Effect of Alloying Additions on Secondary Hardening Behavior of Mo-Containing Steels

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

The effect of alloying additions on secondary hardening behavior in Fe-Mo-C steels has been investigated by means of the successive alloying additions of Cr, Co, and Ni. The Cr additions promote M_3C cementite formation. The Ni additions destabilize the cementite formation, while the Co additions retard dislocation recovery and present the necessary sites for M_2C formation which provides the secondary hardening.

I. INTRODUCTION

SECONDARY hardening steels containing high Co-Ni contents, such as AF1410 (14Co-10Ni-2Cr-1Mo-0.16C)[1] and Aermet 100 (13.4Co-11.1Ni-3.1Cr-1.2Mo-0.23C),[2] were developed for aerospace applications; these steels possess superior toughness even at ultrahigh strength levels and are based on the HY180 (8Co-10Ni-2Cr-1Mo-0.1C).[3,4]

The precipitates providing the secondary hardening are fine M_2C-type carbides which 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, since alloying element 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. In addition, the Cr addition seems to be necessary in the high Co-Ni secondary hardening ultrahigh strength alloy steels with superior toughness, such as HY180,[3,4] AF1410,[1] and AerMet 100,[2] even though Cr could weaken the extent of secondary hardening. However, there are few studies on the effect of Cr addition on hardening and fracture behavior.

Using a base Fe-10Ni steel, detailed research on the effects of alloying additions on strength and toughness for the HY180 steel, which acted as a starting point for the innovation of high Co-Ni secondary hardening ultrahigh strength steels with the high toughness, was conducted by Speich *et al.*[3,4] Although Ni has been well known to improve intrinsic toughness of the matrix, *i.e.*, the resistance to the cleavage, its effect on promoting M_2C carbides is not known.

Recently, research has been reported for the development of the ultrahigh strength secondary hardening steels containing high Co-Ni contents, in which the computer simulation using thermodynamic data was applied to obtain the optimum alloy design for high toughness/strength alloys.[7] While the alloys designed by the compositional modification through the computer simulation exhibited good results in terms of secondary hardening response, the improvement in fracture toughness could not be obtained simply by means of that alloy design.

In contrast, the effect of alloying additions on the secondary hardening behavior has not been systematically analyzed for alloy systems from the basic Fe-C-X ternary system, in which X is the M_2C carbide former, Mo or W, to the multicomponent high Co-Ni alloy system, such as AF1410 and Aermet 100.

The purpose of this work was to analyze the effect of Cr, Co, and Ni additions on microstructure and secondary hardening behavior in a basic ternary Fe-Mo-C system, where Mo exhibits a strong effect on secondary hardening compared with W.[8,9,10] The Cr addition is considered first since Cr can dissolve in the M_2C formed from Mo and contribute to an increase in toughness in high Co-Ni steels. The Co addition which can indirectly influence the formation of M_2C carbides by the modification of matrix composition is considered next. Finally, Ni which has been well known simply as an intrinsic toughness enhancer, but whose effect on secondary hardening has been little known, is added.

II. EXPERIMENTAL PROCEDURE

Plates of different compositions were prepared by the vacuum induction melting and hot-forging processes and were machined to make standard Charpy V-notch impact specimens. 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-quenched

Table I. Chemical Compositions of Alloys (Weight Percent)

Alloy Designation	C	Mo	Cr	Co	Ni
Mo	0.20	4.25	—	—	—
Mo-Cr	0.22	2.10	2.41	—	—
Mo-Cr-Co	0.27	1.95	2.66	14.75	—
Mo-Cr-Co-Ni	0.24	1.55	2.90	14.25	10.80

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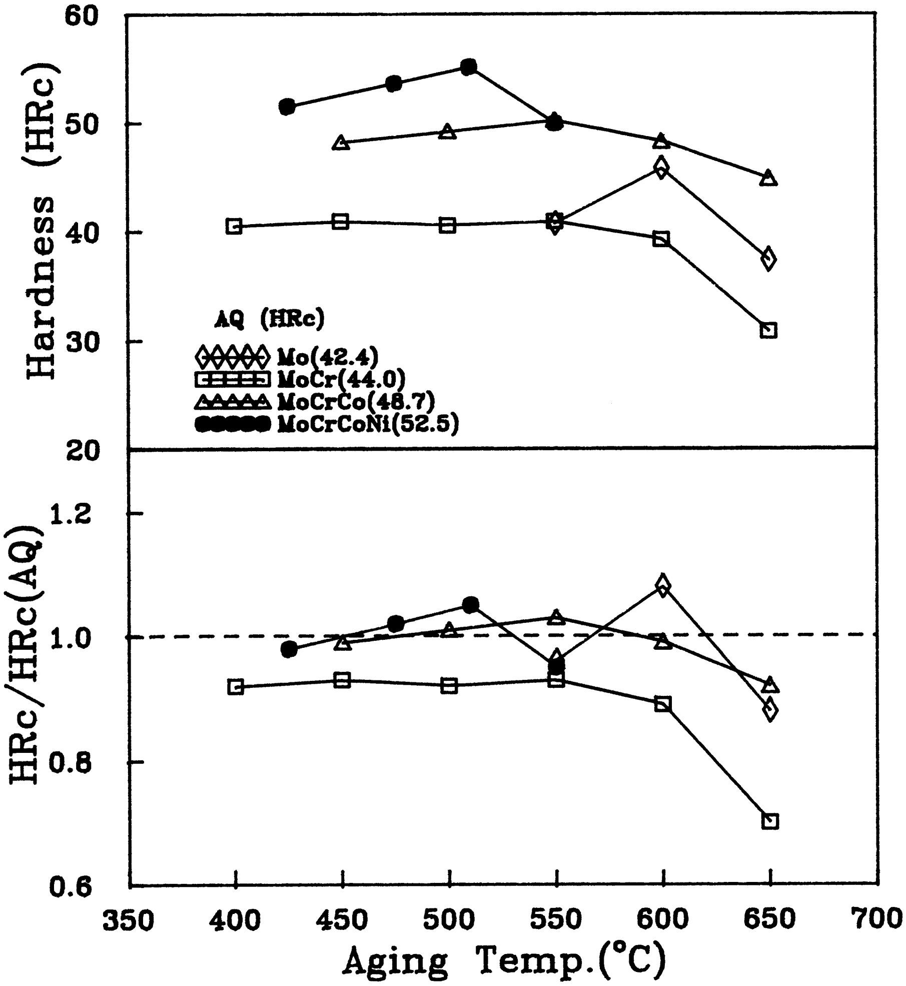

