Fracture Characteristics of 475°C Embrittled 30%Cr Ferritic Stainless Steels*

By Takashi YASUNAKA** and Masao KANAO**

Synopsis

The fracture behavior of 30%Cr ferritic stainless steels subjected to 475°C embrittlement has been studied by means of tensile testing, hardness measurement, acoustic emission technique, and optical and electron microscopies. It has been found that intergranular microcracks are initiated when yield stress increases with aging over the initial twinning stress detected on the stress-strain curve. The unstable fracture occurs with cleavage crack propagation when the criterion for the propagation of these cracks is satisfied. The critical yield stress for the ductile-brittle transition is slightly higher than the initial twinning stress, which varies linearly with the reciprocal square root of grain diameters and is insensitive to the aging temperature. For specimens with coarse grain sizes which have low initial twinning stress, the embrittling time is much affected by the hardening behavior in the early stages of aging. It is suggested that the intrinsic cause of the 475°C embrittlement is due to the planar slip which leads to easiness of cleavage crack formation.

I. Introduction

High-chromium ferritic stainless steels with excellent resistance to stress corrosion cracking in the presence of chloride ions are subjected to severe embrittlement, known as the 475°C embrittlement when the steels are aged in the temperature range of 400° to 540°C. This embrittlement restricts the potential applications of these kinds of steels.

It is now well-accepted that this phenomenon is related to the precipitation of the Cr-rich α' phase on account of a miscibility gap.¹⁻⁶⁾ The direct cause of the embrittlement has been attributed to the formation of deformation twin,^{4,7-9)} because twinning becomes the preferred mode of deformation in embrittled specimens. On the other hand, Grobner¹⁰⁾ has proposed that the embrittlement is caused by the locking of dislocations due to the precipitation of an α' phase on dislocations. The effect of several alloying elements on the 475°C embrittlement has been studied.¹⁰⁻¹⁴⁾ However, in evaluating the effect of the elements on the embrittlement, an important factor in brittle fracture, such as grain sizes, should be considered as suggested by Courtnall and Pickering.¹⁴⁾

The object of this work is to investigate the details of the fracture process in 475°C embrittled 30%Cr stainless steels containing the relatively low levels of impurities and to find the intrinsic cause of the embrittlement.

II. Experimental Procedures

The alloys were prepared from electrolytic iron, electrolytic chromium, metallic titanium and high-nitrogen ferrochromium. After producing 17 kg in-

got by a vacuum induction furnace, the alloys were heated for 1 hr at 1100°C and finally hot rolled to 10 mm round bars. The chemical compositions are listed in Table 1. Titanium was added in Alloy 1 to minimize the solute carbon atoms. All heat treatments mentioned below were performed in salt baths. The specimens were annealed for 1 hr at 900°C, followed by water quenching. Furthermore, two-step annealing was employed to prevent the solid-solution from hardening due to the interstitial elements¹⁵⁾ and to obtain the specimens with different grain sizes: 970°~1100°C for 1/2 hr, followed by quenching into a salt bath at 900°C, holding for 1/2 hr, and then water quenching. The grain sizes have been measured by comparing the samples with the standard chart and are listed in Table 2.

Tensile specimens were aged for various periods of time in the temperature range of 460° to 520°C. Tensile tests were carried out at room temperature on the specimens, 3 mm in diameter with a gauge length of 20 mm, using an Instron tensile machine at a constant extension rate of 0.5 mm/min. As the yield phenomenon was observed in some aged condition, lower yield stress or 0.2% proof stress was defined as the yield stress σ_Y . When sharp drops of load by twinning occurred before yielding, 0.2% proof stress was measured on the load-elongation curves corrected with the elastic elongation which corresponded to the summation of the magnitude of load-drops. The signals of acoustic emissions (AE) were measured to

Table 1. Chemical compositions of specimens (wt%)

Alloy No.	C	N	Cr	Si	Mn	Ti
1	0.002	0.0092	30.34	0.006	0.003	0.013
2	0.009	0.0022	28.67	0.013	0.002	—
3	0.013	0.040	29.84	0.023	0.005	—

