The Effects of Excess Aluminum on Low-temperature Toughness in A302C Steels*

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Synopsis

Low-temperature toughness has been studied through the changes of Al and N contents in A302C steels for reactor vessels by means of Charpy V-notch and press-notch impact tests. The results show that the low-temperature toughness was improved significantly by the elimination of excess Al.

I. Introduction

Low-temperature toughness in A302C steels can be improved by the control of Al and N contents. Excess Al deteriorates the impact properties of the steels.

Mabuchi *et al.*¹⁾ first showed that the absorbed energy in Charpy V-notch impact tests in A533B steels, which have the same compositions as A302C steels, for nuclear reactor vessels increased drastically as the ratio of T.N/T.Al (total nitrogen over total aluminum) increased up to 0.52 (=14/27).

Later, HY130 steel with low Al was shown by Mabuchi and McMahon²⁾ to have lower Ductile-Brittle Fracture Appearance Transition Temperature (FATT) and higher absorbed energy as-quenched and tempered condition than that with high Al.

In order to elucidate further this mechanism, the production heats of A302C steels have been studied with regard to the effect of systematic changes in Al and N contents on the impact properties at low temperatures. The results show that the elimination of excess Al contributes to improvement of low-temperature toughness through the change of the microstructure from upper bainite to mostly ferrite in A302C steels.

II. Experimental Procedures

The steels used in this study were melted by electric furnace and then vacuum cast into 70 to 90 tons ingots. The ingots were forged into 500 mm thick slabs and then rolled into 143 mm thick plates.

The compositions of the A302C steels are listed in Table 1 as ladle analysis, in which the excess Al was approximately estimated by the ratio of T.N/T.Al. The five heats were all commercial steels, which had essentially the same compositions except for excess Al. A special chemical analysis was carried out after the heat treatment of samples, as shown in Table 2, to check the exact excess Al defined by the following equation since the precipitation of AlN would vary with heat treatment.

$$\text{Excess Al} = \text{T. Al} - \text{Insol. Al} - \text{Al as AlN}$$

$$= \text{Sol. Al} - 27/14 \text{ N as AlN} \dots \dots \dots (1)$$

The excess Al decreased in the order of Heats A, B, C, D, and E. Heat A contained the highest excess Al of 0.019% in the five heats. The excess Al was almost removed from Heat E.

Samples were austenitized at 920°C for 4 h and then air cooled. They were tempered as the Post Welding Heat Treatment (PWHT) at 625°C for 17 h and then furnace cooled.

Charpy V-notch (CVN) impact tests and press-notch (PN) impact tests were carried out for three longitudinal specimens taken from the 1/4 t of samples in the five heats at each temperature. The toughness was characterized by the absorbed energy and by the 50% FATT in CVN impact tests and PN impact tests.

The fracture surfaces of CVN impact specimens were subsequently examined by Scanning Electron Microscopy (SEM) to determine the fracture mode.

III. Experimental Results

The absorbed energy measured in CVN impact tests and PN impact tests in the five heats is shown together in Figs. 1 to 6 to compare the effect of excess Al at various temperatures. The absorbed energy in CVN impact tests increased in the order of Heats A, B, C, D, and E at all temperatures. It is important to note that an increase in excess Al deteriorated seriously the absorbed energy in CVN

Table 1. Composition of A302C steels (Ladle analysis, wt%).

Heat	A	B	C	D	E
C	0.20	0.20	0.19	0.20	0.19
Si	0.21	0.21	0.21	0.23	0.25
Mn	1.43	1.43	1.43	1.43	1.43
P	0.007	0.007	0.007	0.009	0.008
S	0.007	0.006	0.006	0.007	0.006
Cu	0.04	0.03	0.04	0.05	0.04
Ni	0.58	0.63	0.59	0.63	0.62
Cr	0.07	0.09	0.06	0.09	0.07
Mo	0.53	0.54	0.52	0.54	0.52
T. N	0.0058	0.0056	0.0060	0.0072	0.0071
T. Al	0.032	0.022	0.021	0.019	0.018
T. N/T. Al	0.18	0.25	0.29	0.38	0.39

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Table 2. Composition of A302C steels (Product analysis, wt%).

