Note

A Comparison of the Effects of Cobalt, Silicon, Nickel and Aluminum on the Tempering Response of a Medium Chromium Secondary Hardening Steel

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(Received on September 1, 2005; accepted on February 1, 2006)

It is well known that cobalt additions can substantially increase the secondary hardening response in a number of alloys.^{1–4)} For steels where secondary hardening is due to the precipitation of Mo_2C or $(\text{Mo}, \text{Cr})_2\text{C}$ particles, cobalt additions result in a finer dispersion of alloy carbides and the enhanced secondary hardening is attributed to this refinement of alloy carbide size and spacing. The finer dispersion of alloy carbides is believed to result from an increased alloy carbide nucleation rate. Chandok *et al.*¹⁾ concluded that cobalt increases the nucleation rate because cobalt increases the activity of carbon in ferrite and thus increases the driving force for carbide precipitation. Speich *et al.*²⁾ observed that cobalt retards dislocation recovery and this would also lead to a higher nucleation rate and a finer dispersion of alloy carbides. Silicon additions also appear to enhance the secondary response in some steels.^{5–7)}

The purpose of this work has been to compare the effects of four elements on the secondary hardening response of a base steel, a 4.4 wt% chromium, 0.4 wt% carbon hot work die steel. This was done primarily to directly compare the effects of cobalt and silicon. Possible effects of aluminum and nickel additions on the tempering behavior of this base steel have also been investigated. The strong effects of aluminum additions on the tempering response of low alloy steels⁸⁾ are similar to those exerted by silicon additions to the same steel, which suggests aluminum may also influence the precipitation of alloy carbides and enhance secondary hardening.

In this work cobalt additions of 4 wt% and 8 wt%, silicon additions of 2 wt%, aluminum additions of 2 wt% and nickel additions of 4 wt% were made to a base hot-work die steel, having a nominal composition (in wt%) of 0.4C/4.5Cr/2Mo/0.5W/0.5V. This base steel was selected on the basis of its excellent toughness after secondary hardening.⁹⁾ The compositions of the six heats utilized are given in Table 1. These alloys were melted using pure starting materials in a vacuum induction furnace and then cast in copper chill molds as 9 kg cylindrical ingots 6.4 cm in diameter. The ingots were upset and cross forged at 1200°C to bars 7 cm wide and 1.75 cm thick. The forged bars were sand blasted and then homogenized at 1200°C in vacuum for 24 h and then furnace cooled. Specimen blanks were cut from the homogenized bars after they had been softened by tempering at 650°C for 2 h. Specimen blanks 7 cm×1.75 cm×2.5 cm were austenitized for 1 h in an argon atmosphere in a vertical tube furnace and quenched in oil. Austenitizing temperatures of 1000°C, 1050°C, 1100°C and 1200°C were used. These blanks were then tempered for 1 h in neutral salt baths and then water quenched. The tempering temperatures used were 200°C, 300°C, 400°C, 500°C, 550°C, 600°C and 650°C. The Rockwell C scale (R_c) hardness values were taken from specimens cut from the tempered blanks using an abrasive saw run at a slow speed under conditions of flood cooling. The reported hardness values are the average of five hardness measurements.

The hardness for each alloy is plotted for the as-quenched condition and as a function of tempering temperatures from 200 to 600°C for the four austenitizing temperatures in Fig. 1(a) through 1(d). In discussing these results the primary interests are the influence of the alloying additions on the peak secondary hardness, the influence of austenitizing temperature on the peak secondary hardness and how the alloying additions influence softening on tempering at temperatures above that associated with the peak secondary hardness.

To compare the influence of the alloying additions on the peak secondary hardness it seems most reasonable to make the comparison after austenitizing at 1200°C where the existence of primary carbides is least likely. These data are shown in Fig. 1(d) and for all alloys the peak secondary hardness occurs on tempering at 550°C. The peak secondary hardness of the base steel is 52.4 R_c . As expected the cobalt additions increase the peak secondary hardness

Table 1. Compositions of Alloys (wt%).