Table 2. Grain size and heat treatment

Heat treatment	Grain size (mm)		
	Alloy 1	Alloy 2	Alloy 3
900°C 1 hr, water quench	0.076	0.053	0.027
970°C 1/2 hr+900°C 1/2 hr water quench	0.11	—	—
1040°C 1/2 hr+900°C 1/2 hr water quench	0.18	0.25	—
1100°C 1/2 hr+900°C 1/2 hr water quench	0.30	—	0.71

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** National Research Institute for Metals, Nakameguro, Meguro-ku, Tokyo 153.

detect the formation of twins and microcracks in a part of tensile specimens. The block diagram of its electronics system is shown in Fig. 1. The transducer made of PZT material with resonance of 140 kHz, was directly attached to the flat surfaces of shoulder section of the tensile specimens. After amplification, the AE signals below 100 kHz were filtered. The load and DC voltage from an RMS voltmeter were recorded on a multi-pen t -Y plotter.

Vickers hardness was measured on the specimens annealed at 900°C and aged in the same temperature range as mentioned above.

Microstructures, slip lines on the specimens compressed 4%, microcracks and fracture surfaces were observed using an electron microscope with an operating condition of 150 kV, a scanning electron microscope and an optical microscope. The thin foils for electron microscopy were prepared by electropolishing them in a solution of 10% perchloric acid in methanol.

III. Results

1. Age Hardening

The hardness changes which resulted from annealing for 1 hr at 900°C and subsequent aging at the indicated temperatures are shown in Fig. 2. The hardnesses of Alloys 1 to 3 were not considerably different from one another on aging for times beyond 100 hr at 480° and 520°C, whereas they were different in the early stages of aging. Especially in Alloy 1, the rapid age hardening was observed in the first 3 hr.

2. Acoustic Emission and Toughness

As aging proceeded, burst-type AE and sharp drops of load on the load-elongation curve began to be detected during the tensile testing. Figure 3 shows the

examples of load-elongation curves and AE signals emitted from the tensile specimens aged at 480°C for various times. The stresses σ_{T_0} and σ_T were defined as the stresses at which the initial burst-type AE was detected and the initial drop of load occurred, respectively. In the stress range σ_{T_0} to σ_T , many AE signals were emitted from the specimens of $\sigma_Y < \sigma_T$ (Fig. 3(a)), whereas much less signals were detected from those of $\sigma_Y > \sigma_T$ (Fig. 3(b)). In the latter case the amplitudes of the signals were small. Furthermore, the stress σ_{T_0} became identical with σ_T (Fig. 3(c)) and finally no signal of AE was found prior to final fracture of the specimens with coarse grain sizes and aged for a long time (Fig. 3(d)). The acoustic emission rate decreased after a peak with increasing strain, and few emissions took place before an unstable fracture in the case shown in Figs. 3(a) and (b).

The variation of σ_Y , σ_{T_0} , σ_T and reduction of area with aging time is shown in Fig. 4. The stress σ_T was almost independent of the aging time. The yield stress σ_Y increased over the stress σ_T with aging, and the reduction of area began to decrease largely. The critical yield stress at which the reduction of area becomes a half of that of the annealed specimen is defined as the critical yield stress σ_{Ye} for ductile-brittle transition as shown in Fig. 4. The stress σ_{Ye} is the yield stress just above σ_T .

The relation of σ_Y to the reduction of area in Alloy 1, which were annealed for 1 hr at 900°C and subsequently aged at various temperatures, is shown in Fig. 5. The relation of reduction of area to σ_Y seems

Fig. 1. Block diagram of instrumentation setup for acoustic emission measurement

Fig. 2. Age hardening curves

Alloy 1
Yield stress : (a) $\sigma_Y < \sigma_T$, (b)~(d) $\sigma_Y > \sigma_T$
Aging time : (a) 10 hr, (b) 21 hr, (c) and (d) 100 hr
Grain size : (a)~(c) $d=0.18$ mm, (d) $d=0.30$ mm
Fracture mode: (a) dimple, (b)~(d) cleavage
Fig. 3.
Load-elongation curve and acoustic emission, aged at 480°C

