The Effects of Excess Aluminum on Mechanical Properties of Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr Steels with Regard to Solute Interactions*

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Synopsis

Mechanical properties have been studied through the changes of Al and N contents in Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr steels with regard to solute interactions between alloying elements by means of Charpy V-notch impact tests, tensile tests and microscopical observations.

The results show that the low-temperature toughness is anomalously deteriorated in Mn-Mo and Mn-Mo-Ni steels but indistinctly related in Mn-Mo-Ni-Cr steel by an increase of excess Al. It is also shown that the tensile strength is remarkably increased, slightly increased and not increased at all by an increase of excess Al in Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr steels, respectively.

I. Introduction

Mechanical properties in low-alloy steels can be improved by the control of solute interactions between alloying elements and impurities.

Very little attention has been paid to the influence of solute interactions on the mechanical properties in practical steel, which is multi-component, due to the complication of microsegregation and due to the incompleteness of thermodynamics in the solid-phase compared with the liquid-phase. However, the influence of solute interactions may be of great importance in understanding the effects of micro-alloying elements on the diagram of continuous-cooling-transformation, and the segregation of alloying elements and impurities at grain boundaries.

The classical studies in the foregoing fields have been carried out on the tendency to form carbides of various alloying elements for Fe-C-M systems by Bain,¹⁾ on the up-hill diffusion of carbon for Fe-C-Si system by Darken,²⁾ and on the banded structure of ferrite and pearlite by previous investigators.^{3,4)} It should be noted that the above studies have been associated with the influence of relatively high-alloying elements for Fe-C-M systems.

It was recently shown by Mabuchi *et al.*⁵⁻⁷⁾ that the low-temperature toughness in an A302C steel is deteriorated by adding a small amount of excess Al (only about 0.010 %) due to the change of the microstructure from fine ferrite to coarse upper bainite because of Al partitioning in bainitic ferrite and because of C enrichment in retained austenite left between bainitic ferrite during continuous-cooling-transformation through a repulsive force between Al-C.

Later, it is demonstrated by Mabuchi and McMahon^{8,9)} that both temper embrittlement and hydrogen embrittlement in an HY 130 steel are

essentially governed not by McLean's equilibrium segregation but by the segregation due to the resultant interactions of repulsive forces between Si-P, Si-N and Si-Al, and of attractive forces between Ni-Si, Ni-Al and Si-Mn during ageing at 480 °C up to 1 000 h.

In order to elucidate this mechanism further with regard to effects of excess Al on mechanical properties, Mn-Mo (A302B), Mn-Mo-Ni (A302C) and Mn-Mo-Ni-Cr (A302C-Cr Mod.) steels have been studied in terms of changes in Al and N contents with the assistance of ideas on solute interactions between alloying elements and on partitioning.

II. Experimental Procedures

The Mn-Mo (A302B) steel was melted by means of a basic oxygen furnace and cast into 40-ton ingots. The ingots were rolled into 300 mm thick slabs and then rolled into 82 mm thick plates. The samples taken from the plates were austenitized as Hot Forming at 910 °C for 6 h and then air cooled. They were stress relieved as Post Welding Heat Treatment (PWHT) at 605 °C for 7 h and then furnace cooled.

The Mn-Mo-Ni (A302C) steel was melted using an electric furnace and then cast into 70 to 90-ton ingots. The ingots were forged into 500 mm thick slabs and then rolled into 143 mm thick plates. The samples were austenitized at 920 °C for 4 h and then air cooled. They were stress relieved at 625 °C for 17 h and then furnace cooled.

The Mn-Mo-Ni-Cr (A302C-Cr Mod.) steel was also melted by electric furnace and then cast into 100-ton ingots. The ingots were forged into 470 mm thick slabs and then rolled into 147 mm thick plates. The samples were austenitized at 920 °C for 3 h and then air cooled. They were tempered at 670 °C for 3 h and then air cooled. They were stress relieved at 625 °C for 22 h and then furnace cooled.

