BII-5

Precipitation-Strengthening and Toughening Effect of Aluminum Nitride on Low-Carbon Structural Steels

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Abstract

A very significant improvement in ductility and low-temperature notch toughness always characterizes the steels that are strengthened by aluminum nitride.

The extent and mechanism of precipitation-strengthening and toughening by aluminum nitride were examined for low-carbon steels and "pure" iron containing aluminum nitride ($A\ell N$) more than about 0.04%, or as nitrogen more than 0.015%.

It was estimated that the toughening effect of aluminum nitride is roughly 400° and 290° C per percent $A\ell N$ in terms of the 2 mm V-notch Charpy transition temperatures of vTr15 (15 ft-lb basis) or vTrS (50% shear fracture basis), respectively. While the strengthening due to aluminum nitride is roughly 100 kg/mm^2 per percent $A\ell N$ by yield point.

1. Introduction

With the advent of so-called aluminum killed steel, a considerable attention has been focused on the improved properties of the steels containing certain amount of aluminum nitride (1, 2). Since much of the improvement was found attributable to the aluminum nitride component, the principle was tried successfully with Thomas converter steel (3).

In the mean time, we at the Ishikawajima-Harima Research Institute have devised methods of raising the nitrogen content of molten steel from the Open-hearth, Electric Arc or LD Converter furnaces at will[2], and also

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[2] Thomas Converters have since some time disappeared from this country.

other pertinent methods in the steelmaking, such as teeming, rolling or heat treatment, for steels that are made to contain large amount of nitrogen and aluminum. A whole family of structural steels of excellent weldability have thus emerged to engross the tensile strength grades of 40, 50, 60, 80 and 100 kg/mm^2(1). Those are collectively called the I-N Steels (4), and being manufactured <u>en mass</u> by the hand of great steel manufacturers of the land under their own tradenames.

As the aluminum nitride steels finish always in finer grained than similarly compositioned (except the nitrogen-aluminum component) commercial steels for the same or equivalent thermal history, however, the effect of aluminum nitride <u>per se</u> in the improvement of the mechanical properties of the steel has remained ambiguous.

In the present paper, the role of aluminum nitride will be examined in the following properties:

(1) the notch toughness in terms of the transition temperatures in 2 mm V-notch Charpy testing;
(2) the elongational ductility, especially of "pure" iron and heat treated high-strength low-alloy steel; and
(3) the yield point of low-carbon steels in comparison with ordinary steels.

2. Precipitation of Aluminum Nitride

Fig. 1 presents some typical cases of precipitation of aluminum nitride in iron and low-carbon steels. In all the cases, the material was solution treated prior to the precipitation treatment.

Several features may be noted. Such as:
(1) contrary to the popularly held belief that aluminum nitride precipitates along the austenite grain boundary, no such trend is evident;
(2) no definite crystallographic precipitation habit is apparent between the aluminum nitride and the matrix, which may be a small wonder for cases (B), (C) and (D) for the matrix underwent transformation, but in the (A) the precipitation took place from ferrite;
(3) the morphology of aluminum nitride precipitates is different in iron from that in steel, <u>e.g.</u> it is triangular, trapezoid or hexagonal as to be expected from the crystalline structure ($P6_3mc$, wurtzite type) in the former, whereas it is rectangular in the latter, even while the X-ray or electron diffraction made on the extracts from either agree well enough with that given in the ASTM X-Ray Powder Data File; and
(4) the size and the distribution of aluminum nitride precipitates can be varied greatly according to the thermal or deformation history.

While some of those may be understood, some others, particularly the apparent lack of definite habit in precipitation, remain unsolved at the moment.

3. The Toughening Effect

Fig. 2 shows the impact transition temperature curves obtained by 2 mm V-notch Charpy specimens for two aluminum nitride steels (IN-4 and IN-15) and for a commercial open-hearth killed steel of ship hull plate grade (KL-1). All three steels were 1" thick, and heat treated under the identical condition in the laboratory (normalized at 930°C for one hour, and air cooled). Compositionwise, those three steels are quite alike except the nitrogen-aluminum component as may be seen in the figure, nevertheless it is seen that the aluminum nitride steels are markedly tougher than the commercial counterpart.