Fig. 1—Absolute hardness values and relative values with respect to the as-quenched hardness as a function of aging temperature in Mo, Mo-Cr, Mo-Cr-Co, and Mo-Cr-Co-Ni steels.

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. The fracture results are reported in a separate article.

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.

III. EXPERIMENTAL RESULTS

A. *Hardness*

The variations in hardness for 4Mo, 2Mo-2.5Cr, 2Mo-2.5Cr-14Co, and 1.5Mo-3Cr-14Co-10Ni steels are shown in Figure 1. The normalized hardness values with respect to the as-quenched value were also compared, since the extent of solid solution hardening with the contents of carbon and alloying elements affected the as-quenched hardness.

The peak hardness appeared at a temperature of 600 °C as a function of the 1-hour aging (tempering) temperature for the 4Mo steel, as reported in previous articles.[11–14] A fine precipitation of M_2C carbides, of course, led to the secondary hardening. A strong hardening effect enhancing the peak hardness by about 10 pct in comparison with the as-quenched hardness was observed.

For the 2Mo-2.5Cr steel in which about 2 wt pct of Mo content in the 4Mo steel was substituted by the Cr, the hardness did not decrease but remained at a similar level in the range of 400 °C to 550 °C, and then decreased at temperatures above 550 °C, in the absence of a clear secondary hardening peak. This infers a great reduction in secondary hardening intensity by the partial substitution of the Cr for 2Mo of the 4Mo steel. This phenomenon was presented in the literature,[5] but a systematic approach was made by Tunney and Ridley,[10] who showed a drastic weakening in secondary hardening intensity with 3Cr addition to the 5Mo steel. This was explained as an inhibition of M_2C carbide formation through the stabilization of M_3C cementite.

Next, the addition of 14Co to the 2Mo-2.5Cr steel resulted in the reappearance of a clear secondary hardening

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with a peak at 550 °C as well as moved the hardness curve considerably upward over the entire temperature range. In most studies, except a study on only Co addition to (2–4)Mo-(0.2–0.4)C steel,[15] Co additions to Mo-Ni and Mo-Ni-Cr steels produced strong secondary hardening *via* a fine dispersion of M_2C carbides in the matrix of high dislocation density. The Co addition up to about 14 wt pct thus has been required to guarantee the ultrahigh strength in AF1410 and Aermet 100 alloys.

Finally, a peak of hardness curve was shifted down to a lower temperature near 500 °C in the 2Mo-2.5Cr-14Co-10Ni steel, compared with 550 °C in the 2Mo-2.5Cr-14Co steel, although the overall level of normalized hardness was maintained at high values in both 14Co and 14Co-10Ni containing steels. The appearance of peak hardness at temperatures near 500 °C was observed in the 4Mo-14Co-10Ni steel in the absence of Cr,[16] as well as in high Co-Ni steels containing both Mo and Cr. Thus, the combined 14Co-10Ni additions to the Mo or Mo-Cr steels decrease the peak hardness temperature from 600 °C to 500 °C. The Ni addition definitely plays a significant role in controlling the secondary hardening behavior, particularly when combined with Co.

B. *Microstructures*

Figure 2 shows the M_2C carbides for the 4Mo steel aged at 600 °C and 650 °C for 1 hour, *i.e.*, in peak-aged and overaged conditions, respectively. In the peak-aged condition, M_2C carbides as fine needles arrayed mainly along the [100] direction are observed. In the overaged condition, on the other hand, coarsened M_2C carbide needles arrayed perpendicular to the $\langle 100 \rangle$ directions are observed. The M_3C appears mostly disintegrated due to the *in situ* formation of M_2C carbides (arrow A).