Hence, Larson-Miller Tempering Parameters of Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr steels are 18.3, 19.2 and 19.5, respectively, by the following equation.

$$TP = T(^{\circ}\text{K})(20 + \log t) \times 10^{-3} \dots\dots\dots(1)$$

The compositions of Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr steels are given as product analysis in Tables 1 to 3, respectively. The three steels were all production heats, which had essentially the same com-

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positions except for excess Al in each steel. Excess Al is defined here by the following equation^{5,7)}, since AlN precipitates would vary with heat treatment.

Excess Al = T.Al–Insol.Al–Al as AlN

= Sol.Al–27/14 N as AlN(2)

Table 1. Composition of Mn–Mo steel. (Product analysis, wt%)

Heat	1A	1B	1C	1D
C	0.19	0.18	0.20	0.17
Si	0.26	0.25	0.24	0.24
Mn	1.45	1.43	1.46	1.46
P	0.017	0.019	0.014	0.019
S	0.003	0.004	0.004	0.004
Cu	0.01	0.01	0.01	0.01
Ni	0.02	0.02	0.02	0.02
Cr	0.03	0.04	0.03	0.03
Mo	0.57	0.58	0.58	0.59
Sol. Al	0.048	0.033	0.022	0.022
Sol. N	0.0108	0.0116	0.0098	0.0108
N as AlN	0.0102	0.0110	0.0090	0.0102
Excess Al	0.028	0.011	0.004	0.002

Table 2. Composition of Mn–Mo–Ni steel. (Product analysis, wt%)

Heat	2A	2B	2C	2D	2E
C	0.20	0.21	0.21	0.22	0.19
Si	0.22	0.21	0.24	0.22	0.27
Mn	1.40	1.38	1.49	1.38	1.41
P	0.008	0.007	0.007	0.009	0.008
S	0.008	0.006	0.006	0.008	0.006
Cu	0.04	0.03	0.04	0.05	0.04
Ni	0.58	0.60	0.57	0.63	0.59
Cr	0.07	0.09	0.06	0.08	0.08
Mo	0.54	0.54	0.51	0.55	0.52
Sol. Al	0.028	0.016	0.014	0.016	0.013
Sol. N	0.0055	0.0051	0.0052	0.0061	0.0064
N as AlN	0.0049	0.0044	0.0044	0.0055	0.0058
Excess Al	0.019	0.008	0.006	0.005	0.002

Table 3. Composition of Mn–Mo–Ni–Cr steel. (Product analysis, wt%)

Heat	3A	3B	3C	3D
C	0.22	0.22	0.23	0.22
Si	0.25	0.24	0.23	0.24
Mn	1.46	1.50	1.44	1.43
P	0.008	0.008	0.007	0.009
S	0.004	0.004	0.004	0.005
Cu	0.04	0.05	0.04	0.04
Ni	0.63	0.63	0.62	0.63
Cr	0.63	0.66	0.64	0.62
Mo	0.57	0.57	0.54	0.52
Sol. Al	0.042	0.027	0.023	0.018
Sol. N	0.0068	0.0058	0.0086	0.0076
N as AlN	0.0060	0.0052	0.0080	0.0068
Excess Al	0.030	0.018	0.012	0.005

In particular, supplemental product analysis for B was carefully carried out in investigating the influence of sol. B on the hardenability of the three steels, but nothing notable was found as reported previously.⁷⁾

Charpy V-notch (CVN) impact tests and tensile tests were carried out for longitudinal specimens, taken from the quarter-thickness portion of samples, at various temperatures and at room temperature, respectively. The toughness of three steels was characterized by absorbed energies at 0 °C (*vEo*) and also by 50 % Ductile–Brittle Fracture Appearance Transition Temperature (FATT) in CVN impact tests.

Optical microstructure and austenitic grain size by ASTM E112 were also observed.

The previous data of Mn–Mo–Ni steel⁷⁾ are employed to compare the present results of Mn–Mo and Mn–Mo–Ni–Cr steels.

III. Experimental Results

The results of tensile tests in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels are listed in Tables 4 to 6, respectively. The excess Al of Mn–Mo steel increased remarkably the tensile strength, and that of Mn–Mo–Ni steel increased slightly the tensile strength, whereas that of Mn–Mo–Ni–Cr steel did not increase the tensile strength at all, as is clearly depicted in Fig. 1.