Alloy	C	Cr	Mo	W	V	Ni	Al	Si	Co	O ₂	N ₂	S
Base	0.38	4.4	2.0	0.49	0.43	0.005	0.008	<0.1	<0.1	0.0024	0.0027	0.0038
Base+Ni	0.39	4.2	2.1	0.50	0.50	4.4	<0.1	<0.1	<0.1	0.0019	0.0026	0.0046
Base+Al	0.38	4.2	2.0	0.50	0.45	<0.1	1.9	<0.1	<0.1	0.0013	0.0013	0.0058
Base+Si	0.40	4.2	1.9	0.51	0.46	<0.1	<0.1	1.85	<0.1	0.0038	0.0045	0.0029
Base+4Co	0.38	4.4	2.0	0.48	0.48	<0.1	<0.1	<0.1	3.9	0.0026	0.0024	0.0032
Base+8Co	0.38	4.3	2.0	0.49	0.49	<0.1	<0.1	<0.1	7.7	0.0019	0.0018	0.0034

The phosphorous levels are all less than 0.010 wt. %.

Fig. 1. The room temperature hardness (R_c) plotted as a function of tempering temperature for the base alloy and the modified alloys for austenitizing temperatures of (a) 1 000°C, (a) 1 050°C, (a) 1 100°C and (a) 1 200°C.

where it is 56.1 R_c and 57.8 R_c for the 4 wt% and 8 wt% cobalt additions, respectively. The peak secondary hardness is highest for the 2 wt% silicon addition and is 60.4 R_c . Surprisingly, the aluminum addition increases the peak secondary hardness to 57.4 R_c and thus the 2 wt% aluminum is almost as effective as the 8 wt% Co addition in increasing the peak secondary hardness. The nickel additions increase the peak secondary hardness by 2.5 R_c to 54.9 R_c .

The peak secondary hardness increases with austenitizing temperature for all of the alloys. The change in peak secondary hardness with increasing austenitizing temperature is similar for the base and base+Ni steels; for these two steels the peak secondary hardness increases by about 2 R_c as the austenitizing temperature is increased from 1 000 to 1 200°C. The peak secondary hardness increases modestly for the base+8Co alloy as the austenitizing temperature is increased from 1 000 to 1 200°C and for the base+4Co steel as the austenitizing temperature is increased from 1 000 to 1 100°C. However, the peak secondary hardness of the base+4Co alloy increases from 53.9 R_c to 56.1 R_c as the austenitizing temperature is increased from 1 100 to 1 200°C; the as-quenched hardness of the base+4Co steel increased from 57.4 R_c to 61.4 R_c as the austenitizing temperature was increased from 1 100 to 1 200°C. The peak secondary hardness of the base+Al alloy increases from 54.3 to 56.8 R_c as the austenitizing temperature increases from 1 000 to 1 050°C; the increase in hardness is more gradual as the austenitizing temperature

is further increased to 1 200°C. The relatively large increase in the hardness of the base+Al steel as the austenitizing temperature is increased to 1 050°C is coincident with the elimination of 10 to 15 vol% ferrite observed in the microstructure after austenitizing at 1 000°C. The peak secondary hardness of the base+Si steel increases dramatically as the austenitizing temperature is increased; the hardness of this steel is 54.3 R_c after austenitizing at 1 000°C and increases to 60.4 R_c after austenitizing at 1 200°C. This increase in hardness with increasing austenitizing temperature for the base+Si steel is coincident with decreasing amounts of primary carbides retained after austenitizing. After austenitizing at 1 000°C the base+Si alloy contains a dispersion of 1–2 μm diameter particles rich in tungsten, molybdenum, vanadium and chromium. It is assumed these particles are carbides. No such particles were observed in the base+Si steel at 1000 $\times$ by light microscopy after austenitizing at 1 200°C.