Microstructures of the Mo-Cr steel aged at 500 °C for 100 hours and 600 °C and 650 °C for 1 hour are shown in Figure 3. Whereas the coarse M_3C cementite platelets present on $\{110\}$ planes still remain stable in the 500 °C and 600 °C aged conditions, coarse M_2C carbide needles are also observed in the 650 °C aged condition where the hardness has decreased considerably. For the 2Mo-2.5Cr steel in which the 2.5Cr substitutes for 2Mo of the 4Mo steel, since Cr stabilizes M_3C cementite at higher temperatures, there is insufficient carbon available to form the M_2C carbides for secondary hardening. In addition, any M_2C carbide which could form in the higher temperature range cannot contribute effectively to the hardening, since the rapid recovery of the dislocation structure at higher temperatures reduces the nucleation sites of M_2C carbides and instead promotes the growth of M_2C carbides.

Figure 4 shows the microstructures of the Mo-Cr-Co steel aged at 550 °C, 600 °C, and 650 °C for 1 hour. In the peak-aged condition, 550 °C, very fine precipitates, which are likely M_2C carbides, are observed. Also, very coarse cementite is present. In the overaged condition, 600 °C, both the fine M_2C carbides arrayed along $\langle 100 \rangle$ directions and the coarse cementite on the (110) plane are present. At 650 °C, the M_2C carbides are observed to have coarsened. Hence, the acceleration of M_2C carbide formation and the reduction of cementite stability occur simultaneously, as compared to the microstructures of the Mo-Cr steel seen in Figure 3. 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 Mo-Cr-Co steel relative to the other steels. Thus, the addition of Co to the Mo-Cr steel promotes the nucleation of M_2C carbides but inhibits their growth.

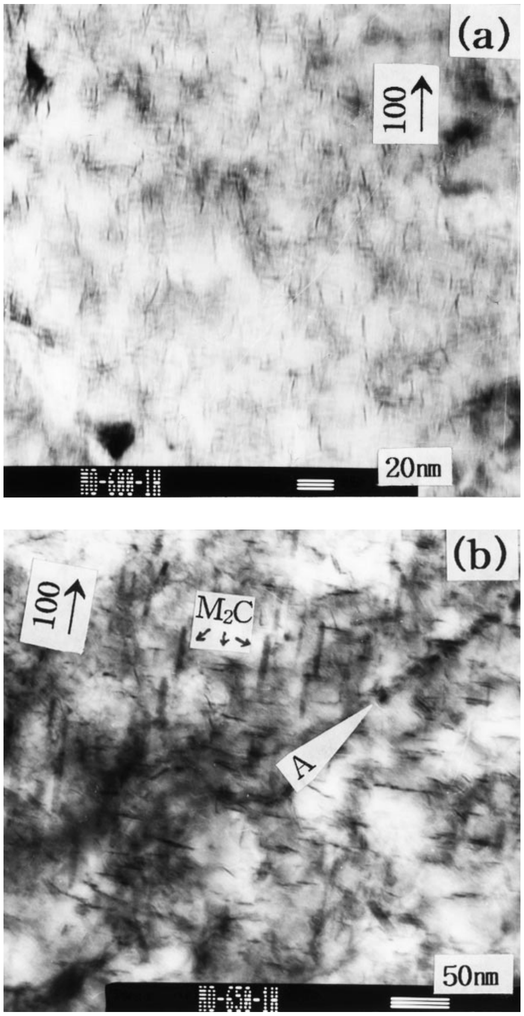

Fig. 2—TEM micrographs of the Mo steel aged for 1 h at (*a*) 600 °C showing fine M_2C along [100] and (*b*) 650°C showing coarse M_2C along $\langle 100 \rangle$ and the disintegrated M_3C along [110] indicated by arrow A.

Figure 5 shows the microstructures of the Mo-Cr-Co-Ni steel aged at 475 °C, 510 °C, and 550 °C for 1 hour. In the underaged condition of 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 remain while some cementite is seen to dissolve. While the M_2C carbides coarsened somewhat in the overaged condition of 550 °C, the dissolution of cementite was mostly completed. The Ni addition accelerates cementite dissolution and provides enough carbon to form M_2C carbides at lower temperatures by Co-Ni combined addition. The presence of Co increases the density of dislocations and increases the driving force for the formation of M_2C carbides which nucleate on the dislocations. The Ni addition plays a dual role in additionally increasing the toughness through the removal of coarse cementite as well as through an increase in intrinsic toughness, *i.e.*, the cleavage resistance of the steel. Until now,