It is also shown in Tables 4 and 5 that the yield strength increased and elongation decreased as the tensile strength increased through the increase of excess Al both in Mn–Mo and Mn–Mo–Ni steels. In particular, it should be noted that the tensile strength of Mn–Mo steel is increased as a logarithmic function of excess Al.

The *vEo* measured in CVN impact tests at 0 °C in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels are shown in Figs. 2 to 4, respectively, to compare the effects of excess Al in semi-logarithmic fashion. It is important to note that the *vEo* of Mn–Mo and Mn–Mo–Ni steels decreased very rapidly with an increase

Table 4. Result of tensile test in Mn–Mo steel.

Heat	1A	1B	1C	1D
Y. S. (kgf/mm ²)	56.1	52.0	44.1	41.6
T. S. (kgf/mm ²)	69.8	65.2	62.6	59.2
El (%)	26	28	30	32

Table 5. Result of tensile test in Mn–Mo–Ni steel.

Heat	2A	2B	2C	2D	2E
Y. S. (kgf/mm ²)	50.8	47.7	50.8	49.6	46.1
T. S. (kgf/mm ²)	63.8	61.5	62.1	63.6	61.5
El (%)	26	24	25	25	27

Table 6. Result of tensile test in Mn–Mo–Ni–Cr steel.

Heat	3A	3B	3C	3D
Y. P. (kgf/mm ²)	55.9	53.4	54.6	53.9
T. S. (kgf/mm ²)	70.0	67.7	69.5	69.5
El (%)	25	26	22	27

of excess Al, and that the slope of the former was two times higher than that of the latter as a function of log excess Al, whereas the *vEo* of Mn–Mo–Ni–Cr steel seems to be almost independent of excess Al in the present range as discussed later.

Figures 5 to 7 show the correlation of the FATT in CVN impact tests with excess Al in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels, respectively. It is obviously shown that the FATT was quickly lowered as the excess Al was decreased both in Mn–Mo and Mn–Mo–Ni steels, and that the slope of the former was higher than that of the latter. However, it is also noted that the FATT of Mn–Mo steel seems to be 20 to 30 °C lower than that of Mn–Mo–Ni steel, since the former had the cooling rate of 10 °C/min in normalizing followed by PWHT with the *TP* of 18.3

Fig. 1. Influence of excess Al on the tensile strength in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels.

but the latter had the cooling rate of 3 °C/min in normalizing followed by PWHT with the *TP* of 19.2.

On the other hand, the FATT of Mn–Mo–Ni–Cr steel was distantly related to the excess Al in the present range as discussed later. It should be noted that the FATT of Mn–Mo–Ni–Cr steel is clearly shown to be lower than that of Mn–Mo–Ni steel when comparing Fig. 6 with Fig. 7, notwithstanding their almost identical conditions in heat treatment as Mn–Mo–Ni–Cr steel had the cooling rate of 3 °C/min in normalizing followed by PWHT with the *TP* of 19.5.

Photograph 1 compares the austenitic grain sizes of heats with the highest excess Al and with the lowest excess Al in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels. No difference at all in austenitic grain size was observed between heats with the highest excess Al and with the lowest excess Al in the three steels. It is then considered that the microstructure is more important than the austenitic grain size in the present case with regard to the effect of excess Al on mechanical properties.

The microstructures of heats with the highest excess Al and with the lowest excess Al in Mn–Mo, Mn–Mo–Ni and Mn–Mo–Ni–Cr steels are shown in Photo. 2 in order to compare the effect of excess Al. Heats 1A and 2A, which contained the highest excess Al in Mn–Mo and Mn–Mo–Ni steels, respectively, had the coarse structure of upper bainite with bainitic ferrite sideplates of Widmanstätten morphology (ferrite with an aligned martensite–austenite constituent), since excess Al tends to retard the ferrite transformation due to the rate control of Al partitioning in the ferritic component of bainite and expels C from bainitic ferrite sideplates into retained austenite left between them as they grow during continuous-cooling-

Photo. 1. Austenitic grains of the three steels in the order: (a) Heat 1A, (b) Heat 1D, (c) Heat 2A, (d) Heat 2E, (e) Heat 3A and (f) Heat 3D containing (a) (c) (e) the highest excess Al and (b) (d) (f) the lowest excess Al in the three steels.

transformation due to a repulsive force between Al-C. It is also important to note that the grain size of upper bainite in Heats 1A and 2A corresponded almost to the grain size of the prior austenite, grain boundaries of which were clearly etched by 5 % nital.

