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Order hardening in nickel–molybdenum and nickel–tungsten alloys

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Order hardening characteristics were studied in Ni–20% Mo, Ni–25% Mo and Ni–20% W. They were processed through quench and reheat cycles and the progress of order hardening was monitored through microhardness measurements. A correlation with the microstructure as observed with polarized light microscopy and transmission electron microscopy was established. Among the various factors, such as degree of order, domain size, coherency strains and dislocations, which can contribute to strengthening, domain size seems to play a major role.

1. Introduction

The increase in strength of alloys with the progress of ordering is an attractive concept in the development of alloys. While its full potential is yet to be realized in practice, there are several significant contributions in this area. The topic has been reviewed by leading researchers in this field [1–4].

In his considerations of strength in isostructurally ordered alloys, Cottrell [5] established the importance of a critical domain size for peak strength. Hence maximum strength can be expected at an intermediate stage of ordering treatment. In disordered alloys, dislocations move singly, while interactions of superdislocations with matrix dislocations and antiphase boundaries (APBs) will lead to an increase in flow stress.

In the 1930s, hardening in neostructurally ordered alloys was a subject of intensive study. There had been a resurgence of interest in this area, after Arunachalam and Cahn [6] reported their careful work on CuAu. There is nearly a doubling of strength in this alloy. The extra hardening may be attributed to the change in lattice symmetry, resulting in substantial misfit stresses.

The early studies on order hardening of Ni_4Mo are due to Dubrovina and Umansky [7]. At 500 and 600 °C, no increase in hardness was observed. The increase observed on ordering at 700 and 800 °C was ascribed to the growth of domains and an increase in the degree of order within them. Snyder and Brooks [8] established correlations between strength and domain size. Chakravarti *et al.* [9] extended this work. They observed a decrease in ductility and intergranular fracture of the ordered phase. They attributed these to the inhibition of cross-slip and the pile up of coplanar dislocation arrays. Ling and Starke [10] have suggested that the high strength is due to the high density of dislocations which are generated to relieve misfit stresses at the interface. Irani *et al.* [11] suggested that order twinning and intergranular fracture operated to relieve stresses in the overaged condition. Chen *et al.* [12] studied the influence of an applied stress on ordering of Ni_4Mo and noted that the number of domain variants within any one grain was affected with a consequent change in mechanical properties.

Recently, Kao [13] measured the strength of ordered Ni_4Mo alloys via the tensile mode. Theirs is perhaps the first and only study relating yield strength and elongation with ageing time at various temperature up to and well beyond the critical temperature of ordering (~ 868 °C). Two initial domain sizes of 24 and 3000 nm were obtained by prior ordering treatment. As expected, a 50% increase in the strength was exhibited by the specimen with smaller domain size. Kao [14], however, ascribed this increase in strength to the degree of ordering rather than domain size. Their studies further revealed remarkable constancy of strength with test temperatures. However, the ductility remained inadequate (~ 1%). A steep rise in elongation values was observed when the samples were tested at temperatures well above the ordering temperature with attendant loss in strength by about 50%. However, there is only one early study of order hardening in Ni_4W by Epermian and Harker [15].

It may be relevant here to note a few significant recent contributions to hardening of CuPt. Irani and Cahn [16] ascribe hardening in CuPt to lattice mismatch and domain size. This paper is also noteworthy for its comparative study of hardening in several noncubic ordered alloys including Ni_4Mo and Ni_4W.

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Mitchell *et al.* [17] believe that hardness changes are dependent largely on the internal strains resulting from the cubic to rhombohedral distortion of CuPt.

2. Experimental procedure

Preparation of alloys consisted of melting the constituents in appropriate amounts in an arc furnace in an argon environment. The strips were cut into small pieces and melted several times to ensure homogeneity in composition. Finally the strips obtained were rolled to 2.5 mm thickness and cut into pieces 10 mm x 10 mm for microhardness measurements and optical microscopy. Specimens for electron microscopic examination were further rolled to 250 μm thickness.

Samples for optical microscopy were etched in aqua regia. A MIM-7 metallograph, in conjunction with a gypsum λ-plate and a birefringent analyser, was used for photomicrography. Specimens for electron microscopy were jet polished in an electrolytic bath containing 40% orthophosphoric acid in distilled water. Microhardness measurements were carried out on a πMT microhardness tester. The load used throughout the investigation was 100 g.

Ni–20% Mo and Ni–25% MO alloys were disordered at 1050 °C for 10 and 5 h, respectively. Ni–20% W specimens were solution treated at 1300 °C for 1 h. Ni–20% Mo and Ni–25% Mo alloys were subsequently aged at 700 and 800 °C for periods ranging up to 100 h. The ordering treatment for Ni–20% W was carried out at 820° and 950 °C for similar periods. Evacuated silica capsules were invariably used for performing heat treatment.

3. Results

3.1. Microhardness measurements

Fig. 1 shows the variation of microhardness values with isothermal ageing time at two temperatures, 700 and 800 °C, for Ni–20% Mo. Both curves show similarities to age-hardening behaviour. At 700 °C signs of overageing are apparent. At 800 °C the curve becomes almost flat after attaining the microhardness values of 510 kg mm^{-2} in 10 min. The peak value of 536 kg mm^{-2} is reached after ageing for 2 h at 700 °C followed by a monotonic decrease in microhardness values, indicating softening of the material. The maximum for 700 °C is slightly higher than that for 800 °C.

The microhardness isotherms of Ni–25% Mo at 700 and 800 °C are shown in Fig. 2. Both curves are of precipitation type and exhibit overageing. The maxima are attained in 8 and 2 h at 700 and 800 °C, respectively. The values of microhardness peaks are at 638 and 572 kg mm^{-2} at respective temperatures. At the lower temperature, there is a tendency towards greater hardening than at the higher temperature. A comparison of Figs 1 and 2 reveals that the maxima are shifted to longer annealing time and also to higher values with the increase in molybdenum content of the alloys.