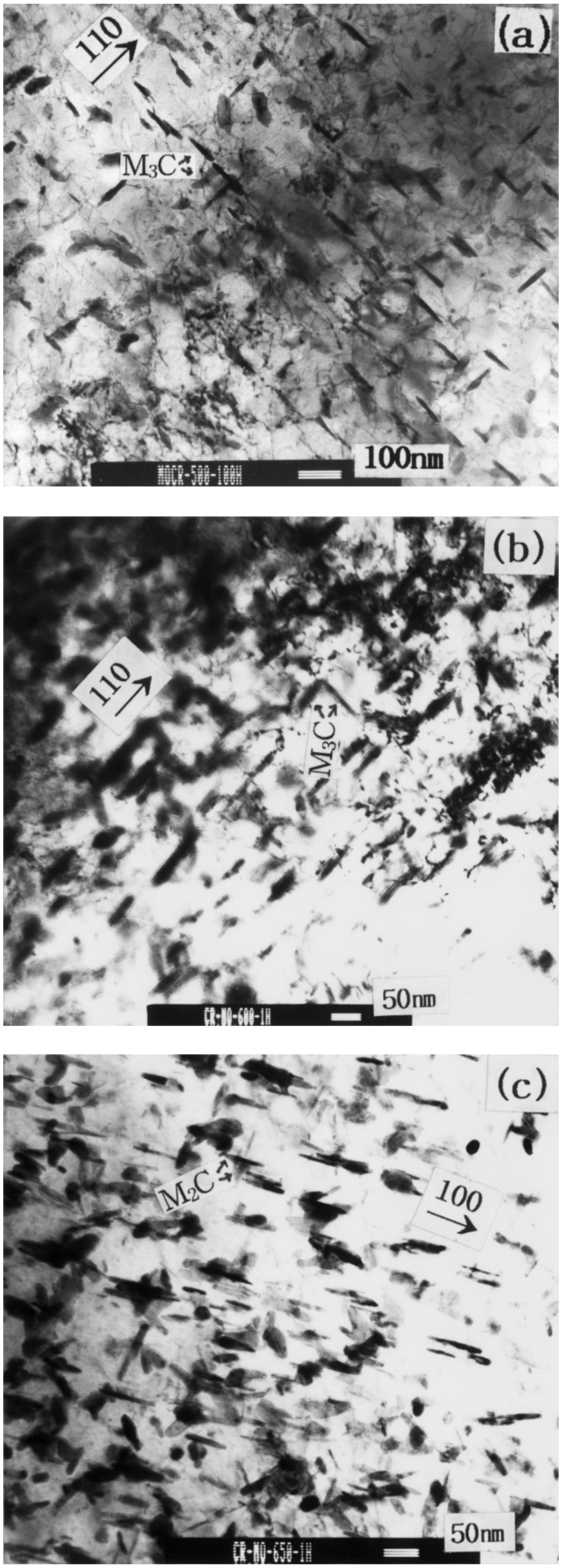

Fig. 3—TEM micrographs of the Mo-Cr steel aged at (*a*) 500°C for 100 h and at (*b*) 600°C for 1 h, showing coarse M_3C along ⟨110⟩ and (*c*) 650°C for 1 h, showing coarse M_2C along ⟨100⟩.

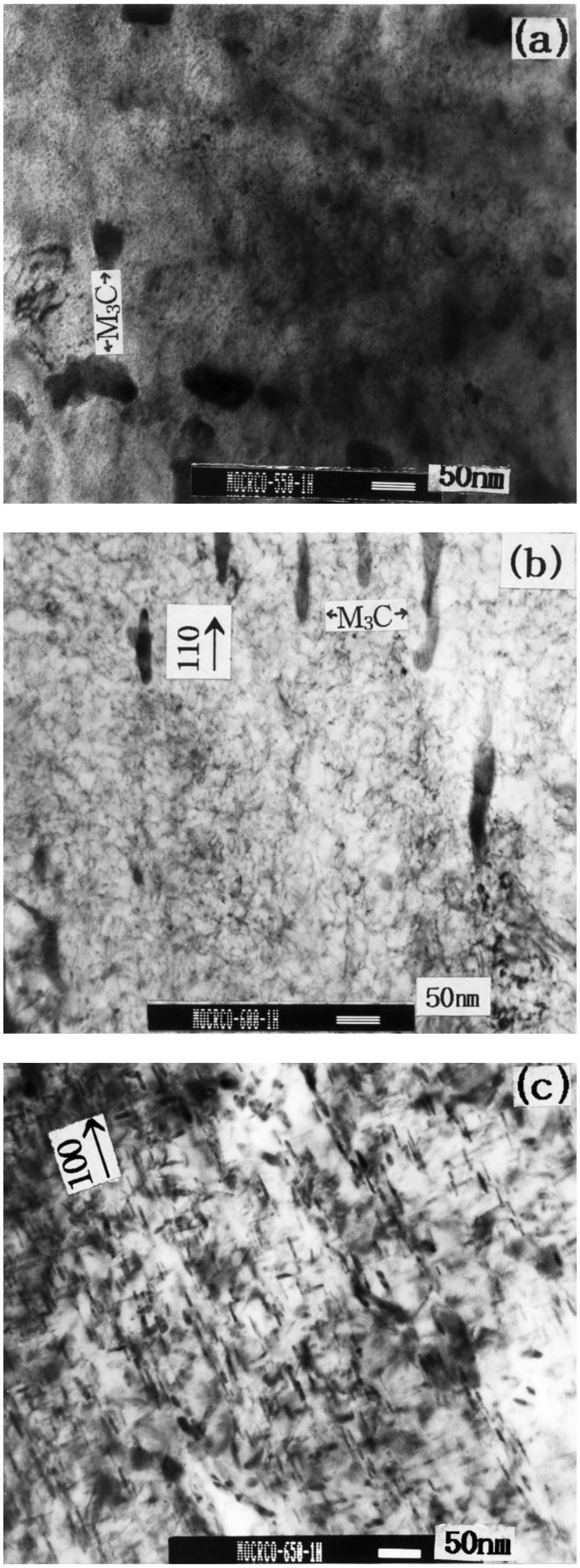

Fig. 4—TEM micrographs of the Mo-Cr-Co steel aged for 1 h at (*a*) 550 °C showing very fine M_2C and coarse M_3C, (*b*) 600 °C, showing fine M_2C along ⟨100⟩ and coarse M_3C along [110], and (*c*) 650 °C, showing coarse M_2C along ⟨100⟩.