On the other hand, Heats 1D and 2E, which contained the lowest excess Al in Mn-Mo and Mn-Mo-Ni steels, respectively, had a fine allotriomorphic structure of ferrite at the grain boundaries of the prior austenite, an idiomorphic structure of ferrite blocks

Fig. 2. Effect of excess Al on the absorbed energy of Mn-Mo steel in CVN impact tests at 0 °C.

Fig. 3. Effect of excess Al on the absorbed energy of Mn-Mo-Ni steel in CVN impact tests at 0 °C.

Fig. 4. Effect of excess Al on the absorbed energy of Mn-Mo-Ni-Cr steel in CVN impact tests at 0 °C.

Fig. 5. Correlation of the FATT in CVN impact tests with the excess Al in Mn-Mo steel.

Fig. 6. Correlation of the FATT in CVN impact tests with the excess Al in Mn-Mo-Ni steel.

Fig. 7. Correlation of the FATT in CVN impact tests with the excess Al in Mn-Mo-Ni-Cr steel.

Photo. 2. Microstructure of the three steels in the order: (a) Heat 1A, (b) Heat 1D, (c) Heat 2A, (d) Heat 2E, (e) Heat 3A and (f) Heat 3D containing (a) (c) (e) the highest excess Al and (b) (d) (f) the lowest excess Al in the three steels.

inside the prior austenitic grains, and a partly developed upper bainitic structure. It is also noted that the structure in Heats 1D and 2E appears to be finer than that in Heats 1A and 2A, although the difference in austenitic grain size was not observed as shown in Photo. 1. It seems then that the influence of excess Al on mechanical properties in Mn-Mo and Mn-Mo-Ni steels is to change the microstructure from mostly fine ferrite to coarse upper bainite.

It follows in Photo. 2 that Heats 3A and 3D in Mn-Mo-Ni-Cr steel had the fine structure of lower bainite without regard to the amount of excess Al, since Ni and Cr seem to weaken the influence of excess Al on the change of microstructure through the reduction of Al partitioning in the ferritic component of bainite. This is due to attractive forces between Al-Ni and Al-Cr, and also Cr appears to retard pearlite transformation due to the rate control of Cr partitioning in cementite, as discussed later.

The fracture mode of CVN impact specimens tested at -20°C for Heats 2A and 2E in Mn-Mo-Ni steel is shown in the previous report⁷⁾ to compare the effects of excess Al. It is reported that Heat 2A, which contained the highest excess Al of 0.019 % in the Mn-Mo-Ni steel, showed almost complete transgranular cleavage, while Heats 2E, from which excess Al was almost removed, showed microvoid coalescence in the initiation region and transgranular cleavage in the propagation region. These observations correspond well with the former experimental results that sufficient excess Al would result the prevention of microvoid coalescence, which could absorb higher energy than cleavage, on account of the change of microstructure from mostly fine ferrite to coarse upper bainite.

It is also shown in Fig. 8, which depicts the continuous-cooling-transformation diagram for Mn-Mo-Ni steels with the highest excess Al and with the lowest excess Al, that excess Al in the austenite tends to retard proeutectoid ferrite and to develop upper bainite with bainitic ferrite sideplates. It should be noted that these results can explain the foregoing experimental observations.

IV. Discussion

It is clearly demonstrated in the results of the present study that the excess Al in Mn-Mo (A302B) steel considerably reduces the low-temperature toughness and increases drastically the tensile strength. The influence of excess Al in the steel on mechanical properties appears to be due to the change in the microstructure of the steel from mostly fine ferrite to coarse upper bainite. It is also shown in Mn-Mo-Ni (A302C) steel that an addition of Ni can moderate the influence of excess Al in the steel on mechanical properties, above all, on the tensile strength.

On the other hand, it is noted in Mn-Mo-Ni-Cr (A302C-Cr Mod.) steel that additions of Ni and Cr almost eliminate the influence of excess Al in the present range on mechanical properties.