Heat	A	B	C	D	E
C	0.201	0.210	0.210	0.215	0.189
Si	0.215	0.210	0.243	0.217	0.267
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
Ti	0.005	0.005	0.005	0.005	0.005
T. B	0.0004	0.0004	0.0003	0.0007	0.0005
Sol. B	0.0001	0.0001	trace	0.0002	0.0002
Insol. B	0.0003	0.0003	0.0003	0.0005	0.0003
T. N	0.0061	0.0057	0.0058	0.0069	0.0071
Sol. N	0.0055	0.0051	0.0052	0.0061	0.0064
Insol. N	0.0006	0.0006	0.0006	0.0008	0.0007
T. Al	0.031	0.019	0.017	0.019	0.016
Sol. Al	0.028	0.016	0.014	0.016	0.013
Insol. Al	0.003	0.003	0.003	0.003	0.003
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

impact tests at temperatures below 40°C. It should be also noted that Heat E, in which the excess Al was almost removed, is shown to induce the highest absorbed energy in CVN impact tests in the five heats at all temperatures. On the other hand, the absorbed energy in PN impact tests was constant with regard to the amount of excess Al and was always lower than the lowest value in CVN impact tests at temperatures below 0°C. The absorbed energy in PN impact tests had the same trend as that in CVN impact tests in the five heats at temperatures above 20°C, although the values in the former were more scattered than those in the latter.

This may be due to the following reasons: Generally speaking, the fracture energy in CVN impact tests consists of energy for crack initiation and energy for crack propagation, while the fracture energy in PN impact tests consists of only the energy for crack propagation at temperatures where work hardening by press notch would make crack start with ease. However, the fracture energy in PN impact tests consists of both of the above energy contributions at higher temperatures where microvoid coalescence would occur in the propagation region of the specimens. It is, therefore, possible to predict that the sufficient excess Al as well as press notch would prevent microvoid coalescence and then would reduce the fracture energy down to the absorbed energy in a complete cleavage fracture at low temperatures.

Figure 7 shows the correlation of the FATT in CVN and PN impact tests with the excess Al in the five heats. It is clearly shown here that the FATT in CVN impact tests was quickly lowered as the excess Al was decreased, while the FATT in PN impact tests was almost constant with regard to the amount

Fig. 1. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at -20°C.

Fig. 2. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at -12°C.

Fig. 3. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at 0°C.

Fig. 4. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at 20°C.

Fig. 6. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at 60°C.

Fig. 5. Effect of excess Al on the absorbed energy of A302C steels in CVN impact tests and PN impact tests at 40°C.

Fig. 7. Influence of excess Al on the FATT from CVN impact tests and PN impact tests.

of excess Al as expected. In particular, it should be noted that Heat *E* with no addition of excess Al had the lowest FATT in CVN impact tests among the five heats.

Photographs 1(A) and 1(E) show the fracture mode of CVN impact specimens tested at -20°C for Heats *A* and *E*, respectively, in order to compare the effect of excess Al. It is important to note that Heat *A*, which contained the highest excess Al of 0.019% in the five heats, showed almost complete transgranular cleavage, while Heat *E*, from which excess Al was almost removed, showed microvoid coalescence in the initiation region and transgranular cleavage in the propagation region as shown in Photos. 1(A) and 1(E), respectively. These observations correspond

well with the former prediction that the sufficient excess Al as well as press notch would prevent microvoid coalescence, which would absorb higher energy than cleavage, at low temperatures as seen in the comparison of the fracture energy between CVN impact tests and PN impact tests.

Photograph 2 shows the austenitic grain size of Heats *A* and *E* after heat treatments by means of ASTM E112 and demonstrates the effect of excess Al. The difference in the austenitic grain size was not observed at all between Heats *A* and *E*. It is then considered that the microstructure is more important than the austenitic grain size in this case with regard to the effect of excess Al on the absorbed energy of A302C steels in CVN impact tests at low temperatures.

