Communications

Effects of Co and Ni on Secondary Hardening and Fracture Behavior of Martensitic Steels Bearing W and Cr

H. KWON, C.M. KIM, K.B. LEE, H.R. YANG, and J.H. LEE

AF1410 (14Co-10Ni-2Cr-1Mo-0.16C)[1] and Aermet100 (13.4Co-11.1Ni-3.1Cr-1.2Mo-0.23C),[2] possess superior toughness even at ultrahigh strength levels. These steels are based on the design of HY180 (8Co-10Ni-2Cr-1Mo-0.1C).[3,4]

The precipitates providing the secondary hardening are fine M_2C-type carbides that are formed by the dissolution of M_3C-type cementite during aging at temperatures near 500 °C for the high-Co-Ni secondary hardening alloy steels. The alloying elements Mo and W form the carbides of M_2C type. In contrast, because Cr alone does not form M_2C carbides but M_7C_3 or $M_{23}C_6$ carbides, hardening with precipitates of the latter carbides could only occur by Cr additions greater than about 9 wt pct.[5,6] However, even the lower Cr contents combined with Mo and/or W additions can contribute to the formation of M_2C carbides in which Cr is also dissolved.

Recently, the effect of alloying additions on the secondary hardening behavior has been systematically analyzed for alloy systems from the basic system of the Fe-C-Mo ternary alloy, which has a strong M_2C carbide former Mo, to the multicomponent high Co-Ni alloy system by means of the stepwise alloying additions of Cr, Co, and Ni.[7]

However, another M_2C carbide former W has been neglected because W has a weak effect on secondary hardening. Because the 14Co-10Ni addition to the 2Mo-3Cr steel, which exhibited little hardening, results in a strong secondary hardening by the fine dispersion of M_2C carbides, there may be a similar effect in W-containing steels. Although the secondary hardening behavior in some W-containing steels, such as 6W,[8,9] 6W-3Ni,[10,11] 6W-6Ni,[11,12] and 3W-3Cr,[13] was studied in our laboratory, no systematic approach to the high Co-Ni steels containing W has been conducted.

In contrast, many studies on the fracture behavior and toughness of commercial high Co-Ni systems containing Mo have been made by Garrison and co-workers.[14,15,16] Kwon and co-workers reported the fracture behavior of both the basic secondary hardening steels containing the M_2C carbide forming elements Mo and/or W[8–13,17] and the MoCr, MoCrCo, and MoCrCoNi steels.[18]

Table I. Chemical Compositions of Alloys, Weight Percent

Alloy Designation	C	W	Cr	Co	Ni
W	0.25	5.47	—	—	—
W-Cr	0.22	2.72	2.44	—	—
W-Cr-Co	0.31	3.33	2.41	15.11	—
W-Cr-Co-Ni	0.24	3.13	3.07	14.18	9.83

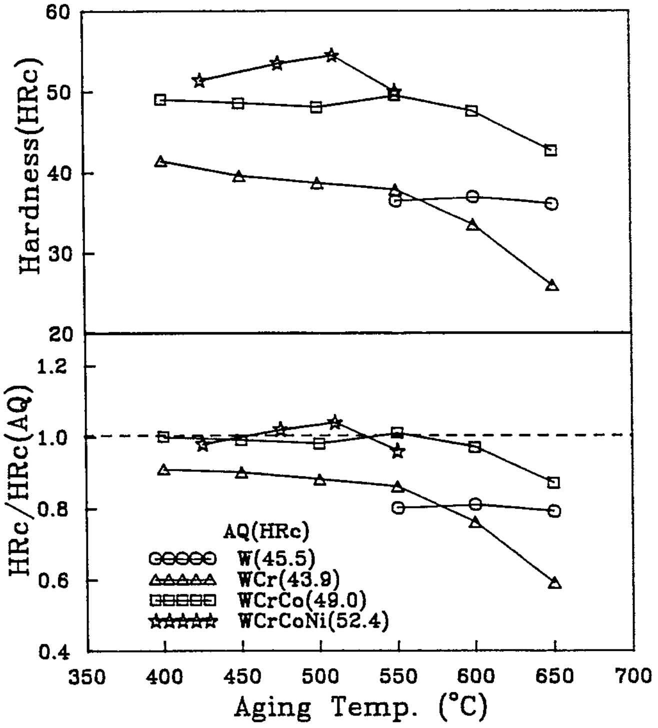

Fig. 1—Hardness as a function of aging temperature in W, W-Cr, W-Cr-Co, and W-Cr-Co-Ni steels.

