Effect of AlN Precipitation on Mechanical Properties of α -Iron*

By Tadashi ICHiyAMA,** Mahito KOIZUMI,** Ikushi YOSHIDA,** Kunio WATANABE,**
and Seiji NISHIUMI**

Synopsis

Two series of Fe-0.01, 0.03, and 0.1%Al alloys that contain 0.015%N and either 0.01 or 0.02%C were used to study the states of AlN precipitates and their effects on the yield point of α -iron. Results obtained were as follows.

(1) AlN precipitates the most in the temperature range between 800° and 900°C during isothermal after solution treatment.

(2) Carbon content affects the total amount, shape, size, and dispersion of AlN precipitates.

(3) Variation of yield point is well explained by the individual contributions of precipitated AlN and dissolved nitrogen.

Investigation on ductility and work hardening of extra low carbon Fe-Al-0.01%N alloys with aluminum contents varying from 0.005 to 1% led to the following conclusions.

(4) The behavior of dissolved nitrogen as revealed by internal friction suggests that the reversion of AlN precipitation occurs.

(5) In the same heat treatment that will cause the intergranular brittle fracture, ductility can be improved by fixing more nitrogen. In the ductile state, on the other hand, the contribution of AlN precipitates to ductility is the greater, the smaller their effect on hardening.

(6) Of the factors that influence work hardening the grain size is the main; nitrogen in solution or fine AlN particles increase the work hardening rate, whereas grown precipitates and quenched-in dislocations decrease it.

I. Introduction

AlN precipitation in steel as viewed in terms of its effects on mechanical properties of the steel has been one of the problems most intensively investigated.^{1),2)} The effects can be classified into two categories, namely the indirect effect of AlN precipitation through structural change of steel and the direct effects. Examples for the former are grain refinement of structural steels^{3),4)} and control of recrystallization texture of low carbon steel sheets by AlN precipitation.^{5),6)} To the latter effects belong lowering of ductility in cast steel at high temperature,^{7),8)} improvement of low-temperature toughness,^{1),5),9)} prevention of strain aging, and so forth.

Relatively few studies have, however, been reported on the effect of AlN precipitation itself. It is also known that the precipitation of AlN in steel is easily

affected by other impurity elements including carbon. One of the aims of the present work is to clarify the direct effect of AlN on the basic properties of α -iron. Dilute Fe-Al-N alloys were used for this purpose, and various states of AlN precipitation were obtained by selecting proper conditions of heat treatment.

Some information about AlN precipitation in α -iron and its relation to yield point of matrix was obtained in the first part of this study using two series of Fe-Al-N alloys that contain respectively 0.01 and 0.002% of carbon; the influence of AlN precipitation on ductility and work hardening of α -iron was investigated in the second part using the other series of specimens of extra low carbon Fe-Al-N alloys.

II. Effect of AlN Precipitation on Yield Point of α -Iron

1. Experimental

The base materials containing different amount of carbon and aluminum were furnished by melting electrolytic iron in vacuum furnace. Their chemical compositions are given in Table 1. The sheets 1 mm thick were prepared by forging, hot rolling, and surface grinding. About 0.015% nitrogen was added by heating specimens in 10% ammonia-hydrogen gas for 5 hours.

Figure 1 shows heat treatment diagram used to obtain various states of AlN precipitation. It was carried out in a vertical furnace equipped with two heating zones, in which specimens were hung from the top with tungsten wire. After solution treatment at 1350°C for 15 min in the higher temperature zone, specimens were quenched into the lower temperature zone kept at a predetermined temperature of between 600° and 1000°C, held isothermally for 30 min, and quenched into oil bath.

The amount and the dispersion of AlN precipitated by the above heat treatment were investigated respec-

Table 1. Chemical composition of material (wt%)

	C	Si	Mn	P	S	Sol. Al	Insol. Al	Sol. N	Insol. N	O
0.01 C-0.1 Al	0.014	0.005	<0.001	0.003	0.007	0.10	0.002	0.017	<0.001	0.009
0.01 C-0.03 Al	0.009	0.003	<0.001	0.003	0.007	0.029	0.002	0.015	<0.001	0.003
0.01 C-0.01 Al	0.012	0.002	<0.001	0.003	0.007	0.008	0.002	0.015	<0.001	0.004
0.002C-0.1 Al	<0.001	0.005	<0.001	0.003	0.003	0.092	0.003	0.012	<0.001	0.004
0.002C-0.03 Al	0.0014	0.006	<0.001	0.003	0.007	0.027	0.004	0.012	<0.001	0.003
0.002C-0.01 Al	0.0019	0.006	<0.001	0.002	0.005	0.010	0.004	0.010	<0.001	0.004

* Originally published in *Tetsu-to-Hagane*, **55** (1969), 1229, in Japanese. English version received March 19, 1970.