The microstructures of Heats *A* and *E* are shown in Photos. 3(A) and 3(E), respectively in order to compare the effect of excess Al. The slight banded

Photo. 1(A).
Fracture mode of CVN impact specimen tested at -20°C for Heat *A* showing (a) (b) in the initiation region, (c) (d) in the propagation region, (a) (c) the magnification of $\times 100$, and (b) (d) the magnification of $\times 1\,000$. ($\times 4/5$)

Photo. 1(E).
Fracture mode of CVN impact specimen tested at -20°C for Heat *E* showing (a) (b) in the initiation region, (c) (d) in the propagation region, (a) (c) the magnification of $\times 100$, and (b) (d) the magnification of $\times 1\,000$. ($\times 4/5$)

structure was seen both in Heats *A* and *E*. Heat *A*, which contained the highest excess Al in the five heats, had the coarse structure of upper bainite with

Widmanstätten ferrite and platelike cementite, which nucleated and grew in the high regions in carbon since Widmanstätten plates rejected carbon into the aus-

Photo. 2. Austenitic grains with the magnification of $\times 100$ in the order: (a) Heat *A* and (b) Heat *E*. ($\times 4/5$)

tenite left between them as they grew, as shown in Photo. 3(A). It is also important to note that the grain size of upper bainite in Heat *A* corresponded almost to the grain size of the prior austenite, grain boundaries of which were clearly etched by 5% nital, although some of the upper bainite are found to have subgrains in several places.

On the other hand, it is shown in Photo. 3(E) that Heat *E*, in which no excess Al was added, had the fine structure of chunky ferrite as allotriomorphs at grain boundaries of the prior austenite, of blocky ferrite as idiomorphs inside the prior austenitic grains, and of upper bainite in the segregated regions. In particular, it should be noted that allotriomorphs seems to dominate in the microstructure of Heat *E*, since the grain boundaries of the prior austenite in Heat *E* were not etched so clearly as in Heat *A*. The grain size of chunky ferrite in Heat *E* is observed to be finer than that of upper bainite in Heat *A* as shown in Photos. 3(A) and 3(E), although the austenitic grain size of both Heats *A* and *E* was much the same as shown in Photo. 2. It is also noted in Photo. 3(E) that the ferrite is seen with no precipitation of carbides inside the grains and that the upper bainite is seen only in the segregated regions due to the slight banded structure and at least partially due to the carbon rejection into the austenite left between ferrite during continuous-cooling-transformation.

It seems then that the influence of the excess Al on the low-temperature toughness of A302C steels is to change the microstructure from chunky ferrite to

upper bainite. It is considered that the difference in the grain size between the upper bainite of Heat *A* and the chunky ferrite of Heat *E* is not essentially important on low-temperature toughness in this case, since the excess Al had almost no effect on the absorbed energy at the upper shelf namely at 60°C, where the fracture mode of CVN impact specimens and PN impact specimens in the five heats was completely ductile, as is shown in Fig. 6.

The morphology of AlN precipitates in Heats *A* and *E* is shown in Photo. 4 by the extraction replica to compare the effect of excess Al. It is clearly noted here that fine and numerous precipitates of AlN are observed both in Heats *A* and *E*. However, Heat *A* with sufficient excess Al tends to induce AlN clusters as the result of difference in diffusivity between Al and N and as the operation of coarsening mechanism, while Heat *E* containing Al in balance with N is shown to induce homogeneous distribution of stable AlN precipitates.

It follows that the influence of the excess Al on the microstructure of the A302C steels is not due to the AlN morphology but due to the activity raise of carbon in steel caused by the excess Al. This is supported by the fact that the blocky ferrites as idiomorphs are not seen at all in Heat *A* as shown in Photo. 3(A) although fine and numerous precipitates of AlN, which may be a potential nucleation site of a blocky ferrite inside the prior austenite during continuous-cooling-transformation, are observed both in Heats *A* and *E* as shown in Photo. 4.

IV. Discussion

The results of this study show that the excess Al in A302C steels can deteriorate drastically the low-temperature toughness due to the change in the microstructure of the steels from fine ferrite to coarse upper bainite. It is also shown that the influence of excess Al on low-temperature toughness disappears in press-notch impact tests.

Interpretation of the foregoing results may be given as discussed below.

1. Effect of Repulsive Interactions between Solutes in Steels

Very little attention has been paid to the effects of repulsive solute interactions in practical steels. However, this may be of great importance in rejecting carbon during continuous-cooling-transformation.