The purpose of this study was to analyze the effect of Co and Ni additions on secondary hardening and fracture behavior of the martensitic steels bearing W and Cr, where W exhibits a much weaker effect on the secondary hardening compared with Mo[19,20,21] and Cr can contribute to an increase in toughness even though the Cr additions weaken the secondary hardening in Mo and W steels.[7,13,22]

The chemical compositions of the alloys used in this study are presented in Table I. Impact specimens were austenitized in a flowing argon atmosphere at 1200 °C for 1 hour and then water- or oil-quenched. Austenitized specimens were aged in a neutral salt bath at 400 °C and 650 °C for 1 hour and then water-quenched.

Fractography was conducted on fracture surfaces cut off the impact-tested samples, while samples for hardness measurements were obtained from a second cut 5 to 10 mm below the fracture surface. Hardness was measured using the Rockwell ''C'' scale (HRc), and average values of five readings are reported. In order to observe martensitic substructures (M_2C and M_3C carbides), thin foils were examined in a JEOL* transmission electron microscope (TEM), operated at 120 kV.

The variations in hardness for 6W, 3W-3Cr, 3W-3Cr-14Co, and 3W-3Cr-14Co-10Ni steels are shown in Figure

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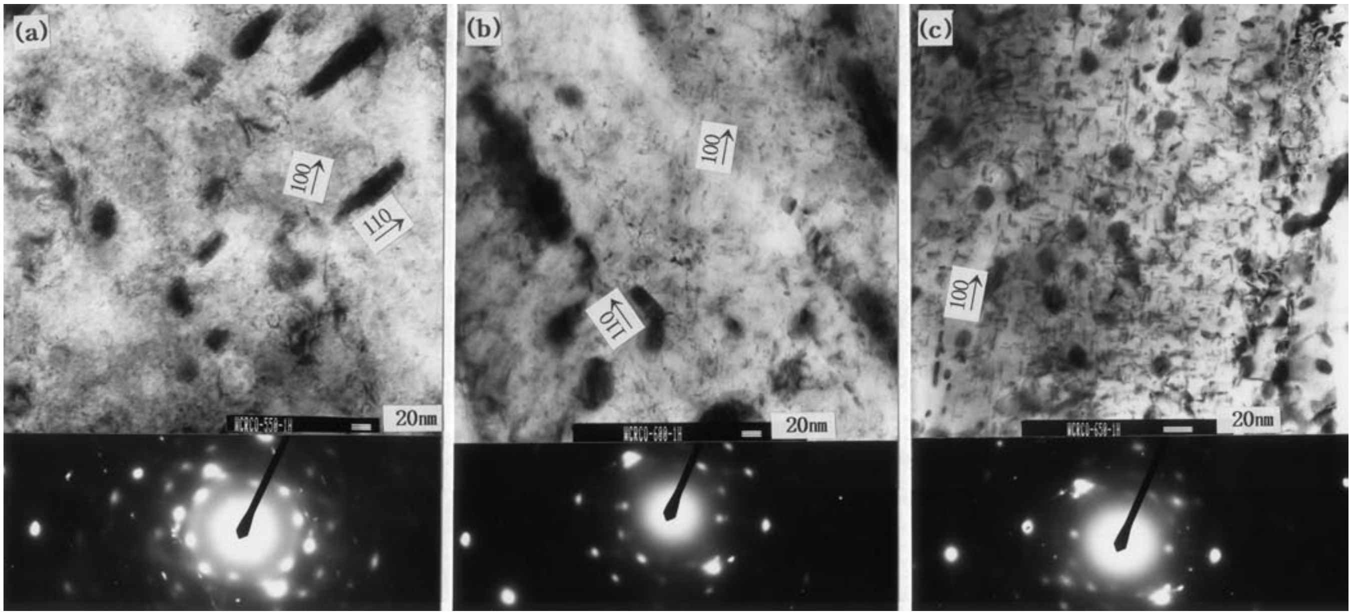

Fig. 2—TEM micrographs of the W-Cr-Co steel, showing fine M_2C carbides and coarse M_3C cementite particles and plates: (*a*) 550 °C, (*b*) 600 °C, and (*c*) 650 °C.