** Central Research Laboratories, Fuji Iron & Steel Co., Ltd. (present Nippon Steel Corp.), Fuchinobe, Sagamihara 229.

Fig. 1. Heat treatment diagram

tively by chemical analysis and extraction replica method of electron microscopy. Change of nitrogen in solution due to AlN precipitation was measured by internal friction. All the tensile tests, for Fe-Al-N alloys as well as the reference unnitrided Fe-Al alloys, were conducted at ambient temperature and at a crosshead speed of 2 mm/min with test pieces of 10 mm width, 50 mm parallel length, and 40 mm gauge length.

2. Precipitation Behavior of AlN

Figure 2 shows AlN precipitation curve obtained by chemical analysis. Precipitation is indicated here by the ratio of the nitrogen bound as AlN to the total acid soluble nitrogen. As the completeness of solution treatment was confirmed by both chemical analysis and electron microscopy, AlN precipitation can be considered to have occurred during the 30 min isothermal heat treatment. The peak of precipitation lies at a temperature between 800° and 900°C. The peak temperature is about 100°C higher than that of an earlier study,¹⁰⁾ which was also of isothermal precipitation of AlN in the cooling process after solution treatment. This is considered due to the difference of A_{r3} point, which depends on the chemical compositions of material.

As the amount of AlN that is precipitated during isothermal holding after solution treatment would be determined by the solubility of AlN and the diffusion rate of aluminum, it might be said that AlN precipitation has a peak at a temperature slightly below the γ - α transformation point where the differences in the solubility and the diffusion rate between in α and in γ would both serve favorably for precipitation of AlN.

Examples of electron-micrographs of each specimen are shown in Photos. 1 and 2. Both the large rod-like and the fine rectangular precipitates were identified as AlN. In order to count the number of precipitates according to their size, from 4 to 6 typical photographs were selected for each specimen. Table 2 shows the volume density, average size of particles, and average interparticle spacing which were calculated using the Ashby and Ebeling's method.¹¹⁾ Volume fraction of AlN was also estimated and compared with that obtained from chemical analysis. The agreement between them, however, was not very good because of the following facts: (1) the precipitates were apt to coagulate during the extraction by carbon replica method; (2) there was an error due to counting all particles smaller than 100 Å in as the particles of 100 Å class; (3) the particles counted in included

Fig. 2. AlN precipitation in Fe-0.01 and 0.002C-Al-N alloys

fine precipitates such as iron nitrides and oxides, especially in the specimens containing 0.01%Al; and (4) where Ashby's method was developed primarily for spherical particles, AlN was in various shapes that render uniform correction impossible.

Besides the causes mentioned above, there existed an analytical error due to filtering through of very fine precipitates, leading to an underestimation in the volume fraction determined by chemical analysis. This also makes the disagreement in the volume fractions as determined by two different methods even greater.

The following points were noticed in the data concerning AlN precipitation.

(1) The temperature at which AlN is precipitated the most does not coincide with that at which the surface density of precipitates are the largest, the latter temperature being generally lower (see Table 2).

(2) The higher the carbon content, the larger becomes the amount, size, and density of AlN precipitated in a given time (see Fig. 1 and Table 2). The cause is probably either the acceleration of AlN precipitation by the coexistence of solute carbon, which reduces the solubility of nitrogen or the precipitation of cementite so as to furnish more nucleation sites for AlN precipitation.

(3) The amount of carbon affects the morphology of precipitates also: many rod-like precipitates, which are typical for AlN, can be found in 0.01%C specimens, whereas many rectangular precipitates, whose aspect ratio is close to unity, are present in 0.002%C specimens (see (a), (b) of Photos. 1 and 2 respectively).

(4) Even when AlN precipitation has been reported as only trace in chemical analysis, particles of about 200 Å can be observed by electron microscope as many as $5 \times 10^8/\text{cm}^2$ (see Photo. 1 (n)).

The change of nitrogen in solid solution due to AlN precipitation was measured by internal friction. The amount of dissolved nitrogen, [N], and the nitrogen bound as AlN, N_{AlN} , are shown in Fig. 3 for specimens containing 0.03%Al and 0.01 or 0.002%C. It is noticed here that the total nitrogen defined as $[N] + N_{\text{AlN}}$ is smaller at 600°C than at 700° and 800°C.

Photo. 1. AlN precipitation in 0.01C-Fe-Al-0.015N alloys. (Carbon extraction replica)

(a)-(e) 0.01%Al, (f)-(j) 0.03%Al, (k)-(o) 0.01%Al. Precipitation treatment temperature (from upper to lower) 1 000°, 900°, 800°, 700°, and 600°C. (Scale—1 μ)

Two possibilities can be considered for this inconsistency in the total nitrogen: either AlN particles precipitated at 600°C were too small to be detected by chemical analysis or not all the nitrogen, except that bound as AlN, was measured by internal friction. If the first possibility is the case, as AlN precipitation shows the minimum at 700°C, it cannot be considered as a simple process controlled by diffusion of aluminum. This point will be discussed later in Chapter III together with the additional result about the behavior of dissolved nitrogen.

3. Influence on Mechanical Properties of α -Iron

It was generally observed that grain size of the

specimens investigated was finer when carbon and nitrogen contents were high and precipitation treatment temperature low except the 1 000°C treatment. Comparison is made here among materials with different contents of carbon (0.01 and 0.002%) and nitrogen (0.015 and 0.001%) at three different aluminum levels.