In order to isolate the contribution of the aluminum nitride effect to this marked reduction in the transition temperature, resort was made to the Boulger and Hansen's analysis method (5). In the work, the authors prepared a total of twenty-nine 500 lb induction-furnace heats of C-Mn type killed or semikilled steels and Si-Al type "Al-killed" steels. The 2 mm V-notch Charpy transition temperatures (vTr15 or the 15 ft-lb transsition temperature, vTrS or the 50% shear fracture (fibrous) transition temperature, and others) and the NRL nil-ductility transition temperatures were evaluated by means of statistical analysis technique as a function of the chemical constituents effect (C, Si, Mn and Al) and the grain size effect.

Two of the Boulger-Hansen's estimation formulae are transcribed below:

$$\begin{aligned} \mathrm{vTr15}\ (^\circ\mathrm{C}) = {} & 185\ \mathrm{C} - 37.0\ \mathrm{Mn} - 149\ \mathrm{Si} + 117\ \mathrm{Si}^2 + 64\ \mathrm{Si{\times}Mn} \\ & - 284\ \mathrm{Al} + 1583\ \mathrm{Al}^2 + 204\ \mathrm{Al{\times}Si} - 10.1\ \mathrm{GS} + 76 \\ & (\text{Standard deviation} = 9.4^\circ\mathrm{C}) \end{aligned}$$

$$\begin{aligned} \mathrm{vTrS}\ (^\circ\mathrm{C}) = {} & 244\ \mathrm{C} - 20.1\ \mathrm{Mn} - 143\ \mathrm{Si} + 137\ \mathrm{Si}^2 + 47\ \mathrm{Si{\times}Mn} \\ & - 208\ \mathrm{Al} + 623\ \mathrm{Al}^2 + 542\ \mathrm{Al{\times}Si} - 10.5\ \mathrm{GS} + 81 \\ & (\text{Standard deviation} = 10.2^\circ\mathrm{C}) \end{aligned}$$

1: first three I-N Steels, <u>i.e.</u> those of tensile strength up to 70 kg/mm^2, may be finished and offered as rolled, while the last two are heat treated.

where, all the chemical components are given in weight percent, Al is the "acid soluble" aluminum, and the GS is the ASTM ferrite grain size number.

Table 1 gives the comparison between five as-rolled aluminum nitride steels[1] (IN-1 to 5) and four of Boulger-Hansen's steels as representative of commercial mild steels (BH steels). In the Impact Properties column, the transition temperatures of vTr15 and vTrS are listed in terms of what was actually observed and as calculated (or what is to be expected) by the Boulger-Hansen formulae above.

It will be seen that the "ΔT", the difference between the observed and the calculated, are evenly dispersed on both the plus and minus sides for BH steels, while those of IN steels are all in the minus side. It will be further noted that the ΔT's for IN steels are about twice the standard deviation given, meaning that the substantial reduction in the transition temperature is real and not due to statistical fluctuations.

Inasmuch as the effects of chemical constituents as well as granular structure are accounted for not only individually but productively, one of the outstanding features of the Boulger-Hansen's analysis, the ΔT should be considered attributable to the remaining factor, i.e. the aluminum nitride component of the steel. Although no definite linear relationship is apparent between the ΔT and the chemically determined quantity of $A\ell N$ in weight percent, it can be shown by taking grand average that the reduction in vTr15 is approximately 400°C per percent $A\ell N$, while that in vTrS is approximately 290°C per percent $A\ell N$.[2]

4. The Enductilization Effect

A quick survey of Table 1 will show that the elongation of the aluminum nitride steels is noticeably greater than that of ordinary steels. One conspicuous phenomenon there is the fact that the yield point elongation is always pronounced in aluminum nitride steels, so much so that it is clearly discernible even in the heat treated low-alloy high-tensile strength steels, whereas it is almost entirely absent from ordinary steels with tensile strengths of above, say, 70 kg/cm^2.