The microhardness versus isothermal annealing time plot for Ni–20% W is shown in Fig. 3 for the temperatures 820 and 950 °C. The highest values of microhardness, e.g. 645 and 620 kg mm^{-2} occur after 4 h and 30 min at 820 and 950 °C, respectively. In this alloy also the peak values are higher at lower temperatures than at higher temperatures. In comparison to Ni–20% Mo, Ni–20% W exhibits greater order strengthening. while at lower temperatures the time to reach maximum hardness is identical, Ni–20% Mo attains its peak value faster at higher temperatures.

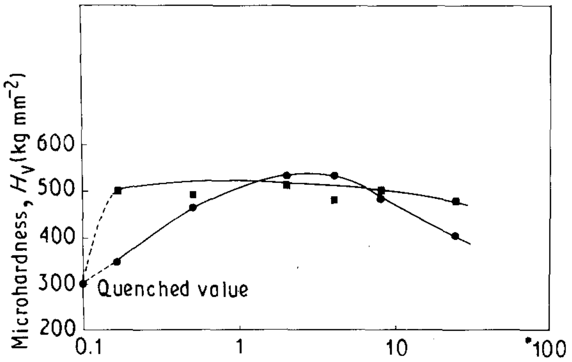

Figure 1 Microhardness isotherms for Ni–20% Mo alloy at (●) 700 and (■) 800 °C.

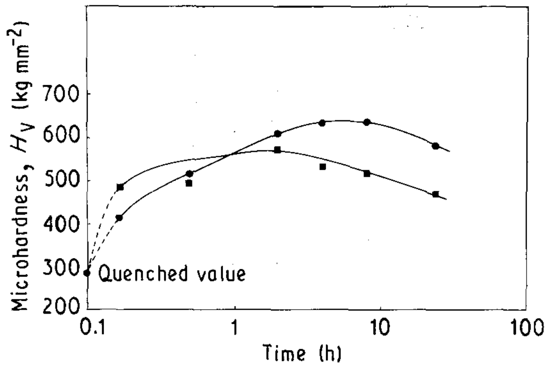

Figure 2 Microhardness isotherms for Ni–25% Mo alloy at (●) 700 and (■) 800 °C.

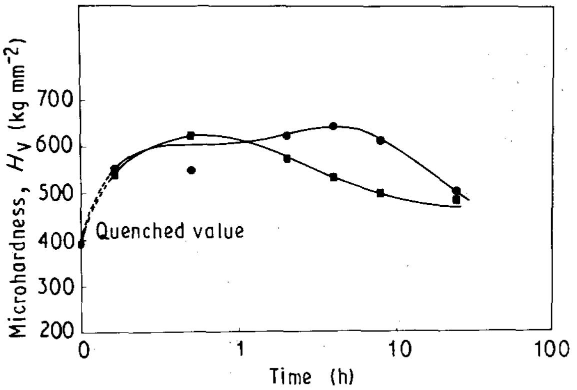

Figure 3 Microhardness isotherms for Ni–20% W alloy at (●) 830 and (■) 940 °C.

3.2. Microstructural changes

The microstructural evolution due to ordering transformations has been described elsewhere for Ni–25%

Mo [18] and Ni–20% W [19]. A detailed report will be made only on Ni–20% Mo. Although the temperatures employed in microhardness measurements and optical metallography, on the one hand, and electron microscopy and diffraction studies, on the other, are slightly different, the observations have been collected together in order to correlate the mechanical behaviour with structural changes both at microscopic and the submicroscopic levels.

The as-quenched alloys after disordering treatment exhibited invariably short-range order as evinced by the presence of diffuse reflections at $\{1\,1/2\,0\}$ positions in the electron diffraction patterns. Dark-field electron microscopic images from these spots revealed microdomains of size ranging from ~ 5–10 nm. Short-range ordering was found to persist for longer periods of time with increase in the ageing temperature for Ni–20% Mo and Ni–20% W alloys. The reverse was observed in Ni–25% Mo. The mode of transition to long-range order has been observed to follow different courses for different alloys and is described below.

3.2.1. Ni–20% Mo

The initial stages of ordering in Ni–20% Mo is marked by the discontinuous appearance of $D1_2$ superlattice spots in the electron diffraction pattern suggesting a heterogeneous mode of transformation. This feature has been observed at both temperatures of ageing, 680 and 780 °C, in which well-developed spherical superlattice reflections corresponding to Ni_4Mo could be noticed. In addition to these, spots corresponding to Ni_2Mo structure are present (Fig. 4). These spots are streaked towards neighbouring Ni_4Mo positions and directions of broadening can be approximated along $\langle 1\,1\,0\rangle^*$. This suggests the formation of Ni_2Mo metastable phase at this stage. The occurrence of this metastable phase in Ni–20% W and Ni–25% Mo has been considered elsewhere [20]. Das [21] reported the presence of Ni_2Mo reflections in Ni–20% Mo after ageing for 8 h at 650 °C. Their presence at this advanced stage of ordering is somewhat surprising in the present studies.

After 4 h annealing at 680 °C, the diffraction pattern of Fig. 5a was obtained. This exhibits superlattice reflections corresponding to Ni_4Mo structure alone. A dark-field image (Fig. 5b) from an Ni_4Mo spot revealed equiaxed precipitates of β-phase having an average size ~ 20 nm. Chakravarti *et al.* [9] reported a somewhat smaller domain size of ~ 7 nm after 3 h annealing at 700 °C. The order domains are uniformly distributed throughout the solid solution matrix indicating homogeneous nucleation. Prolonged annealing at 680 °C led to domain coarsening.

The optical photomicrograph of Fig. 6a has been obtained after isothermal annealing of Ni–20% Mo for 30 min at 700 °C. The lamellar morphology having diffuse contrast is characteristic of perpendicular twin-related domains of type $\{2\,0\,2\}_{fcc}$ and reveals the onset of ordering. There is no sign of domain formation at grain boundaries. Grain-boundary cracking could be clearly discerned in the photomicrograph and arises as a mechanism of stress relief for the cubic to tetragonal change. The striated contrast from perpendicular twins continues up to 24 h annealing. It is evident from the above observations that homogeneous nucleation is predominant at 700 °C.