Yield points and uniform elongations of Fe-Al-0.015%N alloys are plotted against precipitation treatment temperature in Figs. 4 and 5. As regards the yield point, that of 0.01C specimens was 5 kg/mm² higher than 0.002C specimens; it was generally the highest for 1 000°C treatment probably because of the effect of quenching from γ -phase, and the lowest for

Photo. 2. AlN precipitation in 0.002C-Fe-Al-0.015N alloys. (Carbon extraction replica)

(a)-(c) 0.1%Al, (f)-(h) 0.03%Al, (k)-(o) 0.01%Al. Precipitation treatment temperature (from upper to lower) 1000°, 900°, 800°, 700°, and 600°C. (Scale-1 μ)

800° or 900°C treatment; below 800°C, it increased gradually with decreasing temperature. Any consistent tendency was not recognized for the dependence of yield point on aluminum content, hence on AlN amount. As no grain structure difference was observed between the specimens of different aluminum content if the carbon content was equal, the yield point difference among them seems to be mainly due to the precipitation states of AlN.

The treatment at 600° to 700°C lowered abruptly the uniform elongation of 0.002%C specimens, the

brittle fracture becoming pronounced. Since the effect of AlN precipitation on ductility of matrix iron is to be discussed more fully in Chapter III, it is remarked here that ductility peak is situated about at 800°C.

4. Effect of AlN Precipitation on Yield Point of α -Iron

It is worth trying whether the change of yield point in the present experiment can be correlated to various state of AlN precipitation.

Yield point of steel is, in general, given by¹²⁾

Table 2. Density, average size, average interparticle spacing, and volume fraction of precipitated AlN particles

Specimen	Precipitation treatment temperature (°C)	Number of measured particles	Surface density (10 ⁸ /cm ²)	Volume density (10 ⁴ /cm ³)	Average size of particle (Å)	Average interparticle spacing (μ)	Volume fraction of AlN (%)	Volume fraction from chemical analysis (%)
0.01 C 0.01 Al	1 000	287	0.69	0.25	923	1.43	0.435	0.061
	900	300	1.18	0.16	1 426	1.09	1.024	0.115
	800	2 477	15.40	7.22	274	0.30	0.326	0.108
	700	2 311	14.07	6.29	249	0.31	0.214	0.080
	600	1 435	9.53	6.12	208	0.38	0.121	0.034
0.01 C 0.03 Al	1 000	121	0.54	0.38	445	1.60	0.073	<0.007
	900	862	5.16	8.96	312	0.52	0.100	0.061
	800	491	3.41	1.72	379	0.64	0.206	0.060
	700	427	2.37	1.13	344	0.77	0.101	0.03
	600	630	4.23	2.91	222	0.57	0.070	0.01
0.01 C 0.01 Al	1 000	358	1.64	1.24	210	0.92	0.025	<0.007
	900	195	0.83	1.17	793	1.30	1.277	<0.007
	800	193	1.43	1.09	185	0.99	0.015	<0.007
	700	573	5.20	5.80	200	0.52	0.102	<0.007
	600	595	3.51	3.78	222	0.63	0.091	0.007
0.002 C 0.1 Al	1 000	290	1.32	2.26	218	1.03	0.051	0.033
	900	222	1.77	1.85	439	0.89	0.344	0.075
	800	608	3.95	4.17	336	0.59	0.347	0.053
	700	560	3.86	1.44	456	0.60	0.301	0.083
	600	317	0.62	0.27	376	1.50	0.032	0.051
0.002 C 0.03 Al	1 000	961	7.80	19.56	140	0.42	0.117	<0.007
	900	326	2.42	8.37	246	0.76	0.274	0.041
	800	252	1.40	2.16	233	1.00	0.060	0.013
	700	839	8.26	6.78	204	0.41	0.126	<0.007
	600	103	0.63	0.83	307	1.49	0.053	<0.007
0.002 C 0.01 Al	1 000	1 000	3.04	44.91	213	0.68	0.960	<0.007
	900	830	5.46	11.44	267	0.50	0.480	<0.007
	800	497	4.12	2.94	191	0.58	0.045	<0.007
	700	412	2.68	3.95	230	0.72	0.105	<0.007
	600	274	1.36	1.51	192	1.01	0.023	<0.007

Fig. 3. Change of nitrogen-in-solution as measured by internal friction

$$\sigma_y = \sigma^*(T, \dot{\epsilon}) + \sigma_{\mu} + k_y d^{-1/2} \dots \dots \dots (1)$$

where $\sigma^*(T, \dot{\epsilon})$ is the term dependent on temperature and strain rate, and considered to be constant in this experiment; the second and third terms represent respectively the effect of impurity, namely precipitation and solid solution strengthening, and the grain size dependence of yield point. For the convenience of calculation, Eq. (1) is rewritten as

$$\sigma_y = \sigma_o + \Delta\sigma_p + \Delta\sigma_s + k_y d^{-1/2} \dots \dots \dots (2)$$

where σ_o is the sum of the first term and that part of the second term which is due to carbon contribution. Furthermore, the rest of the second term is divided into two terms: the contribution of precipitation strengthening of AlN $\Delta\sigma_p$, and that of solute nitrogen strengthening $\Delta\sigma_s$.