The degree to which the alloying additions improve the tempering response at tempering temperatures above 550°C, the temperature at which the peak secondary hardness is observed, depends on the alloying addition and the austenitizing temperature. While the nickel additions do enhance the peak secondary hardness the hardness of the base+Ni steel is slightly less than that of the base steel after tempering at 600°C and 650°C for all four austenitizing temperatures. On tempering at 600°C the hardness of the base+Al steel is always superior to that of the base steel

but the base+Al steel is always slightly softer than the base steel after tempering at 650°C. The hardness of the cobalt modified steels are substantially greater than those of the base steel after tempering at 600°C. However, after tempering at 650°C the hardness of the cobalt modified steels are the same as the base steel after austenitizing at 1 000°C, but exhibit hardness greater than that of the base steel after tempering at 650°C as the austenitizing temperature is increased. However, only after austenitizing at 1 200°C are the hardness of the cobalt modified steels substantially greater than that of the base steel after tempering at 650°C. The resistance to softening of the base+Si steel on tempering at 600°C and 650°C is actually inferior or comparable to that of the base steel after austenitizing at 1 000°C and 1 050°C. However, the resistance of the base+Si steel to softening is markedly superior to that of the base steel at the two higher austenitizing temperatures, particularly after austenitizing at 1 200°C. After austenitizing at 1 200°C the hardness of the base and base+Si steel tempered at 650°C are 45.6 R_c and 50.1 R_c respectively. The hardness of the base+4Co and base+8Co steels after austenitizing at 1 200°C and tempering at 650°C are 48.9 R_c and 47.6 R_c, respectively, which are less than the hardness of the base+Si steel austenitized at 1 200°C and tempered at 650°C.

The Charpy impact energies have been determined for all of the alloys for each of the four austenitizing temperatures after tempering at 550°C. For the austenitizing temperature of 1 050°C the Charpy impact energies and hardness of the alloys are 46.1 J (51.8 R_c), 16.3 J (56.8 R_c), 32.3 J (54.3 R_c), 13.6 J (53.9 R_c), 6.1 J (56.7 R_c), 14.9 J (57 R_c), for the base, base+Al, base +Ni, base+4Co, base+8Co and base+Si steels, respectively. The Charpy impact energies decrease with increasing austenitizing temperature for all of the steels. Considering the hardness level of the base+4Co alloy the Charpy impact energy of this alloy is very low and the Charpy impact energy of base+8Co alloy is the lowest of all of the alloys considered. The low toughness values achieved for the cobalt modified alloys is somewhat surprising considering the high toughness level of the cobalt containing secondary hardening steels such as AF1410¹⁰) but appear to be consistent with the very adverse effects of cobalt additions of up to 10 wt% on the fracture toughness of secondary hardening steel having a nominal base composition (in wt%) of 0.25C/3.3Ni/3.3Mo/0.55Cr/0.7Mn/0.25Si.³⁾

The carbides precipitated in tempering of the base steel considered here have been investigated by Lechtenberg.⁹⁾ Lechtenberg reported fine MC undissolved carbides were present in the as-quenched condition and at all tempering temperatures. In addition, the carbides precipitated on tem-

pering were reported to be M₃C at 400°C, M₂C and M₆C at 550°C and MC and M₆C at 650°C. The M₆C carbides observed after tempering at 550°C formed by an *in-situ* transformation of the M₃C carbides and were comparable in size to the M₃C particles formed on tempering at 400°C. It is suggested that the significant effects of silicon, aluminum and cobalt on the secondary hardening response of these alloys may involve effects on carbide precipitation beyond the refinement of the size and spacing of the precipitates of M₂C.

In summary, the effects of additions of 4 wt% cobalt, 8 wt% cobalt, 2 wt% silicon, 2 wt% aluminum and 4 wt% nickel on the tempering response of a base hot work die steel have been compared for four different austenitizing temperatures. After austenitizing at 1 200°C all alloying additions significantly enhance the peak secondary hardness. The silicon addition is by far the most effective; the aluminium addition was found to be more effective than the addition of 4 wt% cobalt and nearly as effective as the addition of 8 wt% cobalt. The nickel addition was the least effective, but did increase the peak secondary hardness by about 2.5 R_c. The effectiveness of some of these additions in enhancing the peak secondary hardness was found to be sensitive to the choice of austenitizing temperature. Silicon's influence on the peak secondary hardness was more sensitive to the choice of austenitizing temperature than those of the other alloy additions. Apparently this was because of the dissolution of primary carbides in the base+Si steel with increasing austenitizing temperature. The influence of the additions on the hardness after tempering at 600°C and 650°C depended again on the addition and the choice of austenitizing temperature. It was found that the silicon additions were more effective than any of the other alloying additions in maintaining hardnesses at 600°C and 650°C, provided higher austenitizing temperatures were used.

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