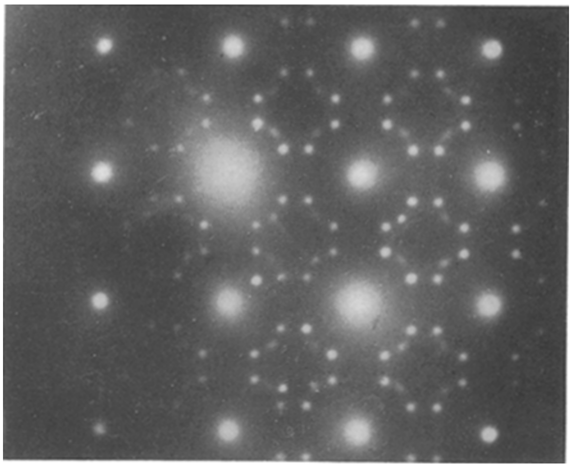

Figure 4 $[0\,0\,1]^*$ SADP obtained after ageing Ni–20% Mo specimen for 45 min at 680 °C. Note the presence of Ni_2Mo superlattice reflections.

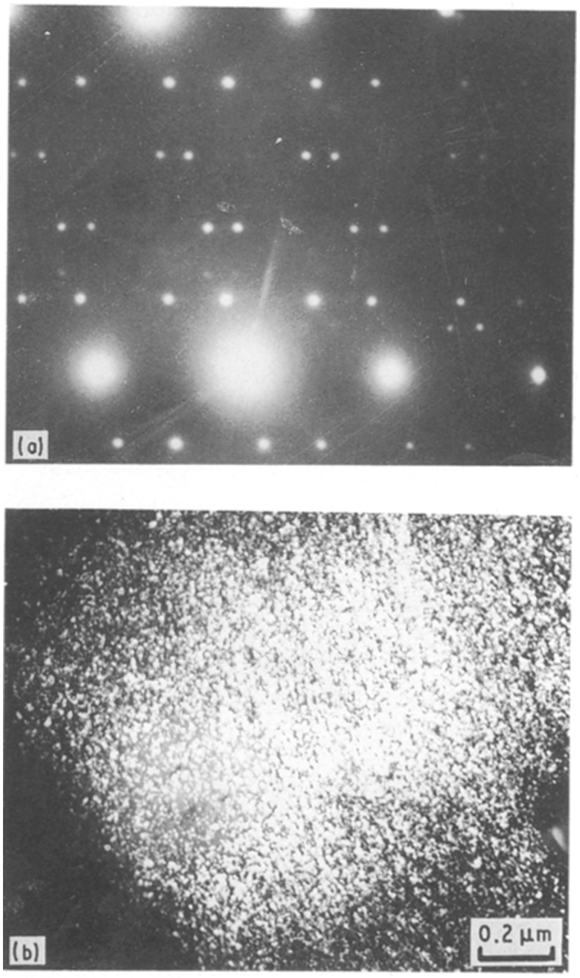

Figure 5 (a) $[1\,\bar{2}\,\bar{3}]^*$ SADP obtained after ageing Ni–20% Mo alloy for 4 h at 680 °C showing Ni_4Mo superlattice spots. (b) Dark-field electron micrograph from a superlattice spot exhibiting Ni_4Mo ordered domain morphology.

The situation is similar when the material is subjected to annealing at 800 °C except that heterogeneous nucleation at grain boundaries sets in at the later stages of ordering. The optical activity of ordered domains remains dormant up to 20 min ageing. Improved optical activity could be noticed after 30 min annealing. On continued annealing for 4 h at 800 °C, a distinct striated structure was observed indicating the presence of perpendicular twins.

Sustained annealing for 25 h at 800 °C produced coarsened twin plates. Fig. 6b depicts thick twin plates across the grain after the above treatment is imparted to the alloy. Striations at the grain boundary along with the cracking of the latter can also be perceived. It can be concluded, therefore, that at 800 °C, ordered Ni_4Mo precipitates are produced by homogeneous nucleation at the early stages of ordering. The heterogeneous mode of nucleation becomes operative at the later stage. The stress generated due to the precipitation of ordered β-phase is relieved via grain-boundary cracking.

The ordering transformation produces an appealing variety of defect structures, as revealed by electron microscopy of Ni–20% Mo aged at 780 °C. Fig. 7a depicts the presence of a number of antiphase boundaries parallel to each other in a specimen of Ni–20% Mo aged for 10 h at this temperature. The dissociated nature of the APBs can be noticed as well. These APBs join in groups of two in the dark-field electron micrograph. The presence of ordered perpendicular twin boundaries could also be perceived where APBs seem to terminate.

Fig. 7b shows the diffraction pattern from the area in which only one portion of the twin plate is available. On the pattern, single domain orientation is disclosed. The Ni_4Mo spots streak profoundly along $[\bar{1}\,1\,0]_\beta$ or $[1\,2\,0]_\alpha$. These streaks are unidirectional and become more pronounced in alternate columns of diffracted spots. This kind of quasiperiodic APBs and associated streaking have been observed previously only in Ni–25% Mo.

After 25 h annealing at 780 °C, a soap-foam structure developed copiously in the specimen. Fig. 8a shows a dark-field electron micrograph from a superlattice spot. The soap-foam structure inside the perpendicular twin plates offers a classical example of homogeneous nucleation and growth. The approximate size of domains at this stage is 0.4 µm. Snyder and Brooks [8] observed smaller domains of size ~ 0.33 µm after 97 h ordering treatment at 775 °C for the same morphology. The ordered domains of Ni_4Mo which are light areas in the dark-field image, are separated by antiphase domain boundaries.