The two terms are given by

$$\Delta\sigma_p = \alpha \mu b / \lambda \dots \dots \dots (3)$$

$$\Delta\sigma_s = \beta c_N \dots \dots \dots (4)$$

Fig. 4. Yield points of Fe-Al-N alloys

Fig. 5. Uniform elongations of Fe-Al-N alloys

where α and β are proportional coefficients; μ and b are respectively the shear modulus and Burgers vector of α -iron.

The yield point can be calculated from Eqs. (2), (3), and (4) with experimentally determined values for three parameters, that is, the mean grain diameter d , the average interparticle spacing A , and the solute nitrogen concentration c_N . It is necessary for calculation, however, to know the values of σ_0 , k_y , α , and β beforehand. Firstly, σ_0 and k_y can be determined by yield point and grain diameter of materials with no nitrogen addition ($\approx 0.001\%$), whose yield point is expressed by Eq. (2) without the second and third terms, or by Petch's relation, where $\sigma_0 = 9.76 \text{ kg/mm}^2$,

$k_y = 0.98 \text{ kg/mm}^{3/2}$ for the 0.01C specimen, and $\sigma_0 = 5.18 \text{ kg/mm}^2$, $k_y = 1.08 \text{ kg/mm}^{3/2}$ for the 0.002C specimen. Furthermore, 0.5 is taken for α , and $1.83 \times 10^2 \text{ kg/mm}^2 \cdot \text{wt}\% \text{N}$ is used from the data of Heslop and Petch¹³⁾ for β .

Values of d , A , c_N , and the both yield points obtained by calculation and experiment are shown in Table 3. The c_N is obtained here by subtracting the nitrogen as AlN from the acid soluble nitrogen. Correlation between calculated and experimental yield point is shown in Fig. 6. This result may be considered as fairly good in view of those various suppositions and experimental errors.

Each contribution of AlN precipitation and dissolved nitrogen to the yield point was calculated and plotted in Fig. 7 versus precipitation treatment temperature. It will be observed in the result that, in regard to the increment of yield point due to aluminum and nitrogen addition, precipitation contribution is dominant in 0.1 Al specimens, whereas effect of dissolved nitrogen becomes more important for 0.01Al specimens.

If the absolute values of strengthening by aluminum and nitrogen are compared among them, it will be seen in Table 3 that they depend greatly on the extent of dispersion of AlN; for example, 0.01C-0.01Al specimen is strengthened the most by AlN dispersion, but there is only a small effect for 0.002C-0.1Al specimen owing to a poor dispersion of particles.

Lastly, it is easily recognized from above data that, given a same amount of nitrogen as solute or as AlN precipitates, very finely dispersed states of AlN are required to achieve greater strengthening effect than that due to solute nitrogen; for example 0.01% solute nitrogen has nearly same strengthening effect as the dispersed states of AlN particles of about 120 Å, which are apart 0.5 μ from each other.

III. Effect of AlN Precipitation on Ductility and Work Hardening of α -Iron

1. Experimental

Chemical compositions of materials before heat treatment are shown in Table 4. Preparation and heat treatment of specimens were same as the previous experiment, except the following points. Carbon content is fixed at one level, namely 0.001%, and seven melts with the aluminum content varying from 0.005 to 1% were used. Nitrogen was added in molten steel, and a material with no addition of aluminum and nitrogen was also prepared as the reference. As regards heat treatment, seven isothermal holding temperatures were chosen at an interval of 50°C between 550° and 850°C to investigate the precipitation behavior of AlN and the corresponding changes of mechanical properties of α -iron in more detail. An attention should be paid to the specimens of 0.5 and 1 Al for which solution treatment for AlN cannot be complete. Nevertheless, if there is some change of mechanical properties owing to different heat treatment after solution treatment with these two specimens, the cause must be attributed to the reprecipitation of

Table 3. Calculation of yield point according to Eq. (2)