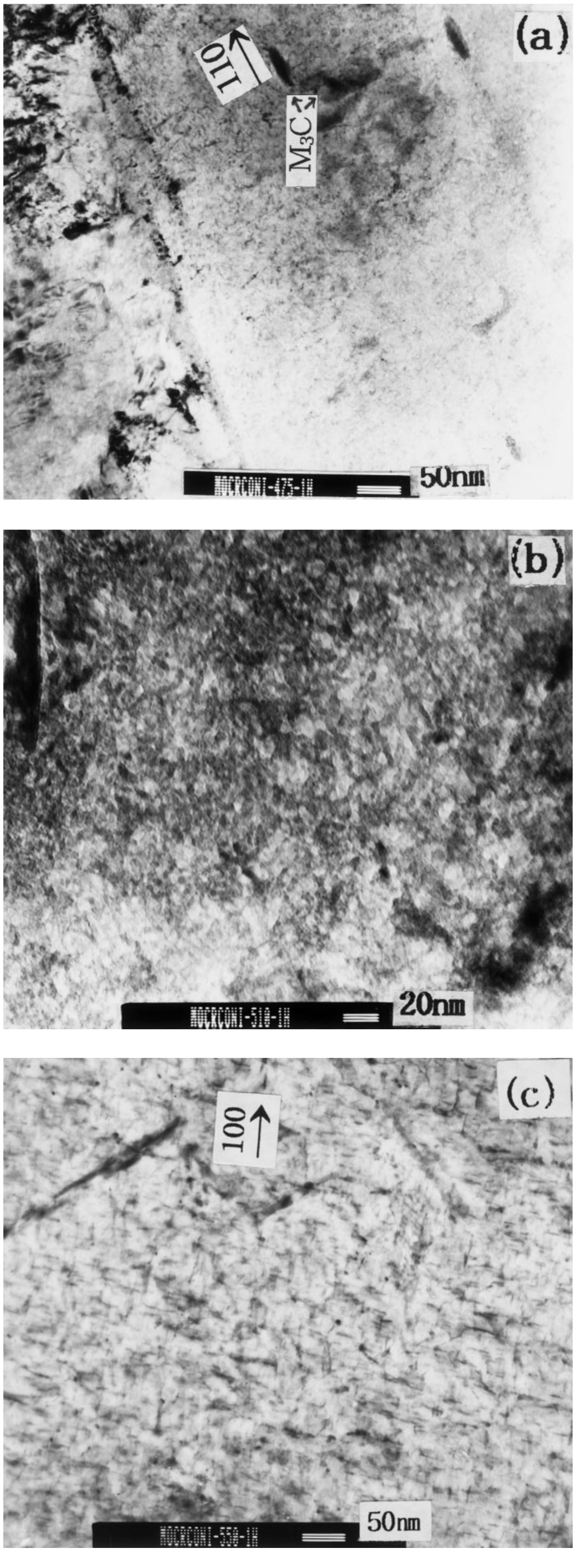

Fig. 5—TEM micrographs of the Mo-Cr-Co-Ni steel aged for 1 h at (*a*) 475 °C showing very fine M_2C and coarse M_3C and (*b*) 510 °C, showing fine M_2C along ⟨100⟩ and coarse M_3C along [110], and (*c*) 550 °C, showing coarse M_2C along ⟨100⟩.

Ni was considered to only enhance intrinsic toughness through a modification of the matrix chemistry.

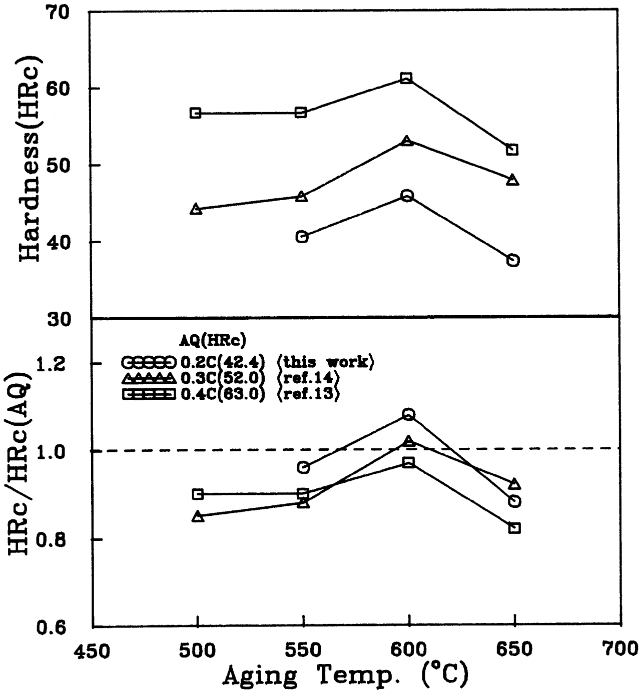

Fig. 6—Absolute hardness values and relative values with respect to the as-quenched hardness as a function of aging temperature in the 4Mo-(0.2 to 0.4)C steels.