Alloy 1, Grain size $d=0.18\text{ mm}$
Fig. 4. Changes in yield stress, twinning stress and reduction of area on aging at 480°C

Alloy 1
Fig. 5. Relationship between yield stress and reduction of area

Fig. 6. Effect of grain size on critical yield stress to ductile-brittle transition and initial twinning stress detected on load-elongation curve

to be insensitive to the aging temperature in the range of 460° to 520°C . The stresses σ_T and σ_{Yc} depend on the grain size as shown in Fig. 6. The stress σ_T is represented as follows:

$$\sigma_T = \sigma_{iT} + k_T d^{-1/2} \dots\dots\dots(1)$$

where σ_{iT} and k_T are constants and have been found to be 32 kg/mm^2 and $9.2\text{ kg/mm}^{3/2}$, respectively. The value of k_T is greater than that of the slope k_Y of the linear relation between σ_Y and $d^{-1/2}$ in the Hall-Petch equation as shown in Fig. 7. The slope k_Y increases

Alloy 1, aged at 480°C
Fig. 7. Effect of grain size on yield stress

Alloys 1 to 3: two-step annealed and aged at 480°C
Solid symbols: dimpled fracture
Open symbols: cleavage fracture
Initial twinning stress from Fig. 6 and range of yield stress are also presented.

Fig. 8. Fracture stress as a function of grain size

with increasing aging time. Figure 8 shows the effect of grain size on the fracture stress of the specimens two-step annealed initially and aged. The range of yield stress and the initial twinning stress obtained from Fig. 6 are also illustrated in Fig. 8. The cleavage fracture stress can be represented as the straight line passing through the origin although the data are scattered in the hatched region on account of the different aging time. The slope of cleavage fracture stress tends to decrease with increasing aging time.

The embrittling time, *i.e.*, the aging time necessary to increase yield stress up to σ_{Yc} is shown in Fig. 9 as a function of grain size for the specimen aged at 480°C . Alloy 2 exhibits longer embrittling times than that of Alloy 1 in this case. The short embrittling time in Alloy 1 with coarse grain sizes is due to the rapid hardening in the early stages of aging. For the specimens of coarse grain sizes which have low σ_{Yc} (Fig. 6),

σ_Y (unaged): 30.5~34.6 kg/mm²

Fig. 9. Embrittling time as a function of grain size, aged at 480°C

Alloy 1, aged for 50 hr at 500°C ($\times 45\,000$)

Photo. 1. General precipitation and preferential precipitation at dislocations

the initial age hardening behavior has great influence on the embrittling time. Since the grain size varies by heat treatment as indicated in Table 2, the conditions of annealing and aging markedly affect the embrittling time.

3. Microstructure and Fracture Surface

Photograph 1 shows the general precipitates of α' phase and the preferential precipitates at dislocations in the specimen aged for 50 hr at 500°C. Photograph 2 shows the precipitates on grain boundaries in the specimens of Alloys 2 and 3 annealed at 900°C and subsequently aged. Note that the morphology of the precipitates differs from each other. Similar preferential precipitates were often observed in all alloys annealed at 900°C and yet unaged, although only a small amount of the precipitates has been found in Alloy 1.

Deformation characteristics also changed with aging: Slip lines were observed on the specimens compressed 4%. The slip lines on the ductile specimen aged for 20 hr at 480°C were very distinct and wavy as shown in Photo. 3, whereas those on the embrittled specimen aged for 100 hr at the same tem-

(a) Alloy 2 (b) Alloy 3

Photo. 2. Precipitates at grain boundary, aged for 50 hr at 520°C ($\times 44\,000$)

(a) Aged for 20 hr, ductile
(b) Aged for 100 hr, embrittled

Photo. 3. Slip lines of Alloy 1 aged at 480°C and compressed 4% ($\times 200$)

Photo. 4. Dislocation substructure in Alloy 1 aged for 100 hr at 480°C and compressed 4% ($\times 40\,000$)

perature were narrowly-spaced straight lines and showed little indication of cross-slip. The configuration of dislocations in the embrittled specimen shown in Photo. 3(b) is illustrated in Photo. 4, where a large number of straight dislocations are seen.