Hence, discussions of the foregoing results in the present study are focussed on the mechanism of the changes in microstructures of the three steels with assistance of ideas on solute interactions in a ternary solid solution and on partitioning of alloying elements during continuous-cooling-transformation.

1. Influence of Solute Interactions in Steel

The interaction parameter $\varepsilon_B^{(C)}$, which shows the solute interaction between elements B and C in a

Fig. 8. Continuous-cooling-transformation diagram for Mn-Mo-Ni steels with the highest excess Al (Heat 2A) and with the lowest excess Al (Heat 2E).

ternary solid solution for an A-B-C system with A as solvent, is defined as the following equation.^{10,12)}

$$\epsilon_B^{(C)} = \alpha_{BC} - \alpha_{AB} - \alpha_{CA} \dots\dots\dots(3)$$

where, α_{ij} : the interaction parameter in a binary solid solution for an i - j system as defined in the quasi-chemical equation.

$$\alpha_{ij} = ZN[\Omega_{ij} - 1/2(\Omega_{ii} + \Omega_{jj})] \dots\dots\dots(4)$$

where, Z : the coordination number in the lattice
 N : Avogadro's number
 Ω_{ij} : the binding energy of an i - j bond in the lattice.

Thus, the solid solution tends to order in the short range or to form compounds due to an attractive force between i - j when $\alpha_{ij} < 0$. In turn, the solid solution tends to cluster in like atoms due to a repulsive force between i - j when $\alpha_{ij} > 0$.

The above interpretation would imply that α_{ij} can qualitatively be predicted with the assistance of the published phase diagrams.¹¹⁾ It is also connoted that the interaction parameter $\epsilon_B^{(C)}$ in a ternary solid solution can have the same influence on an attractive force or on a repulsive force as the interaction parameter α_{ij} in a binary solid solution.

Equations (3) and (4) are generally expressed in the whole range of a ternary solid solution for an A-B-C system with A as solvent, but the present interest in this study is to know the influence of solute interactions in practical steel. Hence, Eq. (3) is changed to the following.

$$\epsilon_B^{(C)} = \alpha_{BC} - \alpha_{FeB} - \alpha_{CFe} \dots\dots\dots(5)$$

where, $\epsilon_B^{(C)}$: the interaction parameter of B and C dissolved in steel for the Fe-B-C system.

By the introduction of Eq. (5), attractive forces in

steel between Si-Mn, Ni-Al, Ni-Si, Cr-Si and Cr-Al due to $\epsilon_B^{(C)} < 0$ and a repulsive force in steel between Al-Si due to $\epsilon_B^{(C)} > 0$ can qualitatively be predicted with the assistance of phase diagrams on stable intermetallic compounds.¹¹⁾ This prediction is confirmed by the cosegregations of Si-Mn, Ni-Al⁹⁾ and Ni-Si^{9,16)} in a 5 % Ni steel, by the cosegregation of Cr-Si in a 2.1/4%Cr-1%Mo steel,¹⁷⁾ and by the site competition of Al-Si in a 5 % Ni steel with high Al⁹⁾ at grain boundaries.

Very little effort has been spent in understanding continuous-cooling-transformation with regard to solute interactions and in obtaining the interaction parameters $\epsilon_B^{(C)}$ dissolved in austenite and ferrite due to experimental difficulties. However, Mori and Ichise¹³⁾ studied the correlation between interaction coefficients, which are equal to interaction parameters over RT ,* of nitrogen dissolved in liquid iron and in austenite for Fe-N-X systems. It implies that the interaction coefficient in austenite can be supposed by the interaction coefficient in liquid iron. It is also noted in the same results¹³⁾ that repulsive forces are held between Si-N, P-N and Ni-N due to $\epsilon_N^{(X)} > 0$, while attractive forces are held between Cr-N, Mo-N and Mn-N due to $\epsilon_N^{(X)} < 0$. This supposition is confirmed by the site competition of P-N in grain boundary segregation at 600 °C for the Fe-P-N system³¹⁾ and by the enhanced segregation of N at grain boundaries due to a repulsive force with Si, in bulk, during short-time ageing in a 5 % Ni steel.⁹⁾