1. The normalized hardness values with respect to the hardness in as-quenched condition were also compared, since the extent of solid solution hardening with the contents of carbon and alloying elements affects the as-quenched hardness.

For the 6W steel, the very weak hardening occurs at a temperature near 600 °C, as compared to the strong hardening for the Mo steels.

For the 3W-3Cr steel, in which about 3 wt pct of W content in the 6W steel was substituted by the Cr, the hardness decreased slowly in the range of 400 °C to 550 °C, but decreased rapidly at temperatures over 550 °C compared with the W steel. In other words, there was a great drop even in the softening resistance by the partial substitution of 3Cr for 3W of the 6W steel. Tunney and Ridley[22] have investigated the drastic weakening in secondary hardening intensity with the 3Cr addition to the 5Mo and 10W steels.

The addition of 14Co to the 3W-3Cr steel resulted in the occurrence of clear secondary hardening with a peak at 550 °C and moved the hardness curve considerably upward over all temperature ranges. It is very interesting that a continuous softening in the range of 450 °C to 600 °C in the 3W-3Cr steel is changed to an actual secondary hardening with a peak at 550 °C by the 14Co addition. In other works, except one on only Co addition to the (2-4)Mo-(0.2-0.4)C steel,[23] the Co additions to Mo-Ni and Mo-Ni-Cr steels produced strong secondary hardening.

A peak of the hardness curve was shifted down to a lower temperature near 500 °C in the 14Co-10Ni containing steel, compared with 550 °C in the 3W-3Cr-14Co steel. The appearance of peak hardness at temperatures near 500 °C was observed in the 4Mo-14Co-10Ni steel with the absence of Cr,[24] as well as in high Co-Ni steels containing both Mo and Cr. Consequently, the Ni addition definitely plays a significant role in controlling the secondary hardening behavior, particularly when combined with the Co addition.

For the 6W steel,[8,13,19] a very weak hardening associated with a much less dense formation of fine M_2C carbides due to slower diffusion of W in the martensite (ferrite) matrix compared with Mo.

For the 3W-3Cr steel, little secondary hardening is due to the cementite stabilization at higher temperatures.[13] There is both a little presence of carbon available to form the M_2C carbides since Cr dissolves up to 18 wt pct within the M_3C cementite, and thus stabilizes the M_3C cementite at higher temperatures,[22] and a slower diffusion of W that delays M_2C carbide formation.

Figure 2 shows the microstructures of the W-Cr-Co steel aged at 550 °C, 600 °C, and 650 °C for 1 hour. In the 550 °C aged condition, *i.e.*, the peak-aged condition, there were very coarse cementite as well as very fine precipitates, which are likely to be the M_2C carbides. In the 600 °C aged condition, *i.e.*, the overaged condition, both the fine M_2C carbides arrayed to $\langle 100 \rangle$ directions and the coarse cementite on the (110) plane were present. In the 650 °C aged condition, the M_2C carbides are observed to have somewhat coarsened, but the coarse cementite was still present. Hence, both the acceleration of M_2C carbide formation and the reduction of cementite stability occurred, as compared to the W-Cr steel. However, the growth of M_2C carbides occurs slowly. This is consistent with the hardness variation in Figure 1, which depicts a slower decrease in hardness in the overaged region of 550 °C to 650 °C for the W-Cr-Co steel relative to the other steels. Thus, the addition of Co to the W-Cr steel may promote the nucleation of M_2C carbides, but inhibit the growth of M_2C carbides. However, the presence of coarse cementite at higher temperatures may reduce the possibility of the stronger secondary hardening by the greater dissolution of cementite.

