

Influence of Nickel and Molybdenum on the Phase Stability and Mechanical Properties of Maraging Steels

M. Ahmed, I. Nasim, and S.W. Husain

The effect of nickel and molybdenum concentrations on the phase transformation and mechanical properties of conventional 18Ni(350) maraging steel has been investigated. Both of these elements act as strong austenite stabilizers. When the concentration of molybdenum or nickel is greater than 7.5 or 24 wt%, respectively, the austenite phase remains stable up to room temperature. In both molybdenum- and nickel-alloyed steels, the austenite phase could be transformed to martensite by either dipping the material in liquid nitrogen or subjecting it to cold working. When 7.5 wt% Mo and 24 wt% Ni were added in combination, however, the austenite phase obtained at room temperature did not transform to martensite when liquid-nitrogen quenched or even when cold rolled to greater than 95% reduction. The aging response of these materials has also been investigated using optical, scanning electron, and scanning transmission electron microscopy.

Keywords

maraging steels, nickel, molybdenum, Charpy impact tests

1. Introduction

CONVENTIONAL maraging steels transform from the high-temperature face-centered cubic (fcc) phase to the body-centered cubic (bcc) martensitic phase when cooled from elevated temperatures. The transformation to martensite in the conventional 18Ni(350) grade occurs at approximately 200 °C and is independent of cooling rate (Ref 1). The lath-type martensite obtained is fairly ductile and can be cold formed into required shapes using processes such as rolling, forging, flow forming, and extrusion. Because the martensite inherently incorporates a very high dislocation density, cold working only marginally increases hardness. For example, in the case of 18Ni(350) grade, the hardness in the annealed condition is approximately 340 HV; after cold rolling (more than 90% reduction), hardness increases to approximately 370 HV.

Strengthening of the martensite is accomplished through precipitation hardening. The steels are aged in the temperature range between 400 and 550 °C to achieve maximum strength (Ref 2-6). The intermetallics that form upon aging include Ni₃Ti, Ni₃Mo, Fe₂Mo, and Fe₇Mo₆. When aging is carried out at temperatures above 550 °C, softening occurs due to overaging and to the formation of austenite that remains stable even

after cooling to room temperature. The austenite so formed is normally referred to as reverted austenite (Ref 3). The deterioration in mechanical properties, however, is accompanied by marked improvement in electrical and magnetic properties (Ref 7, 8). In applications requiring good electrical and magnetic properties along with reasonable mechanical strength (e.g., hysteresis motors), the steels are heat treated in the temperature range between 550 and 650 °C.

The authors' previous work investigated remelting of 18Ni(350) maraging steel scrap and improvement in mechanical properties due to additional alloying with niobium and titanium. Addition of niobium proved beneficial in terms of imparting both hardness and toughness (Ref 9). In the present work, the influence of molybdenum and nickel concentration on properties and phase transformations, with particular reference to austenite stability, has been studied. Aging response of these materials has been investigated at selected temperatures.

2. Experimental Method

Melting was carried out in a vacuum induction melting and casting furnace. The 18Ni(350) maraging steel scrap was first cleaned mechanically using abrasive paper and then washed in soap solution. It was subsequently vapor degreased in carbon tetrachloride. Additional alloying was carried out using high-purity (99.9%) materials. The compositions of the alloys investigated are given in Table 1.

Ingots weighing 12 kg were cast in a yttria-coated and preheated graphite mold. Heating was carried out using a collar-type resistive heater (Fig. 1). The temperatures at the top and

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Table 1 Compositions of the alloys studied

Material	Ni	Co	Mo	Ti	Al	C	Fe
18Ni(350)	17-18	11-12	3.5-4.5	1.6-1.8	0.1 max	0.03 max	bal
Alloy 1	18.20	12.10	5.50	1.56	0.12	0.035	bal
Alloy 2	18.50	11.50	7.50	1.50	0.11	0.032	bal
Alloy 3	22.00	12.00	3.80	1.50	0.10	0.025	bal
Alloy 4	24.00	11.50	3.50	1.55	0.10	0.030	bal
Alloy 5	24.00	11.00	7.50	1.50	0.08	0.021	bal

bottom of the mold were 700 and 300 °C, respectively. The temperature gradient was caused by the location of heater and by the fact that the thickness of the mold wall was kept relatively thin at the top (see Fig. 1). Thick copper plate at the bottom of the mold also helped to attain the gradient.