The sufficient data on interaction coefficients $\epsilon_B^{(C)}$, which were employed for Fe-N-X systems, for dilute solutions of elements B and C dissolved in liquid iron at 1 600 °C were summarized by Elliott *et al.*¹⁴⁾ The foregoing prediction of repulsive force between Al-Si by Eq. (5) is also supported by the interaction coefficient of Al and Si dissolved in liquid iron as

* R : gas constant, T : temperature (K)

shown by Elliott *et al.*¹⁴⁾

It is of particular interest that the interaction coefficients of carbon, dissolved in liquid iron at 1 550 °C for Fe-C-M systems shift periodically along with atomic number.^{12,15)}

On the other hand, Bain¹⁾ reported the tendency to form carbides of various alloying elements in steels as following.

where (Fe) indicates the solvent for Fe-C-M systems.

It is remarkably interesting to note in the comparison of the foregoing results^{12,15)} with Eq. (6) that the values on the interaction coefficients of carbon correspond well with the tendency to form carbides in Eq. (6). It is again implied that the interaction coefficient in steel can qualitatively be supposed by the interaction coefficient in liquid iron. Thus, it is considered that elements on the right hand side of (Fe) in Eq. (6) can not form their carbides in steel since repulsive forces take place between Si-C, Al-C and so on due to $\epsilon_{\text{C}}^{(\text{M})} > 0$, while elements on the left hand side of (Fe) in Eq. (6) have attractive forces with C due to $\epsilon_{\text{C}}^{(\text{M})} < 0$. This prediction would suggest that Al as well as Si raises the activity of carbon in ferrite as also shown by Bain.¹⁾ The repulsive force between Si-C for the Fe-C-Si system was first demonstrated by Darken²⁾ in the study of uphill diffusion. The repulsive force between Al-C was confirmed by the studies of Al partitioning in an A302C steel⁷⁾ and in a dual-phase steel with 1 % Al.¹⁸⁾

The repulsive force between P-C, which can be predicted by interaction coefficients in liquid iron,^{12,15)} is supported by the studies on the banded structure of ferrite and pearlite^{3,4)} and on the site competition of P-C in grain boundary segregation for the Fe-P-C system.³¹⁾

It is consequently confirmed that the tendency to form compounds between metalloid and alloying elements is to be significantly useful in predicting solute interactions in steel.

Kaneko *et al.*²²⁾ reported the tendency to form phosphides of various alloying elements in steel as following.

where (Fe) indicates the solvent for Fe-P-M systems. Aluminum and Si on the right hand side of (Fe) in Eq. (7) can not form their phosphides in steel since repulsive forces take place between Al-P and Si-P. The repulsive force between Si-P is confirmed by the interaction coefficient of P and Si by Elliott *et al.*,¹⁴⁾ by the enhanced segregation of P at grain boundaries due to repulsive force with Si, in bulk in a 2.1/4%Cr-1%Mo steel²⁵⁾ and in a 5 % Ni steel,⁹⁾ and by the U-turn behavior of P in accordance with the accumulation of segregated Si at grain boundaries in a 5 % Ni steel.⁹⁾

It is considered that an attractive force between

Mo-P is preferred to that between Mo-C in practical steel because of the difference in the orders of Mo in Eqs. (6) and (7) to indicate the affinity of Mo with C or P. The above prediction is supported by the fact that the addition of Mo acts to inhibit P-induced temper embrittlement in the series of Mn-Ni-Cr-Mo steel,²⁴⁾ confirmed by Mo apparently being able to act as an effective scavenger and preventing P segregation to grain boundaries until the precipitation of Mo carbides in a 3.5%Ni-1.7%Cr steel,¹⁹⁾ and also proved by the fact that the addition of Mo in the range of 0.5 to 0.7 % can diminish P segregation until Mo precipitation as M_2C in 2.1/4 % Cr steels.¹⁷⁾

