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LETTER

Effect of long-range ordering in a Ni–Mo alloy on its mechanical properties and corrosion resistance

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Ordered alloys and intermetallic compounds are playing an increasingly important role in advanced corrosion applications, e.g. [1]. As design schemes increase in sophistication, the search continues for alloys, which offer higher strength and can handle a larger variety of complex aggressive media in comparison with the conventional alloys. However, the issue of low ductility remains to be an important one and, therefore, efforts are focused on improving ductility and/or innovations in manufacturing technology. Among the most important alloys in this class are the those based upon the Ni–Mo and Ni–Mo–Cr [2, 3, 4]. A common feature of these alloys is that they undergo a series of long-range ordering reactions upon exposure at elevated temperatures [5, 6]. This involves a slight atoms rearrangement on $\{420\}_{fcc}$ planes resulting in closely-related superalattices: $D1_a$ (Ni_4Mo), Pt_2Mo-type: $\{(Ni_2Cr$, and $Ni_2(Cr,Mo)\}$, and DO_{22} (basis for the Ni_3Mo structure) [7].

It was the objective of this study to determine the effect of long-range ordering in a Ni–Mo alloy of commercial grade on its mechanical properties and corrosion resistance. The alloy was processed into sheets about 2 mm in thickness. Its chemical composition is listed in Table 1. Specimens were annealed at 1,065 °C for 20 min and then water quenched. Inorder to induce long-range ordering, annealed specimens were exposed up to 1,000 h at 700 °C and then air-cooled. Mechanical properties were determined from room temperature tensile tests (50.8 mm gage length). Aqueous corrosion rates were calculated from weight loss measurements made on 25.4 mm × 25.4 mm × 2 mm specimens after 24 h immersion in 20% boiling hydrochloric acid. Transmission electron microscopy and diffraction as well as x-ray diffraction were used to characterize the microstructure.

Figure 1 shows the effect of up to 1,000 h of exposure at 700 °C on the room temperature tensile properties and corrosion rate. It is observed that after about 1 h of exposure, the 0.2% yield strength was nearly doubled relative to the annealed condition; however, about 70% of the initial tensile ductility in 50.8 mm gage length was still maintained. Corresponding to these changes there was no significant change in corrosion rate. With continued thermal exposure, the yield strength remained nearly unchanged after up to 1,000 h. In contrast, there was a significant loss of tensile ductility as well as a substantial increase in corrosion rate. Such changes in properties were correlated with long-range ordering to Ni_4Mo as demonstrated below.

Figure 2 shows x-ray diffraction patterns illustrating the effect of exposure time at 700 °C on the average structure. In the annealed condition, only characteristic face-centered cubic (fcc) reflections are observed indicative of a disordered solid–solution. After thermal exposure at 700 °C, characteristic superlattice reflections of Ni4Mo were observed as expected (tetragonal $D1_a$ superlattice: a = 0.5720 nm, c = 0.3564 nm). However, as can be seen the relative intensities of the superlattice reflections remained nearly unchanged as the exposure time was increased from 1 h to 1,000 h. This suggested that ordering was completed after about 1 h of exposure at 700 °C.

An example illustrating the evolution of the microstructure of Ni_4Mo within the alloy matrix is given in Fig. 3. Arrays of discrete particles were observed during the early stages of exposure (Fig. 3a). This was followed by the formation and growth of a mosaic assembly of

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Table 1 Chemical composition (weight %)

Ni	Mo	Cr	Fe	Mn	Si	Co	Al	C
Balance	26.92	0.64	0.93	0.24	<0.02	<0.1	0.19	0.002

twin-related variants along $\{100\}_{fcc}$ planes (Fig. 3b, c). Corresponding to these microstructural changes, the 0.2% yield strength was nearly doubled relative to the annealed condition, however, about 70% of the initial tensile ductility in 50.8 mm gage length was still maintained as demonstrated earlier (Fig. 1). Corresponding deformation substructures are shown in Fig. 4. As expected, in the annealed condition, deformation occurred by slip as shown in Fig. 4a. Slip lines could be clearly distinguished in the deformation substructure with evidence of cross-slip suggesting medium stacking fault energy. However, after long-range ordering to Ni_4Mo, the predominant deformation mode became twinning on the $\{111\}_{fcc}$ planes as shown in the example of Fig. 4b. This observation indicated that was a favorable deformation mode in the ordered

Fig. 1 Effect of exposure time up to 1,000 h at 700 °C on the room temperature tensile properties and corrosion rate in boiling 20% HCl