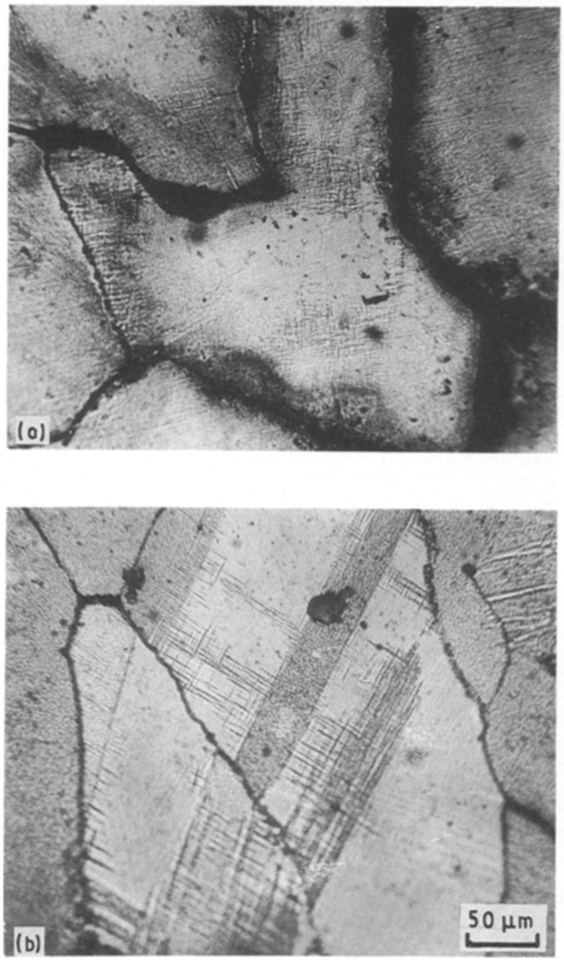

Figure 6 Optical photomicrographs of Ni–20% Mo aged for a 30 min at 700 °C (grain-boundary cracking is revealed) and (b) 24 h at 800 °C (thick plates of ordered twins are revealed).

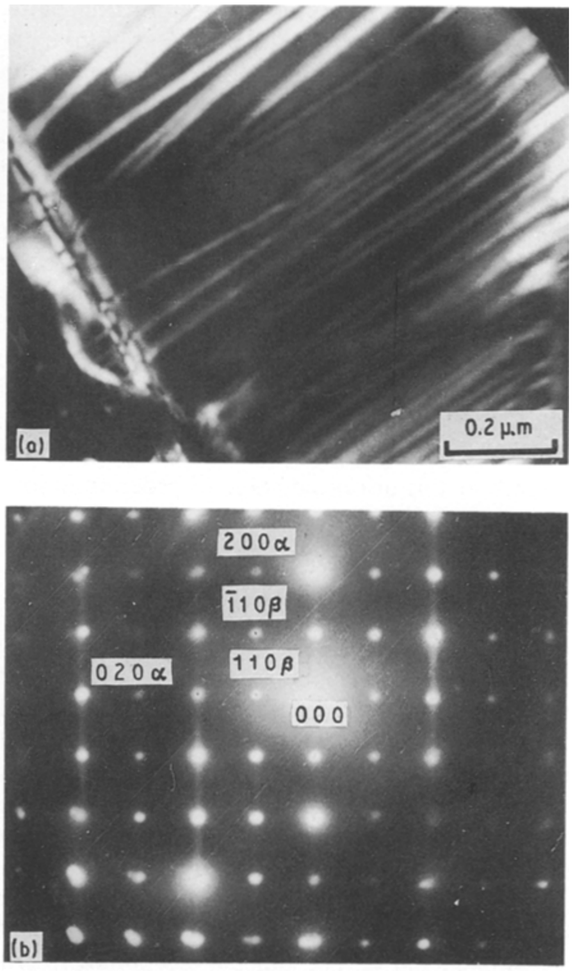

Figure 7 (a) Dark-field electron micrograph exhibiting quasiparallel APBs in Ni–20% Mo aged for 10 h at 780 °C. Note the presence of dissociated APBs. (b) SADP from the same region as in (a). Note the profused streaking of Ni_4Mo spots.

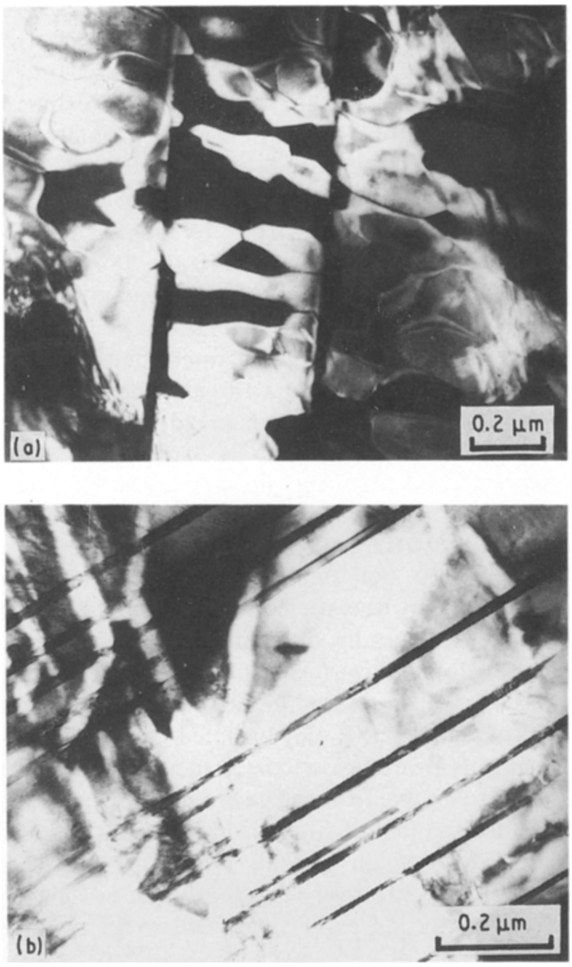

Figure 8 (a) Dark-field electron micrograph showing development of soap-foam structure in a Ni–20% Mo specimen aged for 25 h at 780 °C. (b) Bright-field electron micrograph showing microtwinning in Ni–20% Mo after the same treatment as in (a).