The mold design limited the shrinkage cavity to the top part of the ingot. After cutting of the top part, the ingots were forged using a 500 kg pneumatic hammer. The ingots were first soaked at 1250 °C for 3 h in a gas-fired furnace before forging commenced. After 50% reduction, the forgings were resoaked for a minimum of 1/2 h. The final forging temperature was kept between 700 and 800 °C to achieve grain size on the order of 10 to

20 μm. The final product was in the form of square bars of 12 cm on each side and round bars with a diameter of 13 cm.

Conventionally, maraging steels are produced using a two-stage melting technique. The constituents are first melted in a vacuum induction melting and casting furnace. The ingot produced is remelted in a vacuum arc or electroslag remelting furnace. The second-stage melting is essential to remove macro- and microsegregation (Ref 1). It also reduces the size and number of inclusions. In the present work, however, only single-stage melting was employed. Because the ingot size used in the present study was small and fairly high reduction ratios were employed during hot forging, a reasonable degree of homogeneity was achieved.

Some segregation was visible in the form of banded structure (Fig. 2). (In the as-forged condition, the bands were not visible. They could be delineated clearly only in samples that

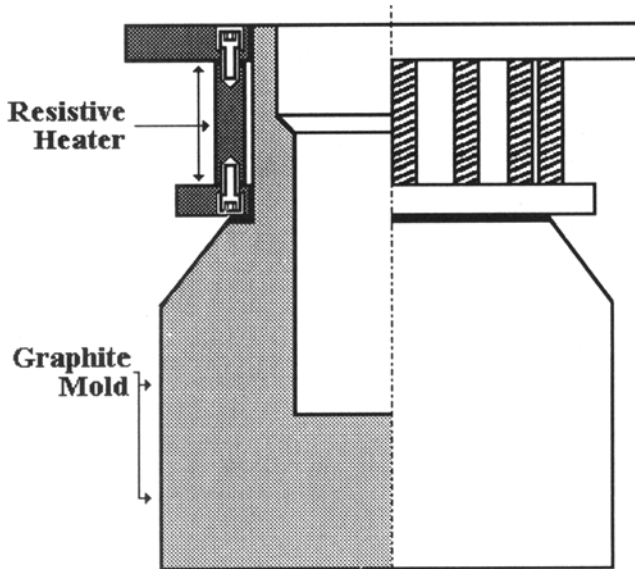


Fig. 1 Schematic showing the graphite mold and the collar-type resistive heater used to heat the mold

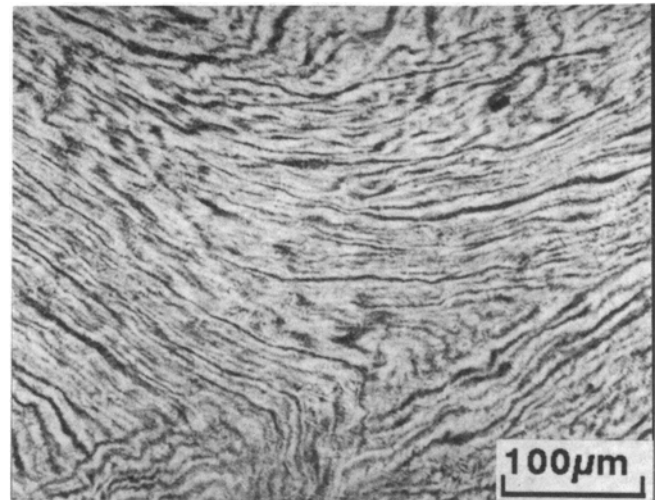
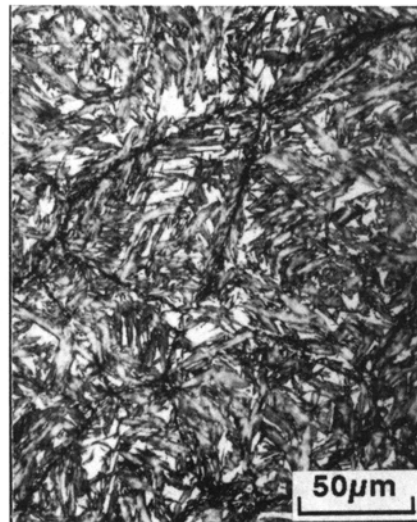