It is also predicted by Eq. (7) that attractive forces can be established between Mn-P, Cr-P and presumably Ni-P. The attractive force between Mn-P is confirmed by the cosegregations of Mn-P in the austenite region of a 3.5%Ni-1.5%Cr steel²⁰⁾ and in a 2.1/4%Cr-1%Mo steel.²⁵⁾ The attractive force between Cr-P is demonstrated by the cosegregation of Cr-P after the Mo carbide of M_2C is formed at the expense of Cr-rich M_7C_3 in 2.1/4 % Cr steels,¹⁷⁾ and by the cosegregation of Cr-P in a 3.5%Ni-1.7%Cr steel.²¹⁾ The attractive force between Ni-P is also shown by the cosegregation of Ni-P in a 3.5%Ni-1.7%Cr steel.²¹⁾

However, it appears that the other elements on the left hand side of (Fe) in Eq. (7) may not effectively interact with P in steels due to the strong affinities with C, N, O or S.

It is then offered that the change in microstructures during continuous-cooling-transformation as well as the segregation of alloying elements and impurities at grain boundaries can be due to the resultant interactions of attractive forces between Ni-Al, Ni-Si, Cr-Si, Cr-Al, Cr-N, Ni-P, Mo-P, Mn-P, Cr-P and so on, and of repulsive forces between Al-Si, Si-C, Al-C, P-C, Si-P, Al-P, Si-N, P-N and so on, as shown by previous works.^{7,9)}

It is eventually rationalized through the present discussions that the solute interactions of a repulsive force between Al-C and of attractive forces between Al-Ni and presumably Al-Cr are of particular importance in addition to the influences of Al partitioning in ferrite and of Cr partitioning in cementite in considering the mechanism on the change of microstructure in the three steels with regard to excess Al as summarized below.

(1) Aluminum, which partitions proeutectoid ferrite (or the ferritic component of bainite),^{7,18)} rejects C into austenite due to a repulsive force between Al-C at higher temperature, and then the retained austenite left between bainitic ferrite tends to contain higher C concentrations during continuous-cooling-transformation. Finally, Mn-Mo (A302B) steel with high excess Al develops into mixed structures of mostly upper bainite and high carbon martensite-austenite constituent left between bainitic ferrite.

(2) Aluminum partitioning in the ferrite-phase can be weakened by Ni due to an attractive force between Al-Ni in the austenite of Mn-Mo-Ni (A302C) steel. Thus, Ni appears to decrease the influence of

excess Al on mechanical properties through the change in microstructure, since C enrichment into retained austenite left bainitic ferrite during continuous-cooling-transformation is indirectly lowered by the reduction of Al partitioning in the steel.

(3) Chromium in Mn-Mo-Ni-Cr (A302C-Cr Mod.) steel appears to have two kinds of role in considering the influence of excess Al. Cr seems to have the same effect as Ni to weaken Al partitioning due to an attractive force between Al-Cr in austenite, while the other is on Cr partitioning in cementite to retard pearlite transformation as discussed later. However, the latter is considered to be more important than the former, since the steel consists not of fine allotriomorphic at grain boundaries but of lower bainite in Mn-Mo-Ni-Cr steel.

2. Influence of Solute Partitioning in Steel

Sato and Nishizawa²³⁾ investigated the partitioning parameter of alloying elements in cementite or in ferrite for Fe-C-M systems, except for Al. The tendency to form carbides in Eq. (6) does not correspond well with the tendency to partition cementite²³⁾ since Cr and Mn can form stable carbides as (Fe, M)₃C but other elements tend to form their own stable carbides as MC. The retardation of pearlite transformation can take place due to the rate control of Cr partitioning between austenite and cementite as shown by previous investigators.²⁶⁻²⁸⁾

J. Y. Koo *et al.*¹⁸⁾ studied Al partitioning in the dual-phase steel of AISI 1010 with 1 % Al and 0.10 % C. They reported that Al partitioned ferrite two times higher than martensite and in turn carbon partitioned martensite in the range of 0.50 to 0.65 %. The Al partitioning parameter of at most 0.1 is derived from the hypothesis that the partitioning parameter of Al is 1/2 in martensite over that in ferrite and the partitioning parameter of Al is at most 1/5 in cementite over that in the ferritic component of martensite employing the above data.¹⁸⁾ The foregoing hypothesis is quite consistent with the previous data on the partitioning parameter by Hultgren.^{32,33)}

Aluminum tends to retard ferrite transformation due to the rate control of Al partitioning between austenite and proeutectoid ferrite as is clearly shown in Fig. 8. It is also supported by Yoshimura and Kobayashi²⁹⁾ that Al dissolved in austenite tends to retard the ferrite transformation resulting in a mostly upper bainitic structure in a 1%Cr-0.2%Mo steel, although the above mechanism is not explained.