Specimens of $\sigma_Y < \sigma_T$ were unloaded after detecting some burst-type AE and many deformation twins were observed. On the other hand, many intergranular

microcracks of about one grain diameter in size together with deformation twins were observed in the specimens of $\sigma_Y > \sigma_T$. It is, therefore, obvious that the burst-type AE is due to the formations of twins when $\sigma_Y < \sigma_T$ and of intergranular microcracks in addition to twins when $\sigma_Y > \sigma_T$.

Photograph 5 shows the twins arrested at the grain boundaries and the microcracks, observed in the fractured specimen aged for 100 hr at 480°C. The specimen was lightly etched with the mixture of hydrochloric and nitric acids in glycerin to delineate the microstructure. Most of the microcracks were intergranular ones and the cleavage cracks were localized only in the grains close to the fracture surface. No cleavage crack was observed at the intersection of two twins.

Photographs 6(a) and (b) show the fracture surfaces of the specimens having yield stress of just below and above σ_{Ye} , respectively. In both cases the predominant fracture mode is quasi-cleavage or cleavage, but a few smooth intergranular fracture surfaces and herringbone structures due to deformation twins are observed in Photo. 6(b). The final fracture of embrittled specimens occurred predominantly by

cleavage even when the intergranular microcracks were initially formed by the deformation twins.

IV. Discussion

It has been reported that a deformation twin often nucleates cleavage cracks, cracks along twin interfaces or intergranular cracks.¹⁶⁻¹⁸⁾ In this study many intergranular microcracks were formed as shown in Photo. 5 when σ_Y became greater than σ_T . Few microcracks, however, were observed when $\sigma_Y < \sigma_T$ although a large number of twins were found. This result indicates that microcracking does not occur when the stress concentrations at grain boundaries due to twinning are relaxed in a certain degree by plastic deformation.

In the early stages of embrittlement, fracture is propagation controlled because microcracking does not lead immediately to unstable fracture. In this case a large deformation precedes unstable fracture. Although many twins were generated at small strain, the frequency of twinning decreased with increasing strain and twinning seldom occurred immediately before unstable fracture (Fig. 3(b)). This decrease in the frequency of twinning would be attributed to the easiness of plastic relaxation due to the increase of the number of mobile dislocations. The predominant fracture mode was cleavage or quasi-cleavage even in this case. Under the condition of severe embrittlement, no signal of AE was detected prior to final fracture (Fig. 3(d)). In this case the fracture is nucleation controlled, i.e., once initiated, a microcrack satisfies the criterion for crack propagation resulting in unstable fracture.

We assume that the intergranular microcrack is a disk-shaped crack of diameter d in a plane normal to the tensile stress and contribute to fracture as a Griffith crack. Fracture stress σ_F is given by Sack¹⁹⁾ as follows:

$$\sigma_F = \{\pi\gamma E/d(1-\nu^2)\}^{1/2} \dots\dots\dots(2)$$

where, γ : the effective surface energy
 E : Young's modulus
 ν : Poisson's ratio.

Taking $E=1.5 \times 10^4$ kg/mm² and $\nu=0.3$, the value of γ derived from the slope of the cleavage fracture stress in Fig. 8 is $2.0 \sim 3.7 \times 10^5$ erg/cm². This value is a reasonable one for cleavage crack propagation.