Specimen	Precipitation treatment temperature (°C)	Mean grain diameter <i>d</i> (mm)	Average interparticle spacing <i>A</i> (μ)	Solute N conc. <i>c_N</i> (%)	$\sigma_0 + k_y d^{-1/2}$ (kg/mm ²)	$\Delta\sigma_p$ (kg/mm ²)	$\Delta\sigma_s$ (kg/mm ²)	Calculated Y.P. σ_{calc} (kg/mm ²)	Experimental Y.P. σ_{exp} (kg/mm ²)	$\frac{\Delta\sigma_p}{\sigma_{calc}}$ (%)	$\frac{\Delta\sigma_s}{\sigma_{calc}}$ (%)
0.01 C 0.1 Al	900	0.70	1.09	0	10.93	0.89	0	11.82	13.0	7.5	0
	800	0.54	0.30	0.001	11.15	3.24	0.18	14.57	15.0	22.2	1.2
	700	0.19	0.31	0.005	11.98	3.13	0.91	16.02	14.9	19.5	5.7
	600	0.35	0.38	0.011	11.41	2.55	2.01	15.97	14.7	16.0	12.6
0.01 C 0.03 Al	900	0.48	0.52	0.005	11.16	1.86	0.91	13.93	10.5	13.3	6.5
	800	0.39	0.64	0.005	11.31	1.52	0.91	13.74	11.9	11.1	6.6
	700	0.28	0.77	0.010	11.61	1.26	1.83	14.70	13.1	8.6	12.4
	600	0.44	0.57	0.013	11.23	1.70	2.38	15.31	13.3	11.1	15.5
0.01 C 0.01 Al	900	0.39	1.30	0.014	11.32	0.75	2.56	14.63	13.6	5.1	17.5
	800	0.28	0.99	0.014	11.59	0.98	2.56	15.13	14.8	6.5	16.9
	700	0.40	0.52	0.014	11.29	1.87	2.56	15.72	15.2	11.9	16.3
	600	0.42	0.63	0.013	11.26	1.54	2.38	15.18	15.3	10.1	15.7
0.002 C 0.1 Al	900	0.56	0.89	0.002	6.60	1.09	0.36	8.05	7.6	13.5	4.5
	800	0.63	0.59	0	6.52	1.64	0	8.16	7.0	20.1	0
	700	0.39	0.60	0.003	6.88	1.62	0.55	9.05	9.0	17.9	6.1
	600	0.58	1.50	0.003	6.56	0.65	0.55	7.76	10.0	8.4	7.1
0.002 C 0.3 Al	900	0.56	0.76	0.005	6.50	1.28	0.91	8.69	8.3	14.7	10.5
	800	0.35	1.00	0.006	6.41	0.97	1.10	8.84	9.7	11.4	13.0
	700	0.45	0.41	0.009	6.61	2.37	1.65	10.63	11.1	22.3	15.5
	600	0.62	1.49	0.008	6.47	0.65	1.46	8.58	10.1	7.6	17.6
0.002 C 0.01 Al	900	0.35	0.50	0.011	6.36	1.94	2.02	10.32	11.5	18.8	19.5
	800	0.45	0.58	0.009	6.76	1.68	1.65	10.09	9.4	16.7	16.4
	700	0.55	0.72	0.012	6.61	1.35	2.20	10.16	11.7	13.3	21.6
	600	0.62	1.01	0.009	6.53	0.96	1.65	9.14	11.0	10.5	18.1

Fig. 6. Correlation of AlN precipitation and dissolved nitrogen to the yield points

Fig. 7. Contributions of AlN precipitates and dissolved nitrogen to the yield point

Table 4. Chemical composition of specimens (wt%)

Specimen	C	Si	Mn	P	S	Sol. Al	Insol. Al	Sol. N	Insol. N	O
R	<0.001	0.006	<0.001	0.002	0.004	0.003	0.005	0.002	<0.001	0.005
0.005 Al	0.001	0.002	<0.001	0.002	0.004	0.004	0.001	0.016	<0.001	0.009
0.01 Al	0.001	0.007	<0.001	0.002	0.004	0.009	0.002	0.015	<0.001	0.003
0.03 Al	<0.001	0.004	<0.001	0.002	0.004	0.03	0.001	0.018	<0.001	0.003
0.06 Al	<0.001	0.003	<0.001	0.002	0.004	0.065	0.003	0.017	<0.001	0.004
0.1 Al	0.001	0.004	<0.001	0.002	0.004	0.09	0.003	0.014	<0.001	0.004
0.5 Al	<0.001	0.007	0.001	0.002	0.004	0.42	0.002	0.006	0.008	0.004
1 Al	<0.001	0.006	<0.001	0.002	0.004	0.98	0.002	0.007	0.010	0.003

that AlN which was dissolved during solution treatment, and not to those precipitates which were left undissolved, because the effect of the latter can be considered equal for the each precipitation treatment.

Amount of precipitated AlN, grain structure, and tensile properties were examined of each specimen. Change in dissolved nitrogen caused by AlN precipitation was determined by internal friction measurement for 0.1 Al specimen. Dislocation structures after tensile deformation of 1, 5, and 10 to 15%, together with that of as quenched state, were examined in an electron microscope for 0.01, 0.1, and 0.5 Al specimens subjected to precipitation treatment at 650° and 800°C.

2. AlN Precipitation in α -Iron

Amount of AlN precipitation of specimens is plotted against precipitation treatment temperature in Fig. 8. A point that deserves a notice is that minimum of precipitation was found in 0.1 Al specimen at 650°C. This was confirmed by the repeated experiment. Figure 9 shows the corresponding change of nitrogen in solution obtained from the data of internal friction. Amount of solute nitrogen becomes the largest at the temperature of precipitation minimum. Similar phenomenon was observed in Section 3 of the last chapter, where no precipitation minimum was detected. The situation, however, is that the precipitation minimum appears, in fact, at the temperature about 650°C for a specimen, thence it would be reasonable to assume the abnormality of AlN precipitation, namely, the AlN particles precipitated at 600°C would have been too small for chemical analysis, as the cause of increased solute nitrogen at a specified temperature.