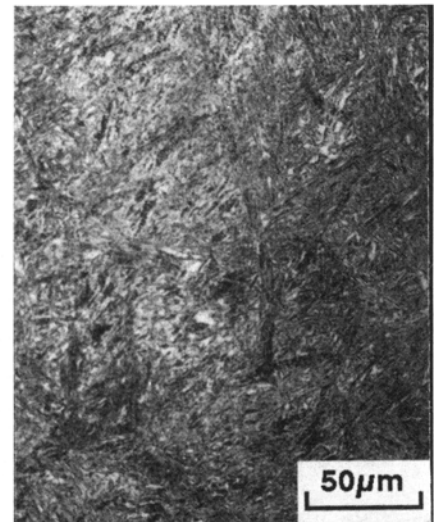
Fig. 2 Macrosegregation in an as-forged specimen of alloy 2



(a)



(b)



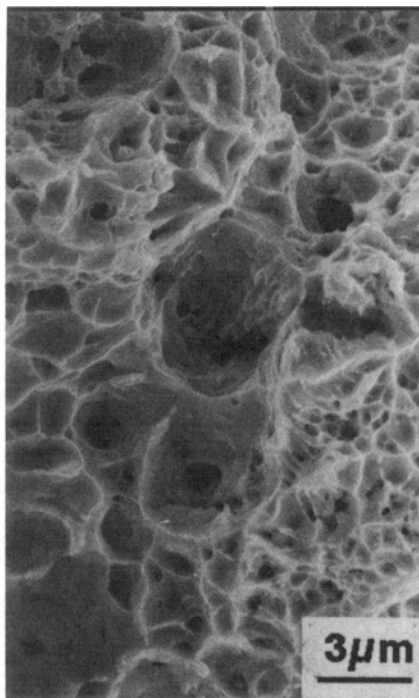
(c)

Fig. 3 Optical micrographs of alloy 2 showing the development of martensite as a function of dipping time in liquid nitrogen. (a) 30 s. (b) 1 min. (c) 15 min

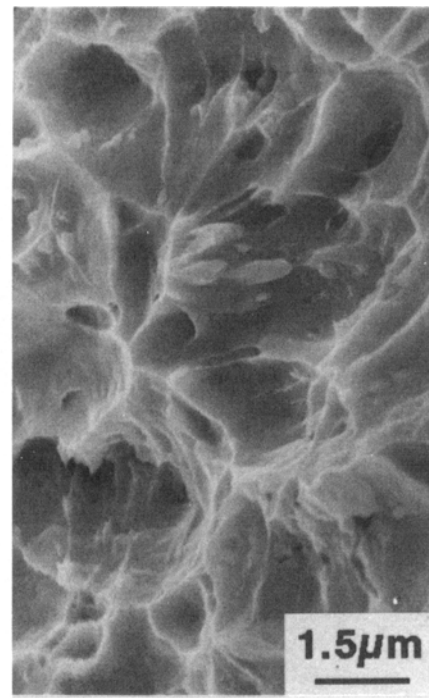
were aged at 500 °C for 15 min or more and then lightly etched with a 2% solution of ferric chloride.) Energy-dispersive x-ray analysis of the bands was carried out. The compositions of different regions were within the experimental error of the technique employed, and no conclusion could be drawn with regard

to the elements being segregated. With regard to segregation, it can perhaps be safely assumed that properties of the alloy investigated will improve when two-stage melting is employed.

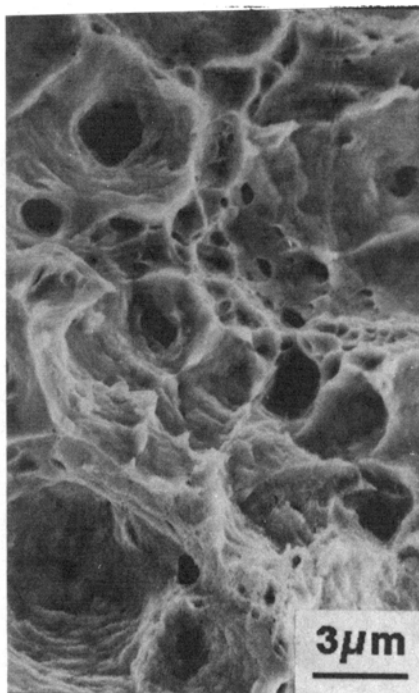
Charpy impact tests and tensile tests were carried out per ASTM specifications. The fracture surfaces were examined us-