Fig. 8b is the bright-field electron image which displays microtwinning of the ordered lattice. If the stress generated during the course of coherent precipitation becomes too large, microtwinning aids in alleviating this stress in the lattice. This can also be interpreted as one of the mechanisms responsible for softening when strain due to lattice mismatch becomes too large.

3.2.2. Ni–25% Mo

The electron microscopic investigations of microstructural evolution on the scale of the period of annealing have been described elsewhere [18]. A brief account of the observations is presented here. Ni_2Mo and Ni_4Mo occur as metastable phases during isothermal annealing in the temperature range 680–880 °C. At temperatures below 800 °C, Ni_2Mo forms first and is followed by Ni_4Mo. At 680 °C ($\approx$ 700 °C) the formation of metastable phases Ni_2Mo and Ni_4Mo is sluggish compared to that at 780 °C ($\approx$ 800 °C). The equilibrium long-range order structure of Ni_3Mo develops after 10 h and 2 h annealing at the lower and higher temperatures, respectively.

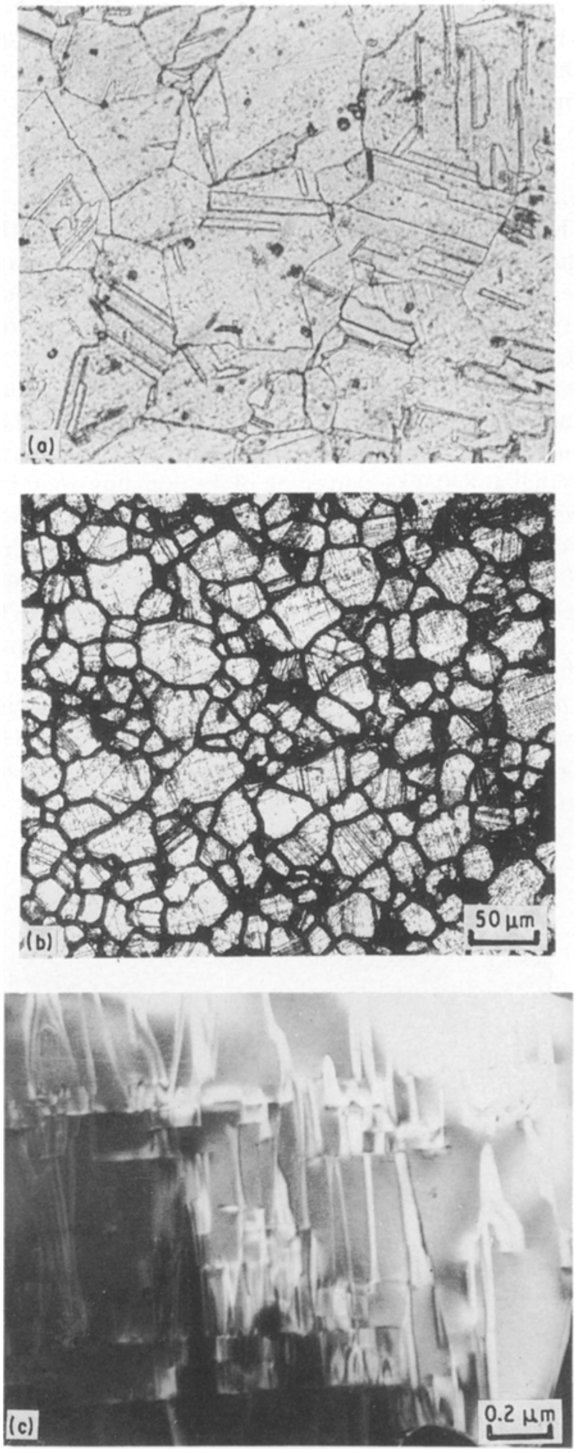

Figure 9 (a) Optical photomicrograph of as-quenched Ni–25% Mo showing single-phase microstructure with a profuse number of annealing twins. (b) Optical photomicrograph of Ni–25% Mo annealed for 30 min at 730 °C showing striations within the grains. (c) Dark-field electron micrograph obtained after annealing Ni–25% Mo specimen for 100 h at 780 °C. APBs can be seen to terminate at structural discontinuities. Note also the parallel nature of APBs in this micrograph.

The optical micrograph of Fig. 9a has been obtained from an Ni–25% Mo specimen solution treated at 1300 °C for 1 h followed by rapid quenching in water. The matrix shows a single phase with a profuse amount of annealing twins. Upon annealing the alloy for 30 min at 730 °C, diffuse striations develop across the grains of Ni–25% Mo solid solution (Fig. 9b). Fig. 9c is the dark-field electron micrograph obtained after annealing Ni–25% Mo specimen for 100 h at 780 °C. APBs can be seen indicating completely ordered domains of Ni_3Mo. These APBs seem to terminate at structural discontinuities. The thermal APBs align themselves to become somewhat parallel. Dissociation of APBs could also be identified in this micrograph.

3.2.3. *Ni–20% W*

The microstructural changes, together with the changes in the diffraction conditions versus the annealing time, form a major theme of other papers [19, 23]. However, it is pertinent to present here a brief account of the investigations. The early stages of transformation are manifested by the abrupt appearance of heterogeneous mode of transformation. The rate of transformation is very fast at 940 °C compared to that at 830 °C. Coarsening of the domains occurs as the annealing period is increased. Transformation from short- to long-range order was complete within 30 min annealing at 830 °C, whereas short-range order spots continued to persist up to 200 h ageing at 940 °C.

Fig. 10a is the optical photomicrograph obtained after annealing Ni–20% W specimens for 2 h at 820 °C. The striated contrast is exhibited together with some indications of grain-boundary reaction. The figure also depicts the spheroids of β-phase. Domain growth with increasing ageing time was also disclosed by optical microscopy, corroborating the electron microscopy observations.