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[1] I-N Steels manufactured by operational open-hearth furnaces; they satisfy all the requirements of Nihon Kaiji Kyokai's Class F, the non-normalization version of Class E.

[2] Since some of the BH steels might have contained as much as 0.012% $A\ell N$, the figure becomes roughly 515° and 375°C per percent $A\ell N$ for vTr15 and vTrS, respectively, if it is to be discounted.

Fig. 2 shows, as an illustration, the stress-strain diagram (engineering) of two high-strength steels, one an aluminum nitride type (IN-90) and the other a commercial steel (HT-90), both heat treated to the same tensile strength of approximately 90 kg/mm^2. Except for the nitrogen-aluminum component, which was 0.013% and 0.04% in the IN-90 and 0.002% and 0.03% for HT-90, respectively, the other alloying elements were almost identical. It will be seen that the aluminum nitride steel is more ductile and tougher than the non-$A\ell N$ counterpart, developing almost twice the working capacity of the latter.

A similar effect was also observed in "pure" iron. In the experiment, an electrolytic iron containing 0.003% carbon was remelted and teemed in vacuo, forged, rolled into 0.05 mm thick foil, and normalized. To a part of the melt, aluminum was added in vacuo, the ingot being similarly finished to the same gauge, then nitrogenized in an ammonia-hydrogen atmosphere. The N-Al iron (0.003% C, 0.016% N and 0.036% sol. Al) was then heat treated in two ways: one, it was heated to 1350°C for fifteen minutes and rapidly cooled so as to leave the nitrogen and aluminum separately in solid solution, two, succeeding the same solution treatment, it was reheated to 850°C for fifteen minutes so as to have substantially all the nitrogen precipitate as aluminum nitride. All the heating and cooling for N-Al iron was done in a hydrogen-nitrogen atmosphere (approximately 1 to 3 by flow rate), while that for the pure iron was dry hydrogen. The final grain size was approximately No. 5 by ASTM for pure iron and solution treated N-Al iron, and was 6 to 7 for precipitation treated variety.

Fig. 4 illustrates the change in elongational ductility of those three irons as measured for various tensile strain rates at liquid nitrogen temperature by the INSTRON tensile tester. It will be observed in the figure that the $A\ell N$ iron remained quite ductile even under the fastest loading rate employed, the fracture mode being perfectly regular in that the parallel portion of the specimen was completely traversed by Lueder's band before rupture which was accompanied by considerable "necking." Whereas the behavior of other specimens was just as expected, i.e. the pure iron is ductile only at a very low rate of deformation, and the solution treated N-Al iron is entirely brittle, probably on account of the free nitrogen. Although the contribution of grain size effect to this phenomenon is unknown, yet it was believed that the greatly improved ductility of the precipitation treated iron is due, at least partially, to the presence of aluminum nitride precipitates.

Finally, by the unusually great yield elongation of aluminum nitride steels, a good linear correlation was found to exist between the yield point elongation and the low-temperature toughness. Fig. 5 gives an example by a 0.11% C-0.021% N-0.076% Al steel, where it is shown that the energy transition temperature[1], vTrE, can be related reasonably well with the yield point elongation. Although the coefficient of correlation is still not very high, the relationship may be used as a working estimation of low-temperature toughness of the steel from simpler room temperature tensile test results. It is hoped also that this correlation will provide a link between the ductility at ambient temperatures and the notch toughness at low temperatures.

5. The Strengthening Effect

The strengthening effect of aluminum nitride was examined by cancelling the grain size effect by Petch's relation. Fig. 6 illustrates the relation between the lower yield point and the inverse square-root of mean grain diameter of two aluminum nitride steels in comparison with four mild steels due to Hahn et al. (6), Petch (7) and Sakui et al. (8), all determined at room temperature. In the figure, a part of the data due to Hahn et al. and to Petch, the part which is indicated by broken line, is the extrapolation based on the published results.

