of the strengthening was investigated, and other possible combinations of alloying elements which have similar strengthening effect were searched. Though the research work has not been completed, the results so far obtained may be summarized as follows.

(1) Among the combinations between an element of titanium, zirconium, and niobium and an element

of chromium, molybdenum, and tungsten, Nb-Mo shows the strongest combination strengthening effect. Ti-Mo, Zr-Mo, and Nb-Cr steels show small combination effect, while little effect is found with Ti-Cr, Zr-Cr, and Nb-W steels.

(2) The combination effect may be due to precipitation of complex carbo-nitride of cubic structure containing a IVa or Va element and a VIa element. This precipitation does not occur in the form of agglomeration but in the form of precipitation of new fine particles.

(3) For the chemical analysis of niobium compound, (1+1) HCl aqueous solution is the best extraction solvent. Any filter whose pore size is smaller than 10⁴ Å is usable for the filtration of niobium residue, and ordinary paper filter is good enough. The solution should be filtered as soon as the matrix is dissolved, otherwise, the amount of extract decreases.

REFERENCES

- 1) S. Kanazawa, A. Nakashima, K. Okamoto, K. Tanabe, and S. Nakazawa: *J. Japan Inst. Metals*, **31** (1967), 165.
- 2) S. Kanazawa, A. Nakashima, K. Okamoto, K. Tanabe, and S. Nakazawa: *J. Japan Inst. Metals*, **31** (1967), 171.
- 3) H. Nakamura, T. Naiki, and T. Kuriyama: *Ishikawajima Tech. Report*, **5** (1965), 239.
- 4) S. Kanazawa, A. Nakashima, K. Okamoto, K. Tanabe, and S. Nakazawa: Study on the Effect of Minute Nb Addition in Steel, (1967), Third report of the basic study group of iron and steel-division of Nb study.
- 5) S. Kanazawa, A. Nakashima, K. Okamoto, K. Tanabe: Preprint of Fall General Meeting, Japan Institute of Metals, (Oct., 1967), 284.
- 6) T. Mori, K. Fujita, M. Tokizane, and K. Yamaguti: *Tetsu-to-Hagane*, **50** (1964), 196.
- 7) K. Kawamura, S. Watanabe, and T. Suzuki: Preprint of Spring General Meeting, Japan Institute of Metals, (Mar., 1969), 130.
- 8) E. Rudy, C. Brukl, and S. Windisch: *Trans. AIME*, **239** (1967), 1796.
- 9) H. Rassarts, F. Benesovsky, and H. Nowotny: *Planseeber. Pulvermet.*, **13** (1965), 199.
- 10) H. Albert and J. Norton: *Planseeber. Pulvermet.*, **4** (1956), 2.
- 11) T. Wallace, C. Gutierrez, and P. Stone: *J. Phys. Chem.*, **67** (1963), 769.
- 12) E. Rudy: *Trans. AIME*, **239** (1967), 1803.

Appendix

Some Investigations on the Analytical Method of Niobium Compound

Though the extraction of niobium compound by (1+1) HCl aqueous solution, which had been examined in detail by Mori *et al.*,⁶⁾ has been popular, whether this method was the most suitable was re-examined with a Si-Mn-Nb steel normalized at 900°C for 1 hr. As extraction solvents, acids such as (1+1) HCl aqueous solution, (1+1) HCl-CH₃OH, and (1+1) H₃PO₄ aqueous solution were used. Also iodine methanol commonly used to extract AlN from steel was tested. An electrolyte with 10% sodium citrate and 1.2% potassium bromide was used in electrolytic extraction method at a constant potential (-400 mV). Figure A shows the results. As shown

C	Si	Mn	Nb
0.18	0.04	1.30	0.034

Normalized at 900°C

Fig. A. Relation between insoluble niobium and various extraction methods

C	Si	Mn	Nb	N
0.18	0.04	1.28	0.034	0.0133

Fig. B. Dissolution rate of niobium precipitates in (1+1) HCl extraction solution

in the figure, (1+1) HCl aqueous solution method recovered the largest amount of niobium residue. This method, therefore, has been judged to be the most suitable one for the extraction,¹⁾ substantiating previous view.⁶⁾

However, there are two problems in this method. One is how soon the filtration should be brought to completion after the matrix has been dissolved. The other is what filter should be chosen. Figure B shows the relation between the time elapsed before filtration after 1 g sample was dipped in 40 cc of (1+1) HCl aqueous solution and kept at room temperature and the amount of residue collected by celafilter M, where 50 hr was the time required for the complete dissolution of matrix. This shows that the filtration should be done immediately after the completion of dissolution.

Recently, filters with 100 Å pore size have become available commercially. A filter with a small pore

Fig. C. Relation between pore size and insoluble niobium extracted by (1+1) HCl

Photo. A. Electron-micrograph of residues extracted by (1+1) HCl aqueous solution

size, however, takes time to finish filtration so that precipitates may dissolve during the operation or washing may become incomplete. Therefore, the analyses were carried out using filters of various pore size. The results are shown in Fig. C. According to this figure, filter with pore size below 10⁴ Å is sufficient to keep the accuracy. The traditional paper filter is also good enough since 0.035% Nb were collected. The precipitates are far smaller than 10⁴ Å, as may be seen in Photo. A, where precipitates smaller than 100 Å are seen in the extracted residue, yet they were collected as residue by a filter of 10⁴ Å pore size. This may be due to the agglomeration of fine precipitates.

The analytical method of niobium compound by (1+1) HCl aqueous solution is the quantitatively reliable technique in the case of Si-Mn-Nb steel. In order to study the possibility to apply this method to the quantitative analysis of duplex carbide, chemical analysis was performed on the niobium content in the residue which had been first extracted with above-mentioned (1+3) H₂SO₄ aqueous solution and then treated with (1+1) HCl-CH₃OH to dissolve cementite in it. Values thus obtained were exactly the same as those of (Nb)₇ or (Nb)₈ in Table 4. Therefore, the analytical method of niobium compound by (1+1) HCl aqueous solution can be quantitatively applied in the case of present investigation.

REFERENCE

- i) S. Kanazawa *et al.*: *Tetsu-to-Hagané*, **55** (1969), 373.