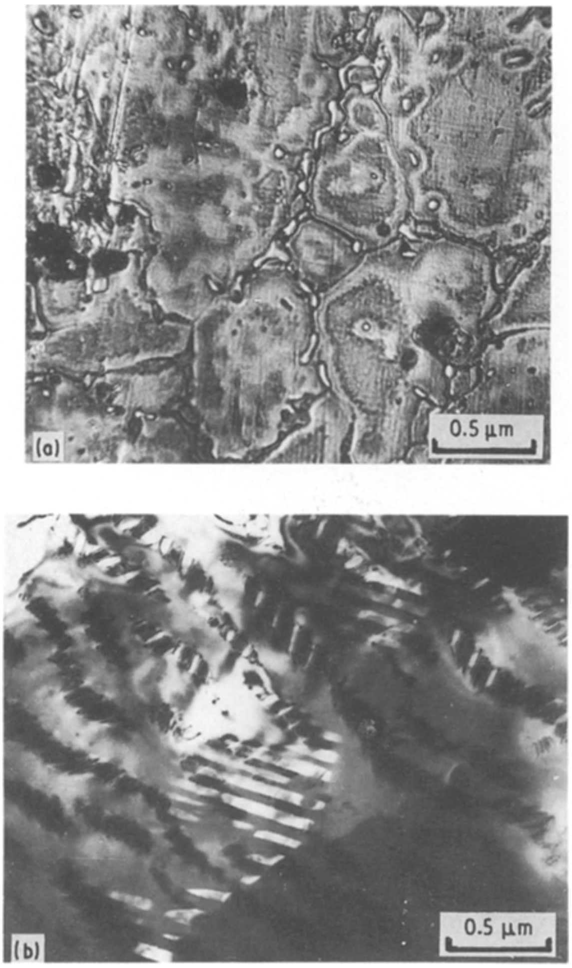

Figure 10 (a) Optical photomicrograph of Ni–20% W aged for 2 h at 830 °C. Striated structure with signs of heterogeneous reaction at the grain boundaries is revealed. (b) Bright-field electron micrograph exhibiting Ni_4W ordered twins in Ni–20% W alloy aged for 100 h at 940 °C. Moire fringes due to precipitates are also depicted.

Continued annealing for 100 h at 940 °C exhibited large twins (Fig. 10b) of size 1 μm approximately, suggesting a heterogeneous mode of nucleation at this temperature. The precipitates of Ni_4W are revealed in the form of Moiré fringes. The average size of Ni_4W precipitates is approximately 0.12 μm. It should be noted that the form and size of the precipitates indicates that a homogeneous mechanism of nucleation is also operative. It may be conjectured that the homogeneous nucleation precedes the heterogeneous process and the latter begins at an advanced stage of ordering.

4. Discussion

It is clear now that one or more of the following mechanisms may be expected to contribute to hardening in neostructurally ordered alloys: (a) degree of order, (b) domain size, (c) misfit stresses or coherency strains, and (d) interfacial dislocations generated due to loss of coherency. It may be noted that the last two mechanisms are exclusive to neostructural alloys. Similarly, it is possible to conceive of the following mechanisms for the loss of strength in advanced stages of ordering; (e) domain growth, (f) intergranular fracture leading to stress relief, and (g) a process akin to recrystallization. In earlier literature, order twinning was conceived of as a mode of stress relief by self deformation of the material. Current theories indicate that such twinning arises from a growth process rather than a deformation process. Hence this mechanism is excluded from the softening process.

It appears to be a worthy goal to evolve a unified theory of order hardening, which will be applicable to a variety of neostructural alloys such as CuAu, CoPt, Ni_4Mo, Ni_4W, Ni_2V and CoPt. The need for this has been emphasized in an evocative paper by Irani and Cahn [16], who have prepared a comparative chart of hardening characteristics of these alloys. As they themselves point out, this task is not easy, as investigations differ widely in the techniques employed and morphological details reported. Their paper serves as a useful starting point for the discussions here.

It has been stated that while CuAu, CoPt and Ni_4W show overageing, Ni_4Mo does not show softening even after long periods of anneal [16]. Our present results show that Ni_4Mo does overage. Fig. 11a and b compare these results with those of earlier investigations by Snyder and Brooks [8], Chakravarti *et al.* [9], Irani *et al.* [11] and Ling *et al.* [24]. There are variations in the absolute values in these studies. These might arise from the temperature from which quenching has been done, the purity of the samples and other experimental variables. Nevertheless, a trend towards overageing can be perceived in the studies of Ling *et al.* [10] at 800 °C. In fact the latter shows more pronounced overageing than our own results.

It is interesting to point out that similar conflicting statements are to be found in the literature about

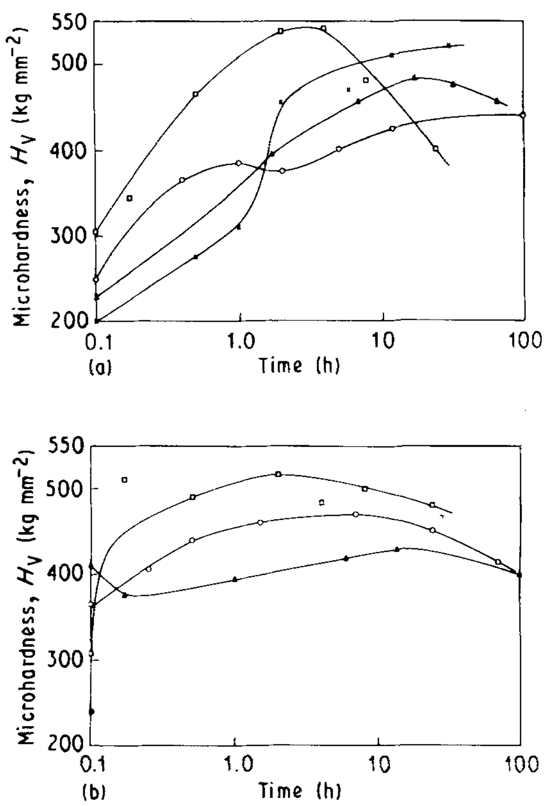

Figure 11 Comparative study of microhardness isotherms for Ni–20% Mo aged at (a) 700 °C, (×) [9], (△) [12], (○) [24], (□) present work, and (b) 800 °C, (△) [8], (○) [11], (□) present work.