On the other hand, Ito *et al.*³⁰⁾ observed in a 1.5%Ni-0.7%Cr-0.5%Mo-15ppmB steel that Si promoted upper bainite, which consisted of a bainitic ferrite plates and martensite-austenite constituent left between them. They attributed this effect of Si to the low partitioning of Si in cementite as shown by previous investigators.^{23,32)} However, it seems better to explain that the above result can be due to the rate control of Si partitioning in the ferritic component of bainite and due to the raise of C activity in the ferrite-phase resulting in the change of carbide morphology and in C enrichment into retained

austenite left between bainitic ferrite plates during transformation through a repulsive force between Si-C.

It is now possible with the assistance of a partitioning parameter to discuss the Al partitioning in the ferrite-phase and the Cr partitioning in the cementite in the three steels as below.

(1) Excess Al partitions proeutectoid ferrite (or the ferritic component of bainite) to retard ferrite transformation resulting in an upper bainitic structure with the assistance of C enrichment into retained austenite left between bainitic ferrite plates during transformation due to a repulsive force between Al-C in Mn-Mo and Mn-Mo-Ni steels.

(2) Chromium partitions the cementitic component of bainite to retard pearlite (or upper bainite) transformation resulting in lower bainitic structure with assistance of the reduction of Al partitioning due to attractive forces between Al-Ni and Cr-Ni, in Mn-Mo-Ni-Cr steel.

V. Conclusions

The influence of excess Al in Mn-Mo, Mn-Mo-Ni and Mn-Mo-Ni-Cr steels on mechanical properties have been studied with regard to solute interactions in solid solution and to partitioning of alloying elements. It is clearly shown in this study that the excess Al of Mn-Mo and Mn-Mo-Ni steels deteriorates the low-temperature toughness and increases the tensile strength due to the change in microstructure from mostly fine ferrite to coarse upper bainite, although the influence of excess Al in the latter steel is weakened more than that in the former steel, whereas the excess Al of Mn-Mo-Ni-Cr steel does not relate both to the low-temperature toughness and to the tensile strength. The mechanisms of the foregoing results are considered due to the following:

(1) Excess Al in austenite tends to partition proeutectoid ferrite (or the ferritic component of bainite) and to retard ferrite transformation because of the rate control of Al partitioning during continuous-cooling-transformation.

(2) Retained austenite left between the bainitic ferrite has a higher C concentration during transformation, since Al in the bainitic ferrite rejects C into austenite due to a repulsive force between Al-C at higher temperature.

(3) Finally, the microstructure of Mn-Mo and Mn-Mo-Ni steels with high excess Al develops (from fine ferrite) into mixed structures of mostly upper bainite and high carbon bainite (or a martensite-austenite constituent).

(4) Aluminum partitioning in the ferrite-phase is weakened by Ni due to an attractive force between Al-Ni in austenite resulting in the reduction of C enrichment into retained austenite left bainitic ferrite plates during transformation, then the influence of excess Al on mechanical properties is lowered by an addition of Ni in Mn-Mo-Ni steel.

(5) Chromium in austenite tends to partition the cementitic component of bainite and to retard pearlite (or upper bainite) transformation because of the rate

control of Cr partitioning during continuous-cooling-transformation, and Al partitioning in the ferrite-phase is also weakened by Cr due to an attractive force between Al-Cr in austenite resulting in the microstructure of lower bainite, then the influence of excess Al on mechanical properties is eliminated by additions of Ni and Cr in a Mn-Mo-Ni-Cr steel.

It is consequently concluded in this study that the change of microstructures can be brought about by a small addition of alloying elements due to the solute interactions during transformation, while the substantial change of morphologies is associated with the differences in the free energy between each phase as a function of concentrations of alloying elements and in cooling rates during continuous-cooling-transformation.

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