It will be seen that the slope of the curve, k, which is generally considered to present the measure of dislocation locking by interstitials, is markedly smaller for IN steels than for reference steels. Nevertheless, in the grain size range below ASTM 8 or thereabout, a strengthening may be noted in the aluminum nitride steels despite their lower carbon contents as compared to Hahn's and Sakui's steels, or their lower free introgen contents as compared to Petch's steel.

Further, the increment in the yield point per ASTM 1 can be read from the curves for IN-6 and IN-15 as to be 1.5 to 2 kg/mm^2. Entering into Table 1 with this knowledge and comparing IN-1, 2 and 5 to BH-4-AR, normalizing the lower yield point to that at ASTM 8, it can be shown that the apparent strengthening effect of aluminum nitride is roughly 100 kg/mm^2 per percent AℓN. With precipitated aluminum nitride of 0.05% a raise of some 5 kg/mm^2 should be observed (Table 1), and such strengthening has actually been obtained in aluminum nitride high-strength steels.

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[1] that temperature at which the energy absorbed by 2 mm V-notch Charpy test piece is the one-half of the maximum absorbed energy (100% shear), which agrees well with the vTrS, see Fig. 2.

6. Discussion of Results

While it is reasonably certain that aluminum nitride contribute greatly to toughen or enductilize the steel, and this effect can be understood, at least qualitatively, by postulating (not without some direct evidences though inconclusive as yet) that the aluminum nitride precipitates act as dislocation source so that there are always significantly more free running dislocations available in the deforming matrix, the effect of the same in strengthening category may need further examination.

For example, as dispersion hardener, the aluminum nitride particles seem to precipitate altogether too far apart to each other to offer any effective blockade for dislocation. In fact, reading the average inter-distance as 6μ from Fig. 1 (C) and (D), and from Orowan's equation (9), the expected increase in the yield point is calculated to be only 0.34 kg/mm^2, a value which is at least one order of magnitude smaller than the estimated contribution of aluminum nitride (the preceding section).

For another, the dispersion of the data points about the least square fit regression line in the grain size versus yield point relationship (Fig. 6) is markedly greater for aluminum nitride steels than it is in other published cases.

Those facts appear to suggest that neither the Petch's model nor the Orowan's would apply to the aluminum nitride steels without modification. It is evident then that more refined insight is needed, for which purpose a research program is in progress. It is hopefully expected that clearer picture of the role of aluminum nitride will be unveiled in due course.

7. Summary and Conclusions

The precipitation behavior of aluminum nitride was reviewed, and the role thereof in improving the properties of steel examined. It was seen:

(1) that the contribution of aluminum nitride to toughening and enductilization is farirly definite, which effect was estimated to be roughly 400°C and 290°C per percent aluminum nitride in terms of vTrl5 and vTrS, respectively;

(2) that a linear relationship holds reasonably well between the low-temperature notch toughness (Charpy V-notch transition temperature) and the room-temperature ductility (yield point elogation);

(3) that the strengthening effect is less certain, nevertheless it was estimated to be roughly 100 kg/mm^2 per percent aluminum nitride in the rise of yield point for grain size of about ASTM 8;

(4) that the aluminum nitride steel donot obey Petch's relation so well as other steels do, nor the strengthening mechanism thereof explained by Orowan's model of dispersion hardening; and

(5) that more insight and research are needed in the clarification of precipitation habits of aluminum nitride and its role in strengthening and toughening of steels.

8. Acknowledgement

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Table 1. Comparison of Aluminum Nitride Steels with Ordinary Low Carbon Killed Steels