CuAu. While the early work of Nowack [25], as well as the reinvestigation of Arunachalam and Cahn [6], showed distinct overageing, Chandra and Ramaswami [26] have claimed that ordering leads to a saturation of hardness values after long anneals. This assertion has been contested vigorously by Arunachalam [27]. The only conclusion that can be drawn is that while CuAu shows overageing after about 1.5 h at 240 °C (T/T_c = 513 K/658 K = 0.78) and CuPt after 3 h at 550 °C (T/T_c = 823 K/1088 K = 0.76), Ni_4W overages after 4 h at 820 °C (T/T_c = 1093 K/1243 K = 0.88) and Ni_4Mo shows overageing after 2 h at 700 °C (T/T_c = 973 K/1141 K = 0.86). Inspite of the higher T/T_c values for these two alloys, the onset of overageing appears to be delayed. Hence some explanation for the retention of strength over long periods is called for.

The present study shows the occurrence of perpendicular twins at the optical and electron microscopic level in both Ni_4Mo and Ni_4W. They arise from a growth process. In earlier literature the occurrence of similar twins in CuAu was attributed to a self-deformation process, whereby the ordered alloys undergo twinning to relieve the stresses arising from the cubic to tetragonal distortion [6, 19]. However, in the analogous CoPt alloy, Pennison *et al.* [29] have shown that the perpendicular twins arise by a growth process. Since then, Arunachalam and Sargent [30] have drawn an analogy with Gleiter's mechanism for the growth of annealing twins [31] and suggested that transformation twins occur as growth faults during the growth of the ordered structure to minimize the transformation stresses. The present observations lend further evidence. The transformation twins are present from an early stage of ordering. There are numerous APBs and antiparallel twin boundaries within them, indicating that impingement plays an equally important role in creating these twin interfaces. In the later stages of domain growth, large perpendicular twins are left behind particularly in Ni–20% W alloy.

It appears that additional light may be thrown on the formation and elimination of domain interfaces by high-resolution electron microscopy. Sinclair *et al.* [32] have shown that the (1 0 1) twin boundaries in CuAu are not atomically smooth, but consist of small {1 0 0} steps. Hence their propagation and elimination may proceed by a ledge mechanism. Similar observations in Ni_4Mo and Ni_4W are required to determine whether the perpendicular twin boundaries are atomically flat. Existing field ion microscopy (FIM) evidence indicates that this is so. Recently, Vasudevan *et al.* [34] have shown that antiphase twins (APTs) are eliminated in the presence of APBs. This was attributed to the higher interface energy associated with APTs. Even atomic exchange along ATP-related ordered domain boundaries favours creation of APBs.

Before turning to the mechanisms of strengthening, it is useful to recount the ordering in Ni–20% Mo on the basis of collated observations of the present study and earlier investigations. At 700 °C the precipitation of Ni_4Mo begins within 2 min but the complete conversion to the ordered state takes more than 1000 min [34]. The domain sizes remain small in the range 3–10 nm in the same time interval. Fig. 12a shows this information drawn from different studies. The misfit stresses have been assessed by X-ray line breadth analysis and indicate that the strains register a rapid increase over the first 100 min, but remain relatively constant afterwards [10]. At 800 °C the reaction is rapid. Precipitation begins within 4 min and is complete within 10 min. Domains are larger at this temperature and grow from about 15 to over 100 nm in 1000 min (Fig. 12a). Unfortunately, no measurements are available of the strains at this temperature.

Domain growth kinetics has been investigated extensively by Vasudevan *et al.* [34, 35] in Ni_4Mo. Johnson–Mehl–Avrami type of equations were also shown to exist in the ordering reaction. A sharp increase in the *n*-value occurred when temperatures were raised above 700 °C.

The present study leads us to believe that domain size plays a crucial role in the hardening achieved in Ni–20% Mo. The maximum registered at 700 °C is higher than at 800 °C. The retention of strength over long periods is also ascribed to the slow change in domain size. The final softening is observed, when domain coalescence leads to larger domain sizes. Grain-boundary cracking operates as a major stress relief mechanism. Recrystallization, observed near grain boundaries by other workers, might also contribute to softening. Our own observations indicate, however, that they may not play a major role.

A comparison with Ni–20% W alloy may now be made. The present study confirms the earlier observations of Ellinger and Sykes [36] and Epremian and