Figure 3 shows the microstructures of the W-Cr-Co-Ni steel aged at 475 °C, 510 °C, and 550 °C for 1 hour. In the underaged condition at 475 °C, very fine M_2C carbides and coarse cementite are observed. In the peak-aged condition of 510 °C, the fine M_2C carbides and the partially dissolved cementite are observed. While the M_2C carbides somewhat

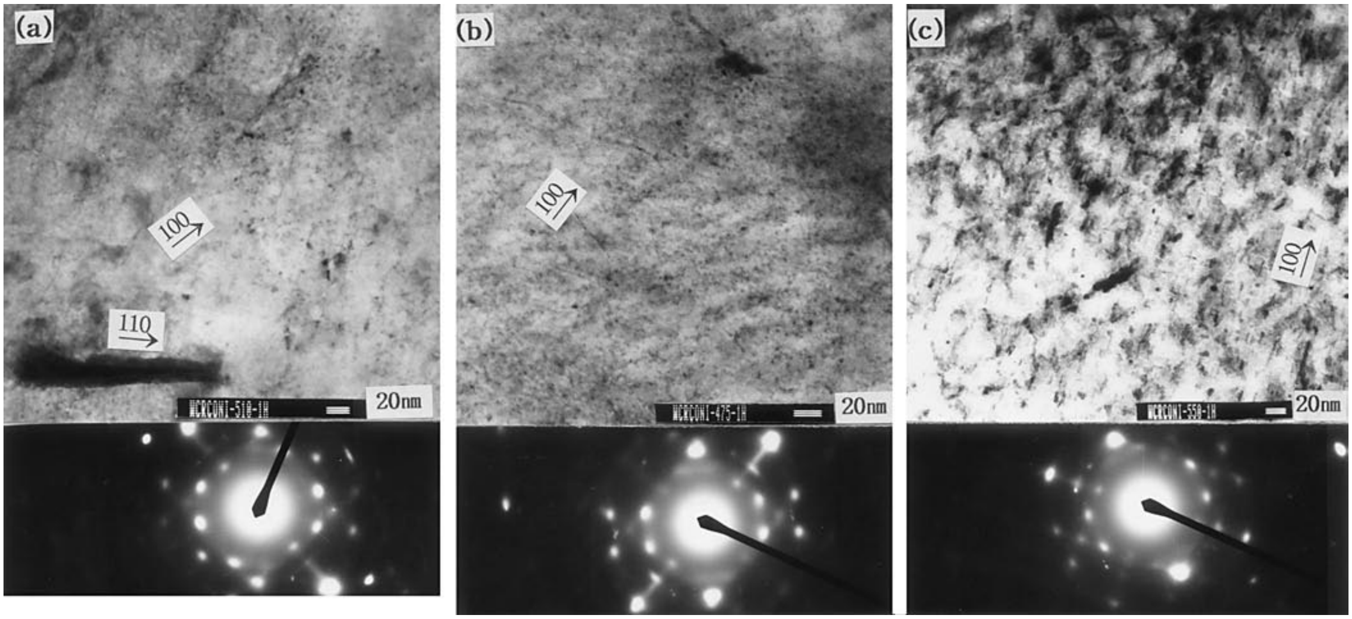

Fig. 3—TEM micrographs of the W-Cr-Co-Ni steel: (*a*) 475 °C, showing very fine M_2C carbides and coarse M_3C cementite plates; (*b*) 510 °C, showing fine M_2C carbides; and (*c*) 550 °C, showing somewhat coarsened M_2C carbides.

Table II. Peak Hardness Temperature, °C

4Mo[8]	2Mo-2.5Cr-14Co[8]	2Mo-3Cr-14Co-10Ni[8]	4Mo-14Co-10Ni[25]	4Mo-9Co[24]
600	550	500	500	no peak
6W[14]	3W-2.5Cr-14Co	3W-3Cr-14Co-10Ni	—	—
600	550	500	—	—

coarsened in the overaged condition of 550°C, the dissolution of cementite was mostly completed. The Ni addition accelerates the formation of M_2C carbides and provides enough carbon to form M_2C carbides at lower temperatures. The 10Ni addition to the W-Cr-Co steel decreased the peak hardness temperature to lower temperatures near 500 °C. On the other hand, the 14Co-10Ni addition to the 4Mo steel shifted the peak hardness temperature from 600 °C to 500 °C.[24] Thus, the Ni addition tends to promote the M_2C carbide formation, especially when combined with Co, which increases both the driving force for the M_2C carbide formation and the density of dislocations where the M_2C carbides can nucleate.