As long as a simple thermally activated process based on aluminium diffusion in α -iron is assumed, no adequate explanation can be given for the fact that AlN precipitation shows minimum at certain temperature, as AlN should then precipitate more with increasing temperature. An alternative possibility would be either (1) AlN with different rate of precipitation or other nitride such as iron nitride precipitate at temperature lower than the specified temperature, in the latter case, however, only the peak of solute nitrogen can be explained, or (2) reversion of AlN precipitated after solution treatment takes place.

Fig. 8. AlN precipitation in Fe-0.001C-0.01N-Al alloys

Fig. 9. Change of dissolved nitrogen in relation to AlN precipitation in Fe-0.1Al-0.01N alloy

Concerning the first possibility, neither morphological change of AlN precipitation nor precipitation of other nitride was found by electron-microscopic examination in specimens that were heat treated at temperatures above or below the precipitation minimum. As to the second possibility, it has been reported that AlN precipitated at ordinary hot rolling temperatures dissolves at temperatures as low as

500°C.¹⁴⁾ If this were the case, the AlN that had already been dissolved would begin to reprecipitate at temperature above 650°C, while the remainder AlN was still in the course of reversion below 650°C, then there would appear a minimum, and this temperature would correspond to that at which the reversion of AlN has just completed. Although the above interpretation needs to be justified by pursuing the chronological change of AlN precipitation at a constant temperature, it would be a very probable explanation for the phenomenon.

For 0.5 and 1 Al specimens, as no internal friction measurement was done, the situation is not so certain,

but that the amount of AlN precipitated at 650°C was a little less than those at other temperature in the 0.5 Al specimen is probably of the same case, and in the 1 Al specimen AlN should have been reprecipitated almost completely. Precipitation of AlN was trace for all treatment temperatures in specimens with aluminum content less than 0.01%, but very fine precipitates were present as observed in Photo. 3.

3. Effect on Ductility of α -Iron

AlN precipitation influences on ductility of α -iron by threefold way: through fixing of solute nitrogen, change of grain structure, and the direct effects of

Photo. 3. Deformation microstructure of Fe-Al-N alloys

0.01Al specimen precipitation treated at 800°C;

(a) As quenched and

(b) Strained 4.8%.

0.1Al specimen precipitation treated at 800°C;

(c) As quenched and

(d) Strained 4.8%.

0.5Al specimen precipitation treated at 800°C;

(e) As quenched and

(f) Strained 4.8%. (Scale—1 μ)

precipitates. The first two effects have been well noted for commercial aluminum killed steel, and as regards the third effect it was also suggested by Ujjiye¹⁵⁾ that that AlN which acts as generator of dislocations contributes to the ductility. In this study, these points will be considered for pure Fe-Al-N alloys.

Change of total elongation according to various heat treatment temperatures is shown against sol. aluminum contents in Fig. 10. The best ductility is obtained for the heat treatment at 800° and 850°C and the aluminum content range between 0.03 and 0.1%. Intergranular brittle fracture, which is the cause of this abnormally low ductility, occurs in the range of aluminum content and precipitation temperature indicated in Fig. 10. It matters much to the ductility of α -iron how the different types of fracture occur; for example, ductility of 0.5 Al and 1 Al specimens, which are not brittle for any treatment, shows relatively small dependence on the treatment temperature.

It should be noticed that ductility of extra low carbon Fe-Al-N alloys depends on both the aluminum content and the heat treatment temperature. As specimens containing 0.01%C are not brittle under the same condition (Fig. 5), the brittle fracture of extra low carbon specimens (0.001%C) could be considered as belonging to the same phenomenon that is known for steels whose carbon is below a certain level.¹⁶⁾ Specimens containing more than 0.5% Al are not brittle, and the transition heat treatment temperature at which the type of fracture changes from brittle to ductile becomes lower as aluminum content increases, while that of the reference material *R* is lower than 700°C. It is concluded from those facts that the brittle fracture characteristics for extra low carbon specimens is closely related to the presence of nitrogen in solution, but the brittle fracture occurs only when the heat treatment is conducted at the temperature in a restricted range. This fact was already pointed out by Hopkins *et al.*,⁷⁾ who suggested the grain boundary segregation of nitrogen to be its cause, although the mechanism of brittle fracture by the presence of solute nitrogen was left unclarified.

Grain size, which is also an important factor to influence ductility, varies much according to material and treatment temperature. Abnormal grain coarsening was seen in specimens *R*, 0.5 Al, and 1 Al; specimens 0.005 to 0.1 Al, on the other hand, had relatively fine grains. No definite tendency exists between the total elongation and the grain size, but it may be said that the specimens whose total elongation is higher than 30% belong to the group of smaller grain size, whereas specimens of very large grain size show relatively low elongation because the blocking effect of grain boundary on crack propagation would be small.