STEEL (*1)	C %	Si %	Mn %	P %	S %	sol.Al %	N %	AℓN %	HEAT TREAT-MENT
	CHEMICAL COMPOSITION								
IN - 1	0.11	0.24	0.92	0.015	0.011	0.067	0.019	0.055	AR(*2)
IN - 2	0.11	0.27	1.00	0.013	0.014	0.050	0.015	0.034	AR
IN - 3	0.15	0.27	1.18	0.017	0.014	0.091	0.018	0.050	AR
IN - 4	0.13	0.27	1.43	0.016	0.011	0.116	0.018	0.054	AR
IN - 5	0.10	0.31	1.44	0.014	0.010	0.121	0.021	0.065	AR
							(*4)		(*3)
BH - 4	0.11	0.22	1.20	0.015	0.026	0.093	0.006	---	AR or N
BH -27	0.13	0.16	1.27	0.016	0.026	0.036	---	---	AR
BH - 3	0.20	0.26	1.31	0.016	0.024	0.038	0.006	---	AR or N
BH - 2	0.19	0.24	0.73	0.014	0.018	0.039	0.006	---	AR or N

STEEL	ASTM G.S. (*5)	TENSILE PROPERTIES			IMPACT PROPERTIES					
		YP kg/mm^2	TS kg/mm^2	EL(*6) %	vTr15, °C(*7) Obs.	Calc.	T	vTrS, °C(*7) Obs.	Calc.	T
IN - 1	9.1	31.4	45.7	40.9	-71	-53.2	-18	-53	-25.1	-18
IN - 2	9.4	29.5	51.2	43.8	-80	-59.6	-20	-48	-28.8	-19
IN - 3	9.1	37.1	52.0	39.0	-78	-50.9	-27	-21	-16.2	- 5
IN - 4	9.2	37.4	52.5	39.0	-76	-57.8	-18	-36	-22.3	-14
IN - 5	8.9	35.8	47.9	40.2	-80	-59.7	-20	-37	-17.7	-19
BH-4-AR	7.5	25.4	41.3	26.4	-47	-42.7	- 4	-11	-10.7	0
4-N	8.1				-37	-48.7	+12	+ 5	-17.0	+12
BH-27-AR	8.2	27.9	46.3	46.0	-57	-44.6	-12	0	-12.6	+13
BH-3-AR	9.4	30.0	50.3	24.7	-29	-45.9	+17	+21	- 9.2	+30
3-N	10.1				-63	-53.0	-10	-26	-16.6	- 9
BH-2-AR	8.0	25.5	45.1	28.4	-28	-21.4	- 7	+ 5	+ 8.0	- 3
2-N	9.3				-45	-34.4	-11	-15	- 5.7	- 9

*1:"IN" steels are N-Al type, while "BH" steels are due to Ref. 5; *2: AR stands for As-Rolled: *3: N stands for Normalization at 1600°F; *4: maximum of the range reported; *5: ASTM ferrite grain size number; *6: Gauge length is 50 mm for IN steels, 8 in. for BH-4, and 2 in. for BH-27, 3 and 2; *7: the standard deviation for the calculated values are 9.4°C and 10.2°C for vTr15 (15 ft-lb transition) and vTrS (50% shear fracture transition) temperatures as measured on 2 mm V notch Charpy, respectively.