The peak hardness temperatures in various alloys containing W or Mo are compared in Table II. It is believed from those data that the combined Co additions, such as Co-Cr and Co-Ni, can play a role of accelerating the M_2C carbide formation, while the only Co addition to the Mo steel can inhibit it. Since the combined Co addition induces not only the delay of dislocation recovery,[25] affording the nucleation sites for the fine dispersion of M_2C carbides, but also the increase in driving force for the nucleation of M_2C carbides,[26] it is necessary to the occurrence of strong secondary hardening. The presence of Co may reduce the solubility of Cr within the M_3C cementite, and the relatively lower stability of cementite thus may provide more carbon available to form the fine M_2C carbides. However, the Co addition decreases the growth rate of M_2C carbides, since Co increases the carbon activity and decreases its diffusivity in ferrite.[26] Hence, Co in the Cr-Co combined addition increases the nucleation rate of M_2C carbides but decreases their growth rate.

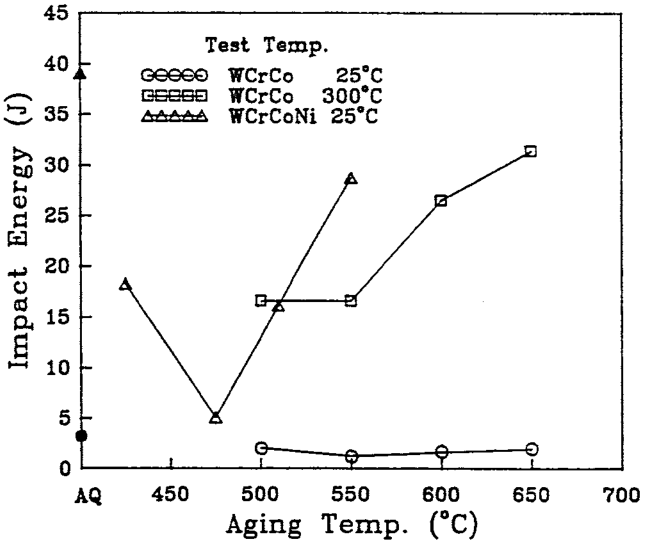

Fig. 4—Variations in impact toughness with aging temperature for the W-Cr-Co steel tested at room temperature and 300 °C and of the W-Cr-Co-Ni steel tested at room temperature.

The Ni addition plays an important role as a cementite destabilizer, which promotes the dissolution of cementite and thus provides the available carbon enough to form the fine M_2C carbides at lower temperatures. Thus, a strong secondary hardening by the combined action of the Ni-Co addition is necessary to effectively obtain the ultrahigh strength at lower aging temperatures.

The 3W-3Cr steel as well as the 2Mo-3Cr steel showed transgranular fracture in the all aging conditions and, thus, clearly showed a transgranular brittle to ductile fracture transition with increasing test temperature.[13]