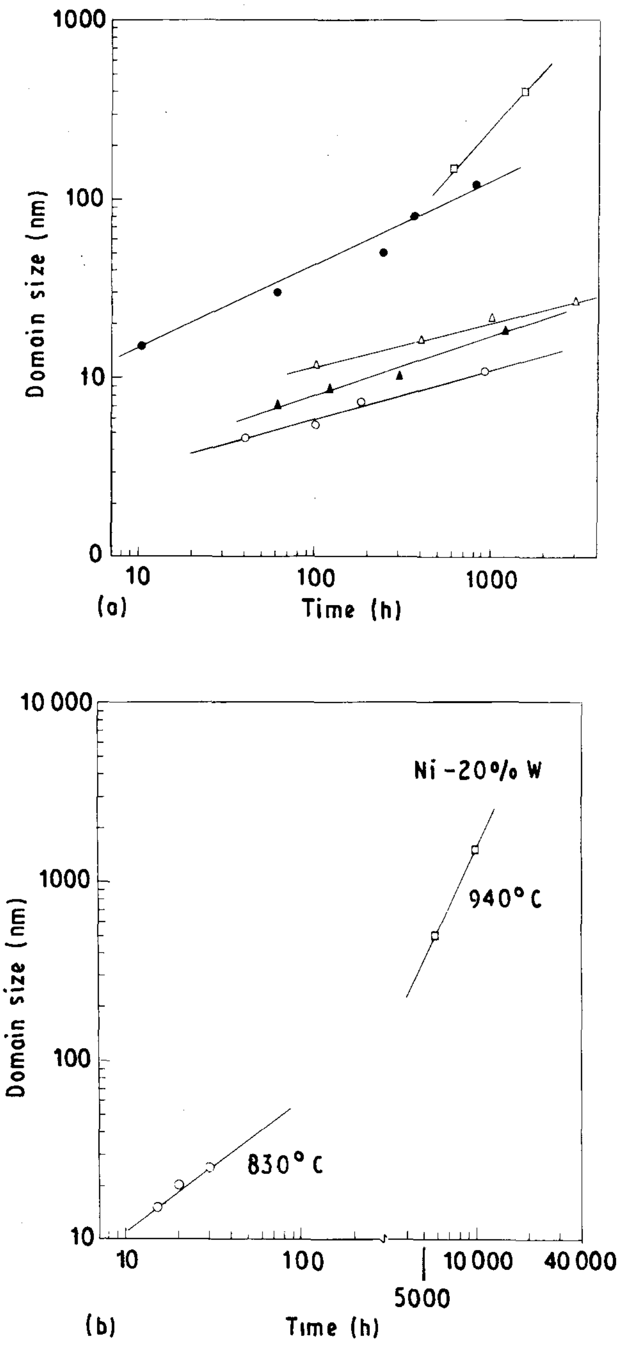

Figure 12 Domain size versus time plot for the growth of (a) Ni_4Mo domains at (△, ▲, ○) 700 and (□, ●) 800 °C; (□) present work, (●) [8], (△) (12), (▲) [24], (○) [9]. (b) Ni_4W domains at (○) 830 and (□) 940 °C.

TABLE I Mechanism of strengthening and softening in neo-structurally ordered alloys

Mechanisms	Alloys	Reference
(I) *Strengthening*		
(a) Domain size	Ni_4Mo	[9]
	CuPt	[16]
	Ni_4Mo	Present study
	Ni_4W	Present study
(b) Misfit stresses	Ni_4Mo	[8]
		[11]
	CuPt	[17]
(c) Interfacial dislocations	Ni_4Mo	[10]
(II) *Softening*		
(d) Intergranular fracture	Ni_4Mo	[9]
		[11]
		Present study
	CuPt	[16]
(e) Strain-induced recrystallization	Ni_4Mo	[9]
		[24]
	CuAu	[37]
	CoPt	[38]
	Ni_2V	[39]
	CuPt	[16]
(f) Domain growth	Ni_4Mo	[8]
		Present study
	Ni_4W	Present study
	CuPt	[16]

Harker [15]. The former workers obtained 28 Rockwell C hardness in the as-quenched condition. This increased to a maximum value of 50 R_c on ageing at 950 °C. There are definite signs of overageing in their curves as well. While Ni–20% W registers higher absolute hardness (Fig. 3) in comparison to Ni–20% Mo (Fig. 1), it is more meaningful to compare fractional increase in hardness. They may be expressed as $(H_{max} - H_D)/H_D$, where H_{max} is the peak value in the ordered condition and H_D is the disordered value. For Ni_4W at 820 °C, this value is 0.75. If the lattice misfit is a major contributory factor to hardening, then Ni–20% W alloy should harden more than Ni–20% Mo. The c/a value is 0.98 for the former and 0.986 for the latter. Irani and Cahn [16] have converted these to a total lattice mismatch and quote values of 0.95% for Ni_4W and 0.5% for Ni_4Mo. These facts again suggest that misfit stresses may not play a major role in strengthening Ni–20% W alloy.

Fig. 12b shows the variation of domain size with ordering time on the basis of the present study. The curves are similar to those of Ni–20% Mo (Fig. 12a). The domain size–time relationship follows $D^n - D_0^n = Kt$, where D_0 is the initial domain size, D is the domain size at time t; n is constant and close to 3. The initial increase in strength is attributed to the increase in the amount of the ordered material and the final softening is due to the domain size. Grain-boundary cracking was noticeably absent in this alloy. Hence large domain size may be the softening factor.

Table I collects together the inferences drawn from the present study of Ni–20% Mo and Ni–20% W and compares them with mechanisms advocated by other investigators for Ni_4Mo, CuAu, CoPt and CuPt. Further work is required, so that some of the conflicting view points apparent in this table may be resolved.

The results for Ni–25% Mo reveal that higher hardness increase occurs for this alloy in comparison with Ni–20% Mo. The microstructural evolution indicates that in the early stages small particles of Ni_2Mo and Ni_4Mo are formed. This will lead to precipitation strengthening. When, at a later stage, the fcc matrix transforms to hcp, the fragmentation of the fcc grains to small hcp platelets takes place. This should lead to strengthening based on grain-size effect. Ultimately the APBs within the hcp platelets become annihilated as a result of domain growth. This will lead to softening. In this alloy, grain-boundary cracking was not observed.

5. Conclusions

The present investigation was concerned with the correlation of strength assessed via microhardness measurements with microstructures produced on ordering in Ni–20% Mo, Ni–25% Mo and Ni–20% W alloys as observed by optical and electron microscopy. These observations have been put in perspective with earlier investigations of Ni_4Mo, and other neostructurally ordered alloys, namely CuAu, CoPt and CuPt. The following conclusions emerge.

1. Ni–20% Mo alloy overages just as Ni_4W, CuAu, CoPt and CuPt do, albeit at a slower rate and with retention of strength up to longer periods.
2. Perpendicular twins form in Ni_4Mo and Ni_4W by a growth process rather than by deformation. Hence they do not contribute as a stress-relieving feature for the later stages of ageing.
3. Domain size seems to play a crucial role in order strengthening of Ni_4Mo and Ni_4W. The small domain size contributes to hardening. Domain growth and coalescence at later stages leads to softening. Grain-boundary cracking appears in Ni_4Mo but not in Ni_4W.
4. The observation of lower fractional increase of hardness in Ni_4W in comparison with Ni_4Mo has been taken to indicate that misfit stresses play a minor role in hardening.
5. The remarkable hardening exhibited by Ni–25% Mo is attributed to the existence of fine grain-size metastable phases Ni_2Mo and Ni_4Mo in the early stages and the fragmentation of fcc grains by hcp platelets. Eventual softening sets in, when domain growth in hcp platelets leads to elimination of APBs.

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