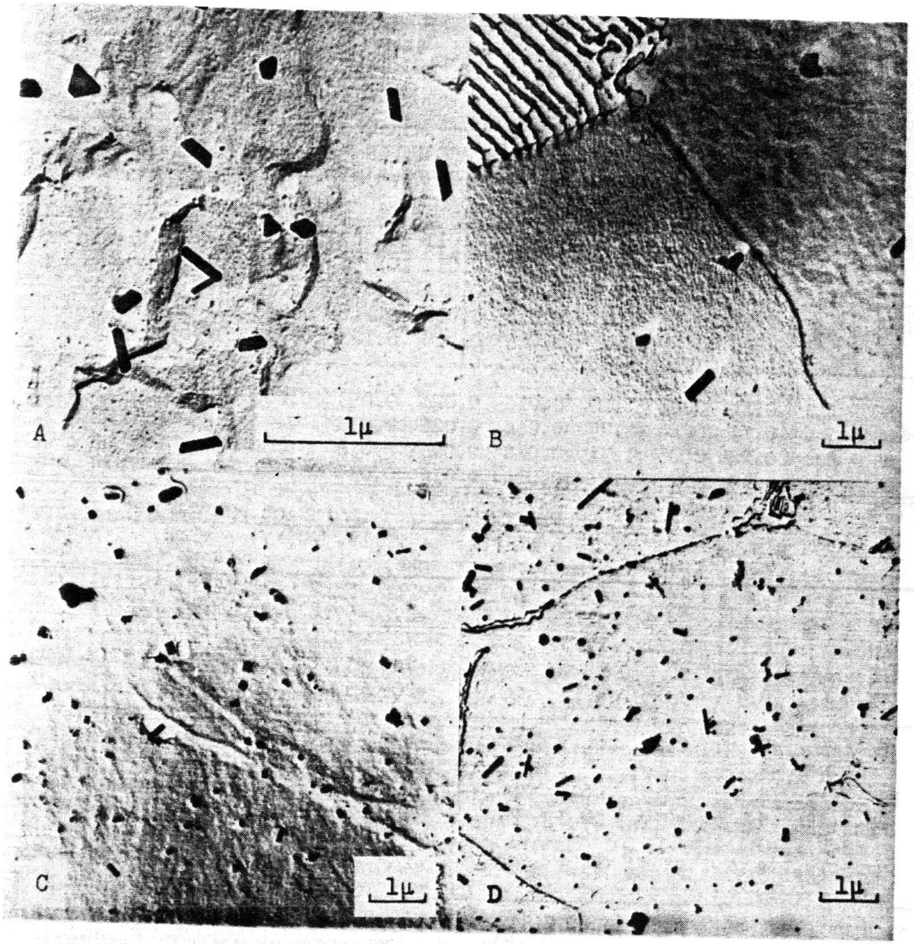


Fig. 1 Aluminum Nitride Precipitates in Iron and Mild Steels

(A) 0.003% C, 0.016% s. Al: 1350° C x 15 min., rapidly cooled, 850°C x 15 min., rapidly cooled.
(B) 0.17% C, 0.25% Si, 0.99% Mn, 0.019% N, 0.064% s. Al; as hot-rolled.
(C) 0.09% C, 0.21% Si, 0.80% Mn, 0.025% N, 0.100% s. Al; 930° C x 30 min., water-quench, tempered at 650° C x 1 h, air-cooled.
(D) 0.09% C, 0.18% Si, 0.79% Mn, 0.019% N, 0.062% s. Al; Modified quench-and-tempering treatment.

	C	Si	Mn	P	S	sol Al	N	AℓN	free N	$Aℓ_2O_3$
IN – 4	0.10	0.30	0.60	0.015	0.037	0.159	0.024	0.059	0.004	0.037
IN – 14	0.14	0.33	0.59	0.014	0.034	0.102	0.035	0.094	0.003	0.014
KL – 1	0.14	0.16	0.61	0.018	0.007	0.012	0.006	0.006	0.004	0.002