Figure 4 shows the variations in impact toughness at

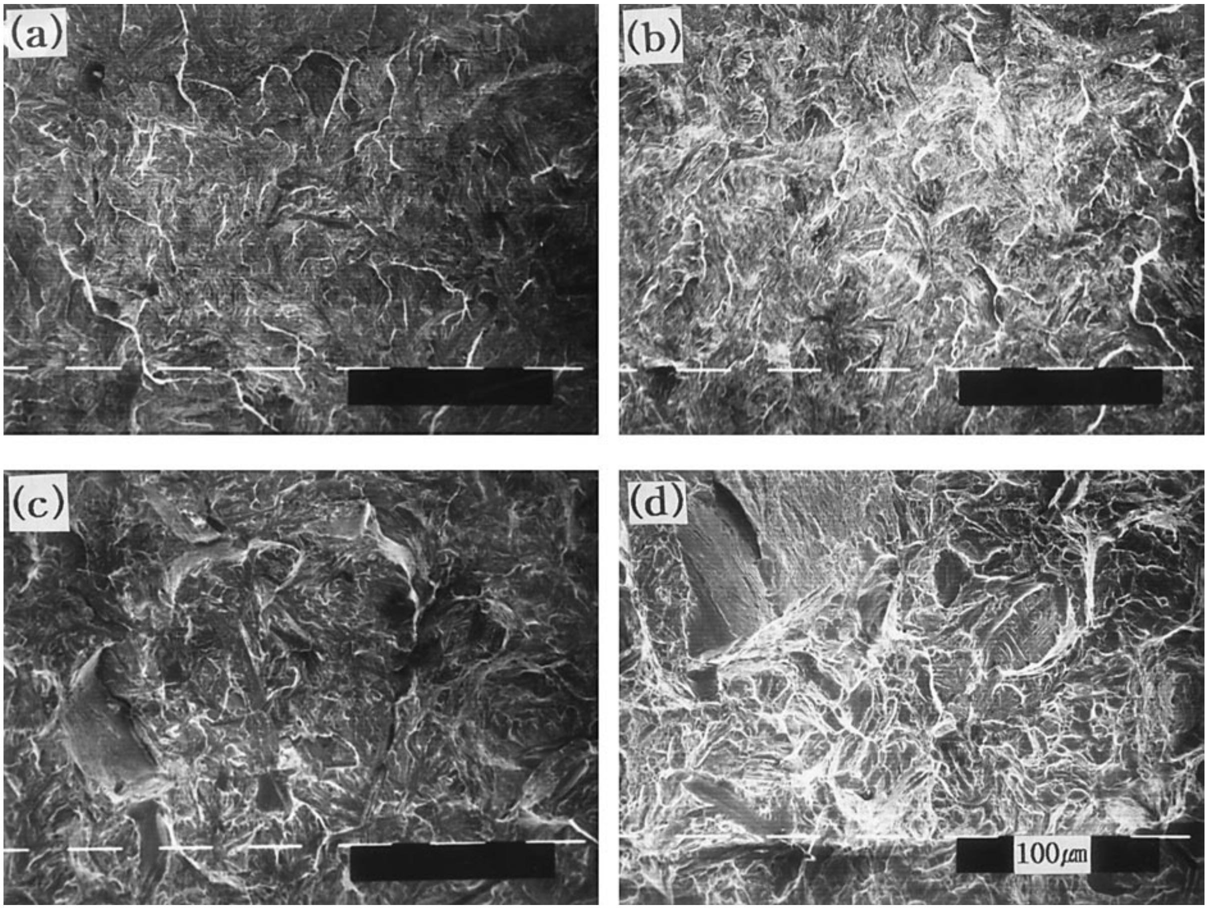

Fig. 5—Fractographs of the W-Cr-Co steel: (*a*) and (*b*) 550 °C, showing the transgranular cleavage when tested at room temperature and 300 °C, respectively; and (*c*) and (*d*) 650 °C, showing the transgranular cleavage with some dimpled areas when tested at room temperature and 300 °C, respectively.

room temperature and 300 °C for the W-Cr-Co steel and at room temperature for the W-Cr-Co-Ni steel.

For the W-Cr-Co steel, the 14Co addition increased the hardness over the entire aging temperature range and led to a secondary hardening with a peak hardness of Rc 50 at 550 °C (Figure 1). The hardness gradually decreased to Rc 45 at 650 °C. While the impact toughness at room temperature represented a very low level of 2 J in the range of 500 °C to 650 °C, the impact toughness at a test temperature of 300 °C was slightly recovered to the constant value of 17 J at 500 °C and 550 °C and continuously increased up to 32 J at 650 °C. The result at 300 °C is different from that for the Mo-Cr-Co steel,[18] which presented still the low constant value of 10 J in the range of 500 °C to 650 °C. Whereas the fractographs in Figure 5 show mostly transgranular cleavage in the specimens tested at room temperature, they contain some dimpled areas in the 650 °C overaged specimens tested at 300 °C. Hence, the 14Co addition results in a severe decrease in toughness of the matrix even though it could increase the overall hardness and produce a secondary hardening.

For the W-Cr-Co-Ni steel, the 10Ni addition accelerated the secondary hardening and shifted a peak hardness temperature down to 510 °C. After reaching the peak value of Rc 54.5 at 510 °C, higher by Rc 3 higher than the as-quenched one, the hardness decreased to Rc 50 at 550 °C. Of course, the 10Ni addition improved the overall impact toughness due to the enhancement in intrinsic toughness of the matrix. While the impact toughness in the as-quenched condition has a high value of 39 J, it decreased to the low values of 18 and 6 J at 425 °C and 475 °C, respectively, but was recovered to 16 J in spite of an increase in hardness up to the peak values at 510 °C and 510 °C and continuously increased to 29 J with a decrease in hardness at 550 °C of the overaged condition.