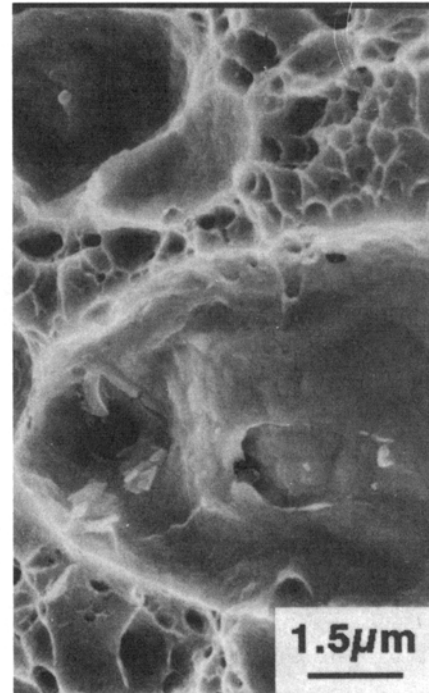
(a)



(b)



(c)



(d)

Fig. 4 SEM fractographs of alloy 2. (a) and (b) Austenite phase. (c) and (d) Martensite phase

Table 2 Mechanical properties of stock material and alloy 1 in the annealed and aged conditions

Property	Stock material		Alloy 1 (remelted, forged, and alloyed with 5.5 wt% Mo)	
	Annealed	Aged	Annealed	Aged
Hardness, HV	340 ± 10	700 ± 10	340 ± 5	700 ± 10
Tensile strength, MPa (ksi)	1205 ± 35 (175 ± 5)	2070 ± 140 (300 ± 20)	1170 ± 35 (170 ± 5)	2480 ± 35 (360 ± 5)
Elongation (25 mm gage length), %	6 ± 2	1.2 ± 0.3	15 ± 5	4 ± 0.5
Reduction in area, %	25 ± 10	2.5 ± 0.5	71 ± 10	8 ± 0.5
Charpy impact strength, J	40 ± 5	4 ± 1	170 ± 5	9 ± 1

Table 3 Results of tensile testing

Material	Phase	Tensile strength		Elongation (25 mm gage length), %	Reduction in area, %
		MPa	ksi		
Alloy 2	Austenite	1000	145	24	74
	Martensite	1124	163	17	69
Alloy 4	Austenite	814	118	23	78
	Martensite	1027	149	19	70

Table 4 Composition of molybdenum-rich precipitates

Condition	Composition, wt%				
	Fe	Ni	Co	Mo	Ti
Before aging	33.8	6.2	7.6	48	3.2
After aging	44.3	13.4	7.4	33.5	1.2

ing scanning electron microscopy (SEM). The microstructural developments were examined using optical microscopy, SEM, and scanning transmission electron microscopy (STEM). Foils for TEM were prepared by electropolishing using 20% perchloric acid in ethanol.

3. Results and Discussion

In previous work (Ref 9), the authors investigated the possibility of gainfully utilizing maraging steel scrap by remelting in a vacuum induction melting and casting furnace. It was observed that about 10% Ti is lost during vacuum processing. Because titanium is the principal hardening constituent, its loss causes reduction in hardness achieved following aging. Addition of pure titanium to offset the loss was not a solution. Some of the titanium became oxidized, and the resulting inclusions adversely affected properties. Molybdenum, as is well known, also forms intermetallics when maraging steels are age hardened. In addition, it minimizes intercrystalline cracking by preventing segregation of impurities at prior-austenite grain boundaries (Ref 10). Additional alloying with about 1.5 to 2 wt% Mo (alloy 1) compensated for the titanium loss and also improved toughness. The important properties determined for alloy 1 are presented in Table 2. The properties obtained for the 18Ni(350) maraging stock material are also given for comparison.

To further improve properties, an alloy containing 7.5 wt% Mo (alloy 2) was investigated. Martensite transformation did not occur in this alloy, and the material exhibited fcc structure following hot forging or after annealing at 820 °C and air cooling. When the steel was quenched in iced brine, only 30% of the

material transformed to martensite. However, when the samples were dipped in liquid nitrogen for time intervals of more than 5 min, more than 95% of the austenite transformed to martensite.