From the relation between AlN precipitation and total elongation shown in Fig. 11, it is seen that elongation becomes larger as the dissolved nitrogen becomes smaller by the virtue of the AlN precipitation, and the highest elongation is obtained in the high treatment temperature range, that is, 800° to 850°C. The precipitation state most favorable to improve

Fig. 10. Total elongation of Fe-0.001C-0.01N-Al alloys

Fig. 11. Effect of AlN precipitation on total elongation

ductility might thus be the one that (1) interacts little with dislocation—namely its precipitation strengthening is small—and (2) can be the source of dislocation multiplication (*cf.* Section 4).

Yield point and work hardening of very ductile specimens were in fact low, and cell structure was not formed up to fairly large strain. The ductility of specimens 0.005 to 0.01 Al was poor because solute nitrogen and fine precipitates interact strongly with

dislocations, making thereby the initial work hardening great. Both coarse grain structure and strong hardening by many precipitates and inclusions were the cause of low ductility of 0.5 Al and 1 Al specimens.

4. Effect on Work Hardening of α -Iron

Work hardening rates of the alloys at 5, 10, and 15% strain are plotted *versus* sol. Al content in Fig. 12. It is characteristic of work hardening that the treatment temperature dependence is rather small in all specimens, and there is no influence of the fracture type. Work hardening rate reaches a maximum for 0.01 Al specimen and decreases gradually with increasing aluminum content. It is a well-known fact that the work hardening of polycrystalline metal depends on its grain size.¹⁸⁾ Work hardening rates showed actually a linear dependence on $d^{-1/2}$, analogous to Petch's relation for yield point, at the initial stage of deformation as seen in Fig. 13. The grain size dependence of work hardening, however, became smaller, the more the material deformed. This indicates that as the deformation proceeds the difference that existed among those structures before deformation disappears gradually, tending to be smaller at later stage of deformation.

The state of AlN precipitation, density, and arrangement of dislocation are also the factors attributable to the undeformed specimens besides their macroscopic grain sizes. The specimens that exhibit different work hardening features were chosen for investigation by transmission electron microscopy of the changes of dislocation structure accompanying the deformation and of the contribution of each factor to work hardening. Some examples of electron-

micrographs are shown in Photo. 3. Dislocation density was measured for each specimen at different deformation stages in 10 photographs. The following points were observed in Fig. 14: in the 0.1 Al specimen the dislocation density was relatively low before deformation, but increased rapidly up to 5% strain,

Fig. 12. Work hardening rates of Fe-0.001C-0.01N-Al alloys

Fig. 13. Relation between work hardening rate and grain size

Fig. 14. Change of dislocation density during plastic deformation

whereas for 0.5 Al specimen, whose density was high even in the as quenched state, it increased very slowly at the initial stage of deformation.

Nextly, an evaluation was made on the factors that influence the work hardening on the basis of experimental data. It has been ascertained by many experiments that for bcc metals the following relation holds between flow stress and dislocation density

$$\sigma = A + B \sqrt{\rho} \dots\dots\dots(5)$$

where *A* and *B* are constants.¹⁹⁾

The flow stress, which is obtained experimentally, is plotted against square root of dislocation density in Fig. 15. Work hardening rate is given from Eq. (5) as

$$\frac{d\sigma}{d\varepsilon} = 1.15B \sqrt{\rho} \frac{d(\log_{10} \rho)}{d\varepsilon} \dots\dots\dots(6)$$

If *B* is interpreted as a coefficient representing interaction between dislocations, the work hardening rate can be expressed as a product of the strength of interaction, the inverse of mean free path (= $\sqrt{\rho}$), and the multiplication rate of dislocations.

Comparison of the work hardening rate, calculated from Eq. (6) by substituting the experimental values of *B*, ρ , and $d(\log_{10} \rho)/d\varepsilon$, with that obtained from tensile tests is given in Table 5 for specimens of 800°C treatment as strained by 0.8 and 4.8%. The work hardening rate at 4.8% strain is large in specimen 0.01 Al, mainly because of the contribution of strong interaction between dislocations, and for 0.1 Al specimen on account of large increasing rate of dislocation rate. Specimen 0.5 Al was of small work hardening at 4.8% because dislocation multiplication had become difficult owing to its high dislocation density.

If the materials were subjected to further deformation, cell structure would form and dislocation density would begin to saturate. Therefore, any difference of work hardening characteristics of specimens that existed initially should diminish as deformation proceeds.

It can be concluded from the results that the most important factor that influences the work hardening of

polycrystal iron is the grain size for grain boundary acts both as the multiplication source of dislocation and as the obstacles against their motion. As regards the effects of precipitation phase on work hardening, fine precipitates interact strongly with dislocations and accelerate cell formation; those precipitates with appropriate size, say, 1 000 to 3 000 Å, on the contrary, offer small resistance to dislocation motion, and so the cell formation is much delayed.

IV. Conclusion

The investigation about the effect of AlN precipitation on mechanical properties of α -iron can be summarized as follows.