IV. DISCUSSION

The 4Mo steel exhibited the peak hardness at 600 °C, due to the formation of fine M_2C carbides. For a given Mo content, however, increasing carbon content can reduce rather than enhance the peak hardness relative to the as-quenched hardness. For example, the peak hardness of the 0.2C steel was increased by about 10 pct but that of 0.4C steel was decreased by about 5 pct, as compared to the as-quenched hardness for the 4Mo steels (Figure 6).[13,14] Although the as-quenched hardness is increased with increasing carbon content, any excess carbon over about 0.25 wt pct, required to form M_2C carbides in the 4 wt pct Mo steel, cannot contribute to the peak hardness due to secondary hardening.

For the 2Mo-2.5Cr steel, the substitution of Cr for half of the Mo content of the 4Mo steel eliminates the extent of secondary hardening. The hardness remains at a similar level in the range of 400 °C to 550 °C but decreases at 600 °C, at which the 4Mo steel exhibited a strong secondary hardening. This effect is also shown in Figure 7, which plots data from Reference 5. The addition of Cr to 2Mo steel increases overall hardness below 600 °C but eliminates any secondary hardening. Eliminating the Cr and increasing the Mo content from 2 to 5 pct provide a pronounced secondary hardening effect and retention of hardness at higher temperatures provided sufficient carbon is present. Tunney and Ridley[10] have suggested that there is little carbon available to form M_2C carbides in the presence of Cr, which dissolves up to 18 wt pct within the M_3C cementite and stabilizes this to higher temperatures. This is shown in Figure 3, where coarse M_3C cementite on {110} planes is retained even at 600 °C. Although cementite dissolves at 650 °C, considerably coarse M_2C carbides present together with

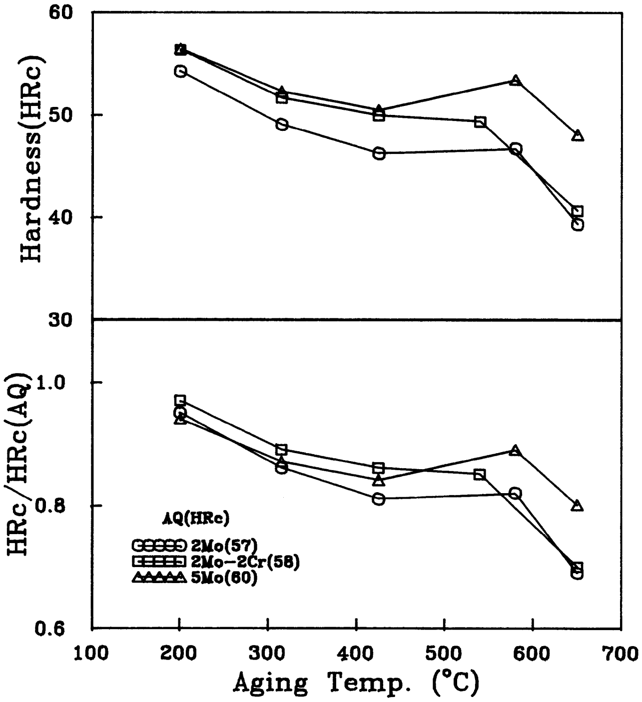

Fig. 7—Absolute hardness values and relative values with respect to the as-quenched hardness as a function of aging temperature in the (2–5)Mo-(0–2)Cr-0.35C steels.[5]

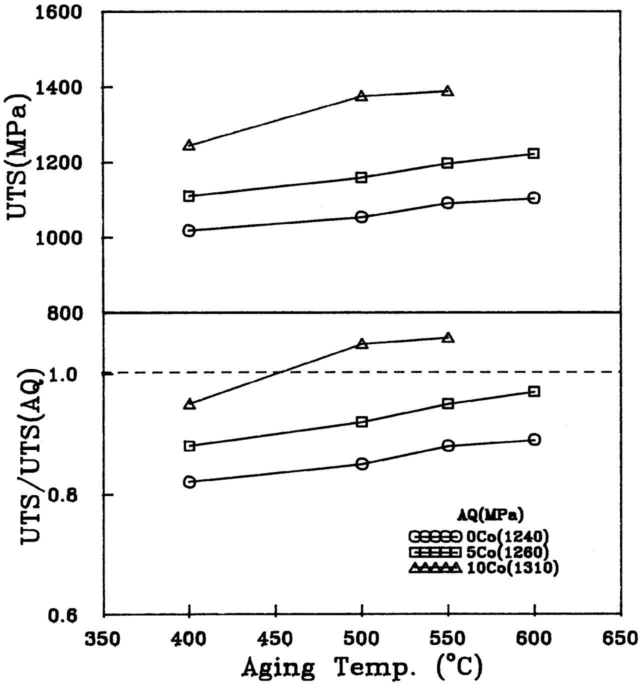

Fig. 9—Absolute tensile strength values and relative tensile strength values with respect to the as-quenched tensile strength as a function of aging temperature in the 3.3Mo-3.3Ni-0.55Cr-(0–10)Co-0.25C steels.[17]