In order to establish the minimum time interval required to complete the transformation to the martensite phase, samples were dipped in liquid nitrogen for different times and the microstructures were examined using optical microscopy (Fig. 3). Martensite needles were first observed after 30 s of dipping time (Fig. 3a). The number density of the martensite platelets increased as the dipping time increased (Fig. 3b and c). The x-ray spectrum obtained from the specimen dipped for 15 min contained no peak from the fcc phase, signifying that the austenite content was less than 5%.

The above experiment used round bars with a diameter of 4 mm. Transformation from austenite to martensite was observed throughout the cross section, and the number density of the platelets increased uniformly across the thickness. (Similar transformations were observed in 24 wt% Ni steels, which are discussed later in this paper.) The austenite-to-martensite transformation could also be induced when the steel was subjected to cold rolling. Almost 100% transformation to martensite occurred when reduction ratios above 80% were employed.

The Charpy impact values in fcc material and following transformation to bcc structure by liquid nitrogen quenching were 290 ± 5 and 215 ± 5 J, respectively. The corresponding hardness values were 215 ± 5 and 300 ± 5 HV, respectively. The toughness of the austenite phase is perhaps one of the highest ever reported in the literature. The difference in impact values between austenite and martensite phases can be associated with the fact that fcc structure, because of its higher number of slip systems, absorbs much more energy before fracturing. The fracture surfaces were examined by SEM and are depicted in Fig. 4. Both sets of micrographs are typical of fractures in highly ductile materials. However, relatively higher material flow is visible in the fcc fracture surfaces (Fig. 4a and b). Tensile testing also showed differences between fcc and bcc in terms of strength, percentage elongation, and reduction in area (Table 3).

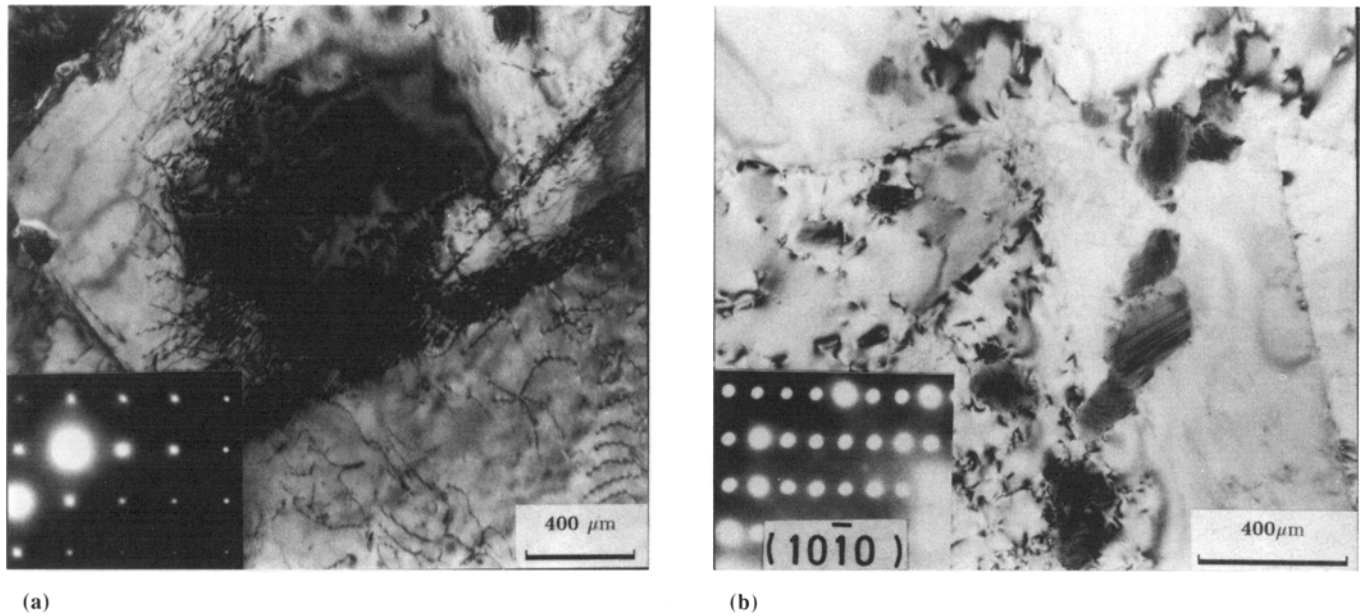


Fig. 5 TEM examination of alloy 2. (a) Austenite phase, with its corresponding diffraction pattern (inset). (b) Precipitates within the grains and along the grain boundaries of the austenite; the inset diffraction pattern was obtained from the precipitate.