The fractographs in Figure 6 show the mostly intergranular fracture at 425 °C and 475 °C. Thus, the loss in impact toughness is tempered martensite embrittlement due to the combined action of impurities and coarse cementite at the grain boundaries. However, the transgranular dimples in the peak-aged condition at 510 °C indicate the enhancement in toughness by the dissolution of coarse cementite degrading the toughness. The Ni addition plays a dual role in additionally increasing the toughness through the removal of coarse cementite degrading the toughness as well as through an increase in intrinsic toughness, *i.e.*, the cleavage resistance.

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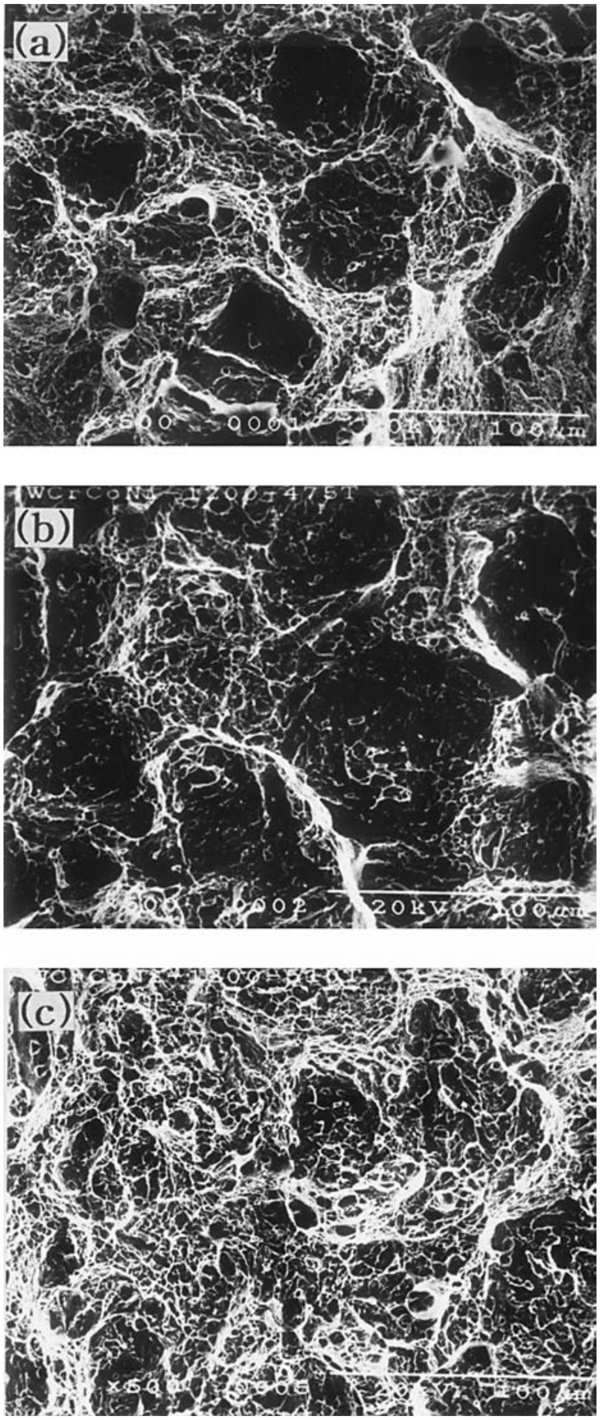

Fig. 6—Fractographs of the W-Cr-Co-Ni steel tested at room temperature: (*a*) 425 °C and (*b*) 475 °C, showing a large amount of intergranular area; and (*c*) 510 °C, showing the mostly transgranular dimples.

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Effect of Small Loads on Crack Growth Rate and Crack Tip Deformation in the Fatigue Process of A537 Steel

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Omission of small cycles is a very cost-effective option when testing materials under long-term random loading histories. Researchers[1,2] have proposed several criteria to identify ''damaging'' and ''nondamaging'' cycles. However, most proposals have been empirical and have lacked rational analysis based on physical mechanisms. In this article, crack tip stress-strain behavior and the effect of small loads superposed upon the major cycle ΔP on the crack growth rate da/dN were studied for A537 steel in the fatigue process.

The chemical composition of A537 steel in weight percent is as follows: C0.13, Mn1.48, P0.012, S0.005, Si0.46,

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