The value of k_T was slightly smaller than that of 3%Si iron, $10 \sim 11$ kg/mm^{3/2} reported by Hull,²⁰⁾ and was greater than that of k_Y as indicated previously. Accordingly, the effect of grain size on σ_Y , σ_T and σ_F can be represented schematically in Fig. 10. The yield stress σ_{Y_0} in the unaged condition increases up to σ_{Y_1} or σ_{Y_2} on aging, and the effective surface energy becomes γ_1 or γ_2 , respectively. The effective surface energy appears to be reduced with aging because of the tendency for the cleavage fracture stress to decrease with increasing aging time (Fig. 8), i.e., $\gamma_2 < \gamma_1$. The stress for propagation of the microcracks is given by the straight line of $\sigma_F(\gamma_1)$ or $\sigma_F(\gamma_2)$ derived from Eq. (2). Intergranular microcracks are formed when σ_Y increases over σ_T . Therefore, the fracture of the speci-

Arrow indicates intersection of twins
Tensile axis is vertical
Sample: Alloy 1
Photo. 5. Intergranular microcracks and deformation twins in the fractured specimen aged for 100 hr at 480°C ($\times 300$)

(a) Aged for 75 hr, $\sigma_Y < \sigma_{Ye}$
(b) Aged for 100 hr, $\sigma_Y > \sigma_{Ye}$
Photo. 6. Fracture surface of tensile specimens of Alloy 1 aged at 480°C ($\times 150$)

Range I: cleavage and nucleation controlled
Range II: cleavage and propagation controlled
Range III: dimple

Fig. 10. Schematic representation of the effect of grain size on σ_F , σ_Y and σ_T . Yield stress increases from σ_{Y0} to σ_{Y1} or σ_{Y2} with aging

mens with grain sizes in Range I is nucleation controlled, whereas in Range II it is propagation controlled. In Range III dimpled fracture occurs. Increasing the strength with aging increases the range of grain size in which brittle fracture occurs. Grain refinement is very effective in increasing the resistance to 475°C embrittlement.

Since large plastic deformation precedes the fracture in the early stages of embrittlement, no satisfactory explanation to this fracture behavior can be given in terms of the locking of dislocations as proposed by Grobner.¹⁰⁾ The restriction of cross slip, as shown in Photo. 3(b), can contribute to cleavage crack formation by producing stress concentration due to the piling-up of dislocations. The similar embrittlement due to planar slip mode was reported for Fe-Co-V,²¹⁾ Fe-Ni-Al²²⁾ and Fe-Ni-Si²³⁾ alloys. Even if microcracking due to deformation twin occurs, cleavage crack will not propagate unless the matrix is embrittled. Although twinning has a close relation with the embrittlement through the crack nucleation and can be one of the major factor for embrittlement, it is considered in the present case that the intrinsic cause of the embrittlement is due to the planar slip mode.

It is believed that the precipitation of α' occurs by spinodal decomposition^{24,25)} inside the spinodal and by nucleation and growth outside it. Since the chromium content, 28.67 to 30.34wt% in the present study, seems to be close to the spinodal curve from the studies using Mössbauer spectroscopy,^{26,27)} it is not clear whether the precipitation of α' occurs by the same mechanism in the three alloys or not. In addition to α' precipitation, the age hardening due to the precipitation of carbides or nitrides probably occurs. Therefore, the conclusive result with respect to the difference of the hardening behavior in the early stages of aging can not be obtained in the present study. The precipitates on the grain boundaries seem to be carbides or nitrides because they were also observed in a part of the unaged

specimens. The stress σ_{Yc} was mainly dependent on the grain size and insensitive to the kind of alloys in spite of the considerable difference in amount of the precipitates on grain boundaries (Fig. 6). Thus, the grain boundary precipitation is not a major factor of the fracture mechanism in this study.

V. Conclusions

(1) When the yield stress increases with aging over the initial twinning stress detected on the load-elongation curve, many intergranular microcracks are initiated during tensile testing. The unstable fracture occurs by cleavage when the criterion for propagation of the microcracks is satisfied.

(2) The critical yield stress to the ductile-brittle transition is a little higher than the initial twinning stress, which is linearly related to the reciprocal square root of grain diameter. The relations of initial twinning and critical yield stresses to grain size are insensitive to the contents of impurities and the aging temperature over the range of 460° to 520°C.

(3) Although twinning contributes to the embrittlement through the microcrack nucleation, it is suggested that the intrinsic cause of the 475°C embrittlement is due to the change of slip mode resulting in restriction of cross slip and easiness of cleavage crack formation by the piling-up of dislocations.

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