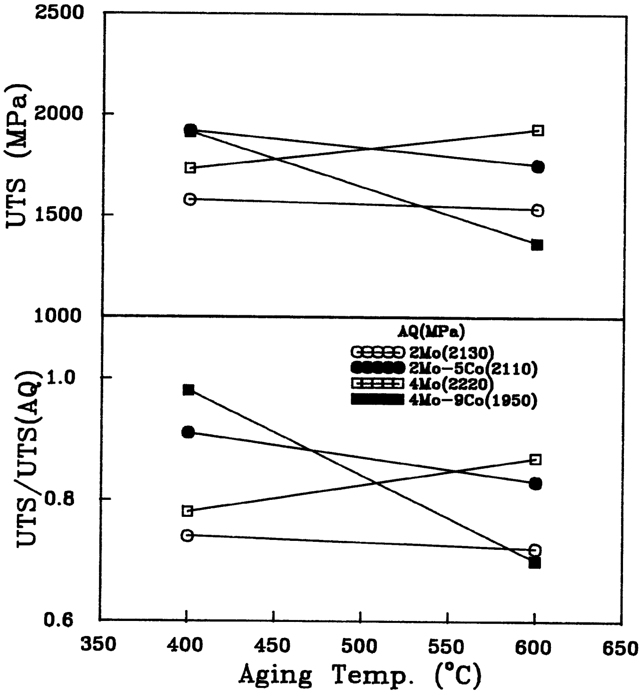

Fig. 8—Absolute tensile strength values and relative tensile strength values with respect to the as-quenched tensile strength as a function of aging temperature in the (2–4)Mo-(0–9)Co-0.4C steels.[15]

a well-recovered matrix cannot produce effective secondary hardening.

An addition of 14Co to the Mo-Cr steel results in a clear secondary hardening peak at 550 °C as well as an overall increase in hardness. When only Co is present, the effect of Co is not necessarily positive. This is shown in Figure 8 from the data reported by Clark and Thomas,[15] who showed the effect of only Co addition to Mo steels without the presence of Cr. While 5Co addition to 2Mo steel increases the overall strength but slightly weakens secondary hardening, an addition of 9Co to 4Mo steel instead leads to a sharp drop in strength at 600 °C. However, when both Cr and Ni are present in Mo steels, the presence of Co has a positive effect. This is shown in Figure 9 in a 0.25C-0.55Cr-3.3Mo-3.3Ni steel,[17] where an increase in Co content enhances not only the overall strength but also the extent of secondary hardening. For 10 wt pct Co, the tensile strength at 550 °C represents a larger value than that of the as-quenched condition. Comparing these two different results with our result on the 14Co addition, it is suggested that the presence of Cr and/or Ni is necessary in order to obtain the strong secondary hardening effect by the Co addition.

The addition of Ni to the Mo-Cr-Co or Mo-Co steel shifts the hardness peak to temperatures near 500 °C. This is shown in Figures 10[16] and 1, respectively. The Ni addition tends to promote M_2C carbide formation and promote M_3C dissolution, especially when Co is present.

The peak hardness temperatures in various alloys are compared in Table II. It is believed that Cr additions prevent M_2C precipitation by tying up the C as M_3C. The Ni additions cause the dissolution of M_3C and provide C for M_2C precipitation. The Co additions delay dislocation recovery[17] and provide the nucleation sites of M_2C formation when this can occur.[19] The Co additions also lower the growth rate of M_2C, since they increase the carbon activity and decrease its diffusivity in ferrite,[19] and in addition, they reduce the solubility of Cr in M_3C to reduce the stability of M_3C.

The Ni addition has until now been considered to only increase toughness. Although the addition of Ni is neces-

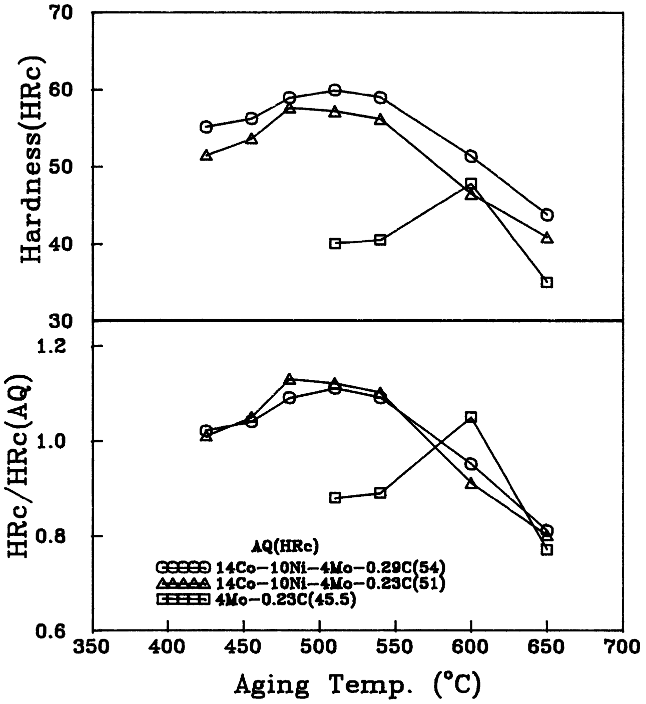

Fig. 10—Absolute hardness values and relative hardness values with respect to the as-quenched hardness as a function of aging temperature in the 4Mo steels with and without 14Co-10Ni addition.[16]