Examination of the austenite phase by TEM revealed that a fairly high dislocation density exists even in the annealed state (Fig. 5a). In addition, precipitates were present along the grain boundaries and within the grains (Fig. 5b). The diffraction pattern from the precipitates, obtained using an energy-dispersive x-ray analyzer in the STEM mode, is given in Table 4. The precipitates were of the Fe_2Mo type. The high density of dislocations and the precipitates most likely contributed to the high toughness.

Recently, Sha et al. (Ref 6) have carried out a detailed analysis of the precipitation process in maraging steel grade C-300. Using atom probe analysis and thermochemical calculations, they have shown that Fe_7Mo_6 is a more stable phase than Fe_2Mo . They have also noted that the diffraction patterns of Fe_7Mo_6 and Fe_2Mo are quite similar; it is difficult to separate the two phases on the basis of electron diffraction patterns alone. In TEM energy-dispersive x-ray analysis, contributions from the matrix can never be ruled out. However, in the annealed state the precipitates were fairly large and the contribution of the matrix was minimized. From the chemical information obtained in the present work, it is likely that the precipitates observed in the annealed austenite were Fe_2Mo rather than Fe_7Mo_6 .

Charpy impact values decrease sharply when the steel is aged following quenching in liquid nitrogen. The values obtained after aging at 450 and 550 °C for 1 h were 8 ± 1 and 5 ± 1 J, respectively. The corresponding hardness values were 600 and 680 HV, respectively. The tensile strength after aging at 550 °C for 1 h was 2400 MPa (350 ksi). Charpy impact and tensile strength values of the deformation-induced martensite could not be obtained because of rolling machine size limitations. Only small pieces could be rolled, from which standard specimens could not be prepared. A maximum hardness of 810 ± 10 HV was achieved after aging at 525 °C for 1 h. The im-

proved hardness resulted from complete transformation to the martensitic phase following cold rolling; normally, some austenite is expected to be retained even after several hours of dipping in liquid nitrogen. The additional defects incorporated during cold rolling also helped to achieve a finer distribution of precipitates, which further contributed to higher hardness.

Detailed analysis of the precipitation process that occurs during aging is not within the scope of this paper and will be discussed elsewhere. However, in light of recent identification of the Fe_7Mo_6 phase, a brief discussion of the molybdenum-rich precipitates in the aged condition will be presented. As the molybdenum content in alloy 2 is quite high, molybdenum-rich precipitates were observed in all the specimens aged in the temperature range from 450 to 700 °C. At aging temperatures up to 600 °C, due to the small precipitate size, representative analysis of the precipitates could not be obtained. However, at aging temperatures above 640 °C, the precipitates were large enough to be analyzed individually with relatively little contribution from the matrix. Occasionally, because of the different etching behaviors of the precipitates, some of them protrude at the edge of the foil and are ideally suited for analysis. The chemical information obtained from such a precipitate in a specimen aged at 640 °C is also given in Table 4. These precipitates are enriched in nickel but depleted in molybdenum when compared with precipitates observed in the annealed condition. Based on analysis of diffraction patterns and chemical information, it appears that even in the aged condition the precipitates are of the Fe_2Mo type.

Nickel is also an important constituent of maraging steel. It imparts toughness and is known to decrease the martensite start (M_s) temperature. When these steels are aged, nickel combines with titanium and molybdenum to form Ni_3Ti and Ni_3Mo precipitates (Ref 3). In the early years of maraging steel development, alloys containing 25 wt% Ni were developed. These alloys possessed fcc structure following cooling from elevated