The classical study of this kind of interaction is the uphill diffusion of carbon in the Fe-Si-C system first shown by Darken.³⁾ This experiment demonstrated that silicon raises the activity of carbon in ferrite.

Mabuchi and McMahon²⁾ first predicted that aluminum as well as silicon should drive carbon out of ferrite into austenite due to their repulsive interaction with carbon in practical steels, according to the tendency to form carbides of various alloying elements in steels by Bain⁴⁾ as following.

$$\begin{aligned} & \text{Ti} > \text{Nb} > \text{V} > \text{Ta} > \text{Mo} > \text{W} > \text{Cr} > \text{Mn} > \text{Co} \\ & > (\text{Fe}) > \text{Ni} > \text{Al} > \text{Si} \dots\dots\dots(2) \end{aligned}$$

Photo. 3(A). Microstructure of Heat *A* showing (a) the magnification of $\times 100$, (b) magnified view of the segregated region $\times 400$, and (c) magnified views of the low carbon region ($\times 400$). ($\times 4/5$)

Photo. 3(E). Microstructure of Heat *E* showing (a) the magnification of $\times 100$, (b) magnified view of the segregated region $\times 400$, and (c) magnified view of the ferrite rich region ($\times 400$). ($\times 4/5$)

Photo. 4. AlN precipitates with the magnification of $\times 17\,000$ (a) Heat *A* and (b) Heat *E*. ($\times 4/5$)

where (Fe) is the solvent. This prediction would lead that aluminum raises the activity of carbon in ferrite as also shown by Bain.⁴⁾

It is shown in Fig. 8 as a schematic *G-X* diagram that aluminum would partition the ferrite-phase rather than the Fe-carbides in an Fe-C alloy. This would raise the free energy curve of the ferrite-phase with aluminum and carbon contained together, and in turn would lower the solubility of carbon in the ferrite-phase, so that the ferrite transformation would occur at higher temperatures.

The mode of formation of upper bainite in A302C steels with excess Al may be explained as follows⁵⁾:

In the presence of excess Al, ferrite nucleates at

Fig. 8. Schematic curves of free energy *vs.* bulk concentration of carbon in Fe-C and Fe-Al-C alloys analogized with Darken's result.³⁾

grain boundaries and grows out of them as Widmanstätten plates, when it is cooled to approximately 450°C. Only the acicular ferrite can grow due to the slow diffusion of carbon. Since the ferrite plates with excess Al reject carbon as they grow rapidly at higher temperatures, the austenite left between them tends to contain more carbon. As a result, carbides nucleate and grow into platelike morphology in these regions. The final structure of A302C steels with excess Al develops into coarse upper bainite with Widmanstätten ferrite and with obviously platelike carbides as shown in Photo. 3(A).

It is then brought about that the effect of excess Al on low-temperature toughness in A302C steels is to change the microstructure from chunky ferrite to upper bainite, which has less toughness than ferrite or lower bainite, due to the raise of the carbon activity in ferrite-phase with excess Al. In principle, however, it is also important to consider the influence of Si as well as excess Al on low-temperature toughness with regard to the repulsive interaction with carbon.

2. Influence of Work Hardening on Low-temperature Toughness

The effect of excess Al on low-temperature toughness may not be seen by a press-notch impact test in the temperature range, at which microvoid coales-

cence occurs only in the region of the crack initiation in a Charpy V-notch impact test, since press notch can cause work hardening in the limited region only.

It seems then that the absorbed energy at low temperatures as well as the FATT in A302C steels happened to be constant with excess Al in the case of press-notch impact tests under the conditions such as these compositions, heat treatments and plate dimensions.

However, it is still important to consider the effect of work hardening on the low-temperature toughness in the stress design and the failure analysis, since work hardening is occasionally applied to the whole section of practical steel by forming such as bending, rolling and pressing.

V. Conclusions

It is clearly shown in this study that the low-temperature toughness in A302C steels may be improved drastically by the elimination of excess Al. It is then rationalized that the influence of excess Al on low-temperature toughness in A302C steels is to change the microstructure from fine ferrite to coarse upper bainite through the raise of carbon activity in ferrite-phase by the introduction of excess Al.

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