Table II. Peak Hardness Temperature (°C)

4Mo	2Mo-2.5Cr	2Mo-2.5Cr-14Co	1.5Mo-3Cr-14Co-10Ni	4Mo-14Co-10Ni[16]	4Mo-9Co[15]
600	?	550	500	500	no peak

sary to get the high intrinsic toughness of the matrix, *i.e.*, the high resistance to the cleavage, its role in secondary hardening has not been identified. Nickel has now been shown to play an important role as a cementite destabilizer, which promotes the dissolution of cementite and thus provides enough carbon to form fine M_2C carbides at lower temperatures, as shown in Figure 5. Furthermore, when Co is also present, the inhibition of dislocation recovery by the Co addition results in the finer dispersion of M_2C carbides which nucleate at the dislocation. Thus, the combined action of the Ni and Co is necessary to effectively obtain the ultrahigh strength at lower aging temperatures.

V. CONCLUSIONS

The effect of Cr. Co, and Ni additions on secondary hardening behavior in Mo steels has been systematically investigated.

1. Secondary hardening behavior is obtained by M_2C carbide formation and dissolution of M_3C.
2. The Cr additions eliminate secondary hardening by causing M_3C to stabilize.
3. The Co additions reduce the stability of Cr in M_3C and also prevent recovery of dislocations which are the sites for M_2C nucleation. The peak hardness temperature is reduced by 50 °C over only Mo containing steels.
4. The Ni additions to Mo-Cr-Co or Mo-Co steel reduce the peak hardness temperature to a lower temperature by another 50 °C to 500 °C. The Ni causes the cementite to destabilize, which provides the carbon needed to form the fine M_2C carbides at lower temperatures.
5. The combined actions of the Ni and Co are needed to effectively obtain the ultrahigh strengths at lower aging temperatures in steels containing Mo.

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REFERENCES

1. C.D. Little and P.M. Machmeier: U.S. Patent 4,076,525, 1978.
2. R. Ayer and P.M. Machmeier: *Metall. Trans. A*, 1993, vol. 24A, pp. 1943-55.
3. G.R. Speich, D.S. Dabkowski, and L.F. Porter: *Metall. Trans.*, 1973, vol. 4, pp. 303-15.
4. G.R. Speich: *Innovations in Ultrahigh Strength Steel Technology*, Proc. 34th Sagamore Army Materials Research Conf., G.B. Olson, M. Azrin, and E.S. Wright, eds., U.S. Army Materials Technology Laboratory, Watertown, MA, 1990, pp. 89-110.
5. E.C. Bain and H.W. Paxton: *Alloying Elements in Steels*, ASM, Metals Park, OH, 1966, pp. 197-222.
6. F.B. Pickering: *Physical Metallurgy and The Design of Steels*, Applied Science Publishers Ltd., London, 1978, pp. 133-40.
7. *Innovations in Ultrahigh Strength Steel Technology*, Proc. 34th Sagamore Army Materials Research Conf., G.B. Olson, M. Azrin, and E.S. Wright eds., U.S. Army Materials Technology Laboratory, Watertown, MA, 1990.
8. A.T. Davenport and R.W.K. Honeycomb: *Met. Sci.*, 1975, vol. 9, pp. 201-08.
9. R.J. Tunney and N. Ridley: *Met. Sci.*, 1979, vol. 13, pp. 585-90.
10. H. Kwon: *Metall. Trans. A*, 1991, vol. 22A, pp. 1119-22.
11. J.J. Irani and R.W.K. Honeycomb: *J. Iron Steel Inst.*, 1966, vol. 203, pp. 826-33.
12. D. Raynor, J.A. Whiteman and R.W.K. Honeycomb: *J. Iron Steel Inst.*, 1966, vol. 204, pp. 349-54 .
13. M.K. Tseng, D.Y. Lee, and H.L. Marcus: *Mater. Sci. Eng.*, 1983, vol. 60, pp. 73-77.
14. H. Kwon: *Scripta Metall.*, 1989, vol. 23, pp. 1001-04.
15. R.A. Clark and G. Thomas: *Metall. Trans. A*, 1975, vol. 6A, pp. 969-79.
16. M. Schmidt and R. Hemphil: *Innovations in Ultrahigh Strength Steel Technology*, Proc. 34th Sagamore Army Materials Research Conf., G.B. Olson, M. Azrin, and E.S. Wright, eds., U.S. Army Materials Technology Laboratory, Watertown, MA, 1990, pp. 239-60.
17. J.R. Holloway and A.D. Hopkins: *J. Iron Steel Inst.*, 1971, vol. 209, pp. 813-18.
18. G.B. Olson: *Innovations in Ultrahigh Strength Steel Technology*, Proc. 34th Sagamore Army Materials Research Conf., G.B. Olson, M. Azrin, and E.S. Wright, eds., U.S. Army Materials Technology Laboratory, Watertown, MA, 1990, pp. 3-66.
19. V.K. Chandhok, J.P. Hirth, and E.J. Dulis: *Trans. ASM*, 1963, vol. 56, pp. 677-93.