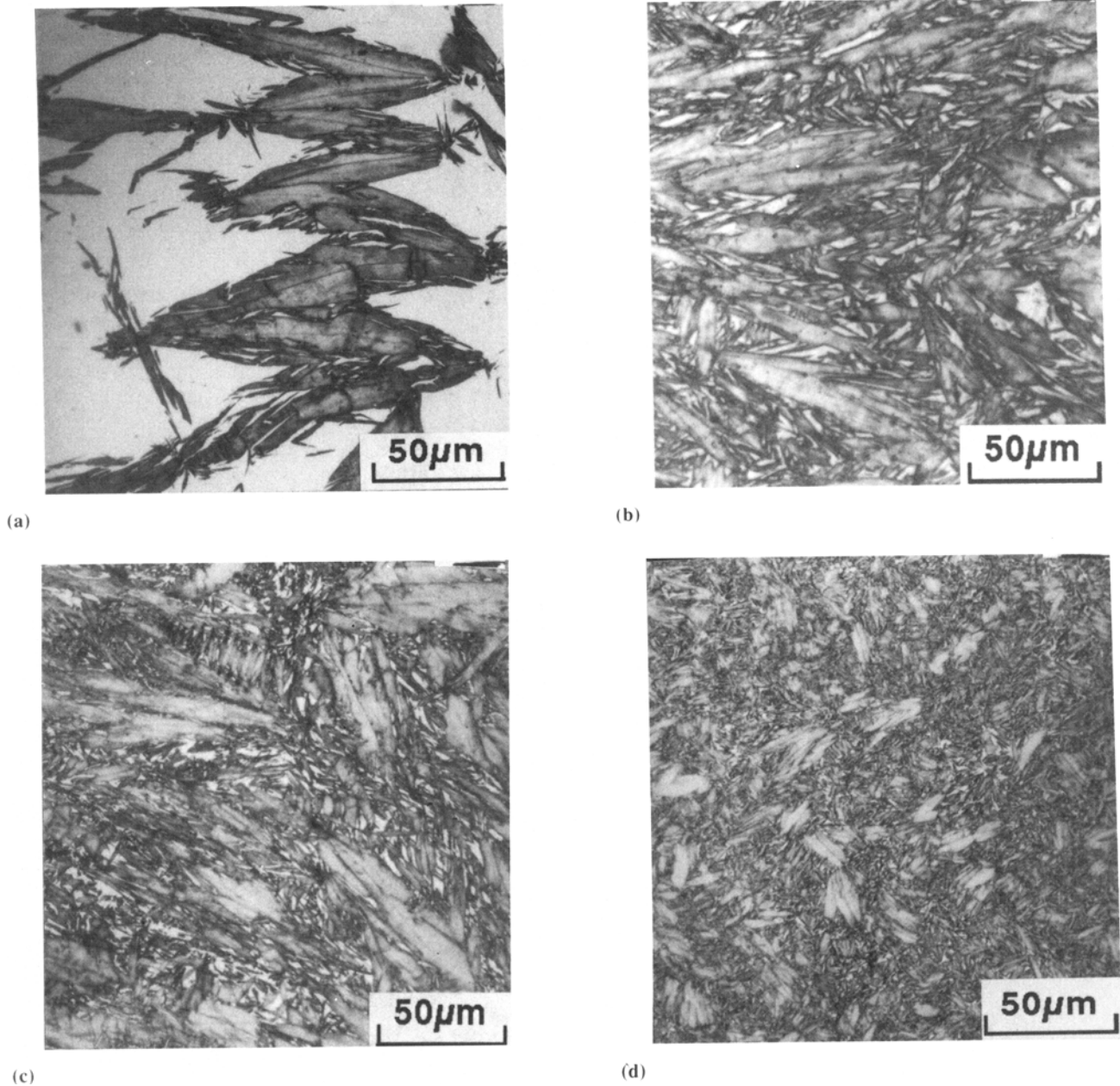


Fig. 6 Optical micrographs of alloy 4 depicting the number density of martensite platelets as a function of dipping time in liquid nitrogen. (a) 10 s. (b) 30 s. (c) 1 min. (d) 15 min

temperatures. Double-stage heat treatment was employed to increase hardness (Ref 10). However, due to the complexity of heat treatment and rather unpromising properties, work on these steels was discontinued. In the present study, high-nickel steels have been reinvestigated.

Alloy 3, containing 22 wt% Ni, exhibited a martensitic structure. Hardness in the annealed condition was 300 HV. A maximum hardness of 640 HV was obtained after aging at 500 °C for 1 h. Charpy impact strength in the annealed and in aged conditions was 215 ± 5 and 8 ± 1 J, respectively. The increase in nickel by 4 wt%, compared with the stock material, significantly improved toughness in both the annealed and the aged conditions.

When the nickel concentration was increased to 24 wt% (alloy 4), the austenite-to-martensite transformation did not occur following hot forging. Similarly, there was no transformation to martensite phase after the specimens were annealed at 820 °C and air cooled. However, when the samples were quenched in iced brine, 50% transformation to martensite was observed. When the 24 wt% Ni steel was dipped in liquid nitrogen, most of the austenite transformed to martensite.