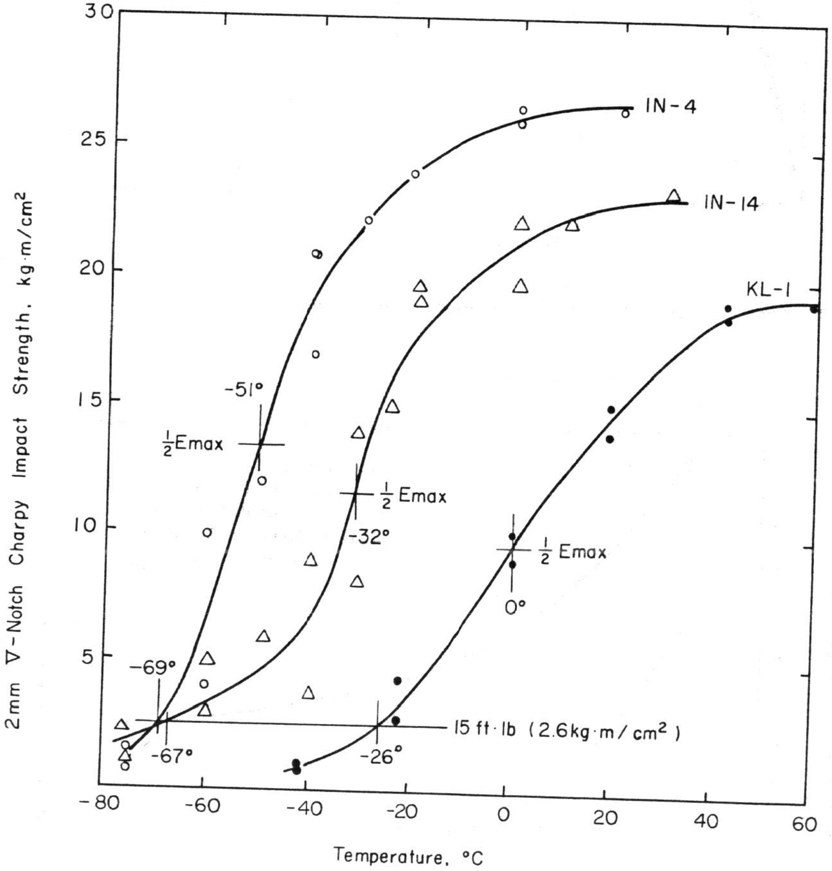


Fig.2 Impact Transition Curves of N-Al Steels and an Open-Hearth Killed Steel, All as Normalized (930° C x 1h, A.C.)

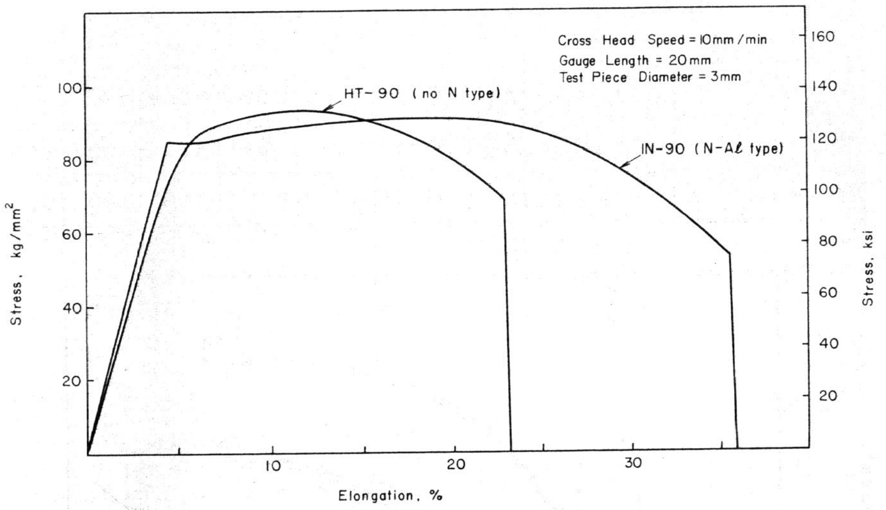


Fig. 3 Stress—Strain Diagrams for Heat Treated High-Tensile Strength Steels.