With two series of Fe-Al-N alloys containing 0.01 or 0.002% carbon and subjected to isothermal heat

Fig. 15. Relation between flow stress and dislocation density

Table 5. Comparison between calculated and experimental work hardening rates

		<i>B</i> (10 ⁻⁴ cm• kg/mm ²)	$\sqrt{\rho}$ (10 ⁻⁴ cm ⁻¹)	<i>d</i> (log ₁₀ ρ)/ <i>dε</i>	<i>dσ/dε</i>		<i>d</i> ⁻¹ (mm ⁻¹)
					Value obtained from dislocation density and its increasing rate (10 ² kg/mm ²)	Value from tensile tests (10 ² kg/mm ²)	
$\varepsilon=0.8\%$	0.01Al 800°C	5.2	3.8	8	1.8	1.8	3.6
	0.1Al 800°C	4	2.6	17	2.0	2.0	2.0
	0.5Al 800°C	6.8	4.5	5.3	1.9	1.8	0.7
$\varepsilon=4.8\%$	0.01Al 800°C	9.4	4.4	2.6	1.2	1.5	3.6
	0.1Al 800°C	5.2	3.3	5.1	1.0	1.2	2.0
	0.5Al 800°C	6.2	5.3	2.5	0.9	1.0	0.7

treatment at 600° to 1 000°C after solution treatment:

(1) The peak of AlN precipitation lies in the temperature range between 800° and 900°C. The peak temperature is affected by chemical composition.

(2) The difference is recognized of total amount, shape, size, and dispersion of AlN precipitation by the difference of carbon content.

(3) Yield point and ductility of α -iron change considerably according to various states of AlN precipitation.

(4) Yield point of Fe-Al-N alloys is well explained by taking account of the contributions of both precipitation and solute nitrogen strengthening.

With another series of specimens containing 0.005 to 1%Al and heat treated at 550° to 850°C:

(5) Behavior of AlN precipitation and the corresponding change of dissolved nitrogen in α -iron at around 650°C strongly suggest that the reversion of AlN takes place.

(6) Among the specimens that are subjected to heat treatments not inducing the intergranular brittle fracture, the ductility is improved by precipitating out AlN of such sizes that the strengthening effect is small.

(7) The brittle fracture that is characteristic of extra low carbon materials is closely related to the state of dissolved nitrogen, and it does not appear in the specimens containing more than 0.5% of aluminum.

(8) AlN precipitation has only a secondary effect on work hardening, which depends strongly on grain size. Dissolved nitrogen and fine precipitates increase work hardening rate, but grown AlN has small contribution to it. The dislocation density before deformation also has some effect on the work hardening.

Acknowledgment

The authors wish to thank Dr. Shōzō Watanabe, the Director of Central Research Laboratories of Fuji Iron & Steel Co., Ltd., for permission to publish this paper. The acknowledgments are also due to Dr. Takashi Furukawa for helpful discussions and Mr. Toshihiro Nakada for cooperation in experiment.

REFERENCES

- 1) N. Ujjiye: *Bull. Japan Inst. Metals*, **5** (1966), 17.
- 2) M. P. Sidey: *Iron Steel* (U.K.), (1967), 168 and 269.
- 3) K. Born and W. Koch: *Stahl u. Eisen*, **72** (1952), 1268.
- 4) K. J. Irvine, F. B. Pickering, and T. Gladman: *J. Iron Steel Inst.*, **205** (1967), 161.
- 5) W. Jolley: *J. Iron Steel Inst.*, **205** (1967), 321.
- 6) I. J. Michalak and R. D. Schoone: *Trans. AIME.*, **242** (1968), 1149.
- 7) S. Hasebe: *Tetsu-to-Hagané*, **48** (1962), 761.
- 8) S. Hasebe: *Tetsu-to-Hagané*, **48** (1962), 1575.
- 9) J. A. Rinebolt and W. J. Harris: *Trans. Amer. Soc. Metals*, **43** (1951), 1175.
- 10) H. Nakamura and M. Fukagawa: *Zairyo Kagaku*, **2** (1965), 30.
- 11) M. F. Ashby and R. Ebeling: *Trans. AIME*, **236** (1966), 1396.
- 12) H. Conrad: *Iron and Its Dilute Solid Solution*, (1961), 315, Interscience, N. Y.
- 13) J. Heslop and N. J. Petch: *Phil. Mag.*, **1** (1956), 866.
- 14) F. A. Hultgren: *Blast Furn. Steel Pl.*, **56** (1968), 149.
- 15) N. Ujjiye: *Trans. ISIJ*, **7** (1967), 278.
- 16) N. P. Allen, W. P. Rees, B. E. Hopkins, and H. R. Tipler: *J. Iron Steel Inst.*, **174** (1953), 108.
- 17) B. E. Hopkins and H. R. Tipler: *J. Iron Steel Inst.*, **177** (1954), 110.
- 18) B. Jaoul: *Étude de la Plasticité et Application aux Métaux*, (1954), 451, Dunod, Paris.
- 19) A. S. Keh: *Direct Observation of Imperfections in Crystals*, (1963), 213, Interscience, N.Y.; *Phil. Mag.*: **12** (1965), 9.