As in the case of high-molybdenum steels, the samples were dipped in liquid nitrogen for different time intervals and the microstructures examined in an optical microscope (Fig. 6). Martensite needles were first observed after 10 s of dipping (Fig. 6a). The number density of the martensite platelets in-

creased as the dipping time increased (Fig. 6b to d). It is interesting to note that as the dipping time increases, the needles become smaller and more dense in number. The large needles that form in the initial stages shrink, and new, densely packed, smaller needles form. This aspect is not clearly seen in the molybdenum-alloyed steel. It is important to mention here that all the specimens had similar grain size. The large needles that form in the initial stages extend up to the grain boundaries. At longer dipping times, the larger needles shrink and give way to smaller, more densely packed platelets.

As before, 4 mm diam specimens were used in the above experiment. Lack of thermal equilibrium can also influence transformation. In order to reduce this, thin specimens (0.5 mm thick) were also subjected to the liquid nitrogen quenching. A similar trend was observed; however, the transformation occurred at a much faster rate. Relatively large needles were first observed after 2 s of dipping. The number density of the needles increased rapidly as the needle size decreased. After 30 s of dipping, no further change was observed. On the basis of this test, it is difficult to establish whether the transformation is isothermal or athermal. Both types have been observed in Fe-Ni martensites (Ref 11, 12).

Hardnesses of 160 ± 5 and 300 ± 10 HV, respectively, were obtained in the austenite phase and the liquid-nitrogen-transformed martensite phase. Charpy impact values of 260 ± 5 and 120 ± 5 J, respectively, were obtained in the annealed condition and after dipping in liquid nitrogen for 15 min. Tensile strengths in the annealed condition and after transformation to the martensite phase following dipping in liquid nitrogen are given in Table 3. The austenite-to-martensite transformation could also be induced when the steel was subjected to cold rolling and reduction ratios greater than 80% were employed. A maximum hardness of approximately 760 HV was achieved in the cold-rolled material after aging at 525 °C for 1 h.

It has been demonstrated that both molybdenum and nickel act as strong austenite stabilizers. On a weight percent basis, molybdenum appears to be about four times stronger than nickel in terms of shifting the M_s temperature to lower values. The austenite produced by adding molybdenum and nickel can be transformed to bcc by cold forming or dipping in liquid nitrogen. However, this is not the case when nickel and molybdenum are added together (24 wt% Ni, 7.5 wt% Mo) (alloy 5). In this alloy, the fcc phase obtained remains stable regardless of the treatment imparted. It does not transform even after being subjected to reduction ratios greater than 95%. Dipping in liquid nitrogen for several hours also does not transform the Ni-Mo-rich austenite. The hardness and Charpy impact strength of alloys were found to be 220 HV and 250 J, respectively.

Alloys 3, 4, and 5 possess fcc structure at room temperature. As such, these alloys do not respond to heat treatment and must be treated in liquid nitrogen or by cold working. This may be undesirable from a practical point of view. However, there are applications where this can be used to advantage—for example, when thin tubes have to be cold extruded or flow formed. The relatively soft fcc austenite will easily flow under load and, in the process, transform to bcc phase. Subsequent aging would most likely produce a material of very high strength. This claim can be made on the basis of the hardness achieved in samples that were aged after cold rolling. In the case of alloy 5, the ma-

terial would remain fcc even after deep drawing and perhaps be suitable for nonmagnetic and cryogenic applications.

4. Summary

The effect of molybdenum and nickel concentrations on the phase stability of maraging steel has been investigated. The results are summarized below:

- Both molybdenum and nickel act as strong austenite stabilizers. When the concentration of molybdenum or nickel is greater than 7.5 or 24 wt%, respectively, the austenite phase remains stable up to room temperature.
- The austenite possesses exceptionally high toughness. The Charpy impact strengths of molybdenum- and nickel-stabilized austenite were found to be 290 and 260 J, respectively.
- When molybdenum and nickel are added together (7.5 wt% Mo and 24 wt% Ni), the austenite phase that forms does not transform to martensite either by dipping in liquid nitrogen or by cold rolling to greater than 95% reduction.

Acknowledgments

The authors would like to thank Mr. Mehrab Gul for his help in preparation of the alloys and Mr. M. Afzal for his help in the photography laboratory.

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