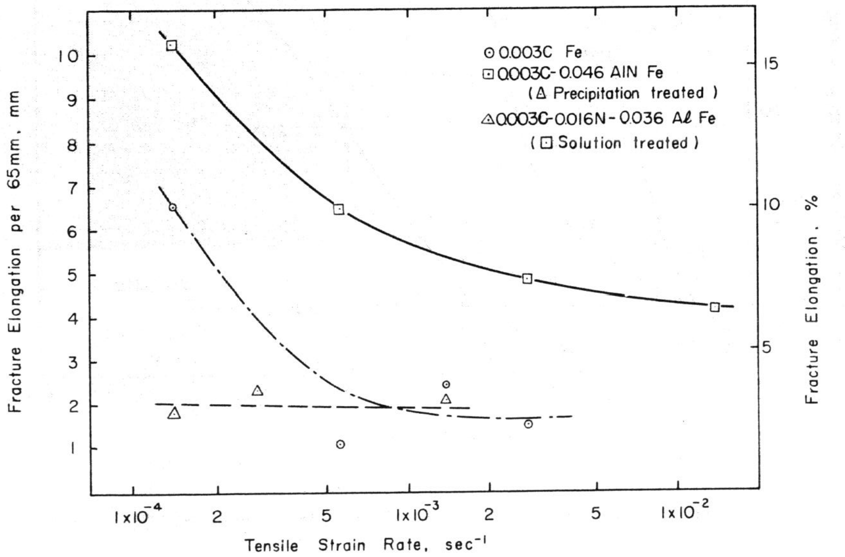
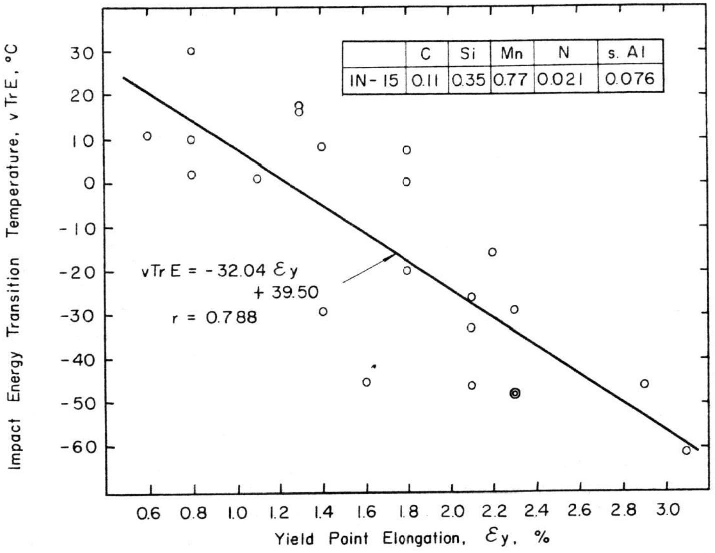


Fig. 4 Tensile Ductility of Various Irons at − 197°C

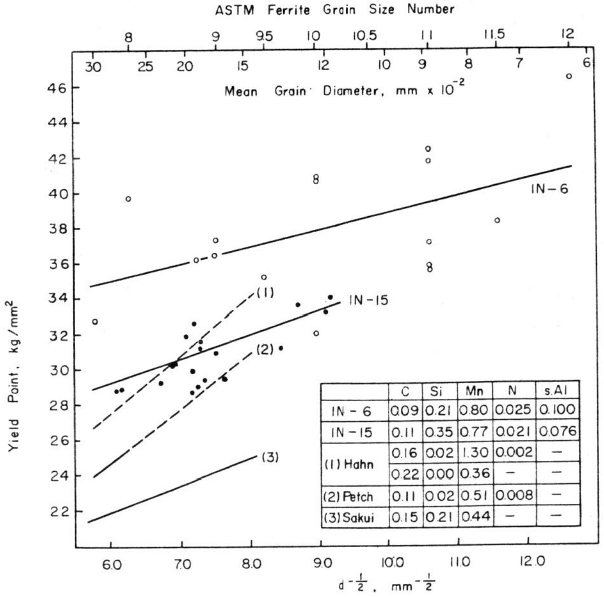


	C	Si	Mn	N	s. Al
IN-15	0.11	0.35	0.77	0.021	0.076

$$vTrE = -32.04\,\mathcal{E}y + 39.50$$

$$r = 0.788$$

Fig. 5 Correlation Between Room Temperature Tensile Ductility and Notch Toughness in an N-Al Steel



	C	Si	Mn	N	s.Al
IN - 6	0.09	0.21	0.80	0.025	0.100
IN - 15	0.11	0.35	0.77	0.021	0.076
(1) Hahn	0.16	0.02	1.30	0.002	—
	0.22	0.00	0.36	—	—
(2) Petch	0.11	0.02	0.51	0.008	—
(3) Sakui	0.15	0.21	0.44	—	—

Fig. 6 Grain Size Dependence of Yield Point of N-Aℓ Steel in Comparison with Mild Steels.