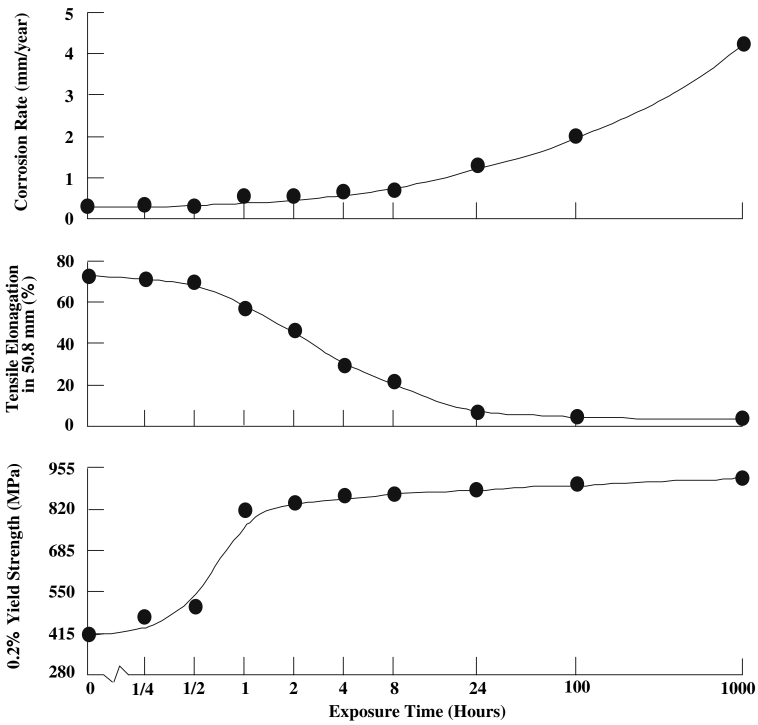
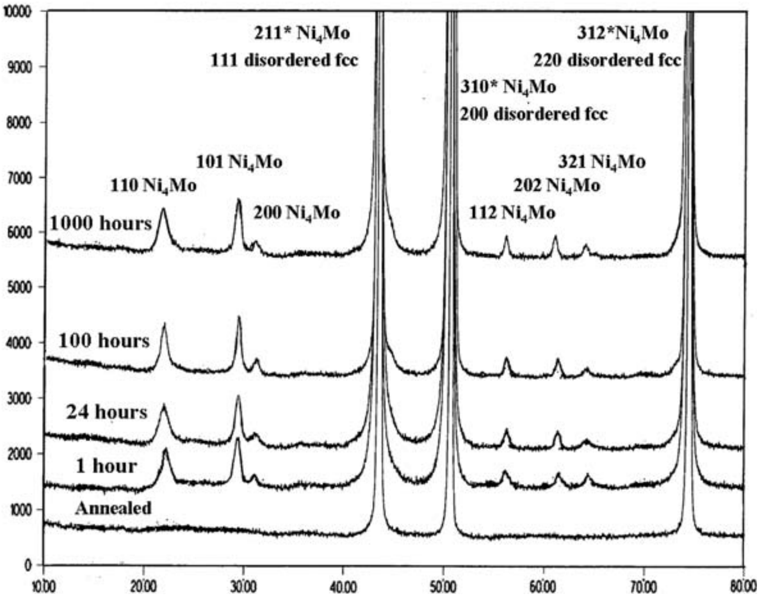


Fig. 2 Comparative X-ray diffraction patterns derived from an annealed sample and samples exposed for different times at 700 °C



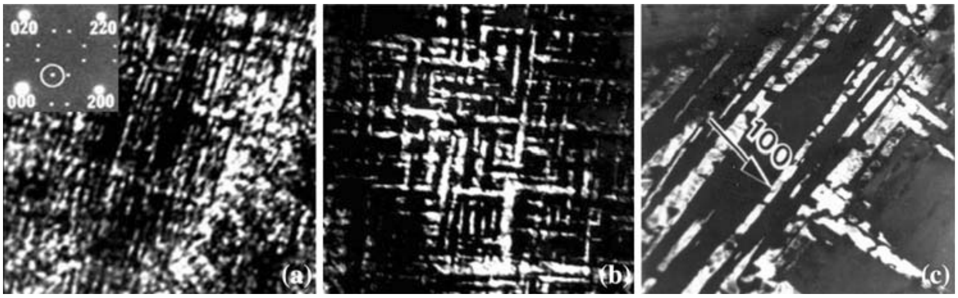


Fig. 3 Dark-field TEM images formed with the 1/5 <420> superlattice reflection to illustrate the effect of exposure time at 700 °C on the microstructure of Ni_4Mo. (**a**) 1 h. (**b**) 24 h. (**c**) 1,000 h

state consistent with the crystallographic features of the fcc (disordered) → $D1_a$ superlattice (Ni_4Mo). It can readily be shown that all {111} <110> slip systems are suppressed in the ordered state, however, eight of the {111} <112> twinning systems remain to be energetically favorable [8]. Corresponding to these changes in tensile properties, there was only a slight increase in corrosion rate, which could be interpreted in terms of Mo-depleted zones in the vicinity of Ni_4Mo domains, as reported in an earlier study [2].

After extended exposure corresponding to almost complete loss of tensile ductility (1,000 h at 700 °C), only $\{111\}_{fcc}$ stacking faults were observed in the deformation substructure as shown in Fig. 4c. Noting that a stacking fault is a thin layer of a twin, this observation indicated that fracture occurred prior to the development of deformation twins. Figure 5 illustrates characteristic morphologies of tensile fracture surfaces as functions of exposure time at 700 °C. As expected, in the annealed condition (Fig. 5a), the fracture mode was transgranular (dimple-type rupture). Also, after 24 h of exposure the fracture mode remained to be transgranular, however, the dimples became rather shallower indicating less strain prior to fracture. Although after 1,000 h of exposure, the fracture mode became interngranular, dimples were observed at separated grain facets (Fig. 5c) indicating highly localized deformation alongside grain boundaries. This behavior is usually associated with alloy depletion in the vicinity of grain boundaries as demonstrated in Fig. 6. The respective values of Mo concentrations were obtained from concentration profiles derived by in-situ fracture and sputtering of aged specimens in an Auger spectrometer. The value of 4.7 atomic % corresponds to a freshly exposed grain boundary, which is to be compared with the bulk value of 19.1 atomic %. It is observed that ordering in the vicinity of grain boundaries occurred by a discontinuous mechanism resulting in alternating lamellae of Ni_4Mo and

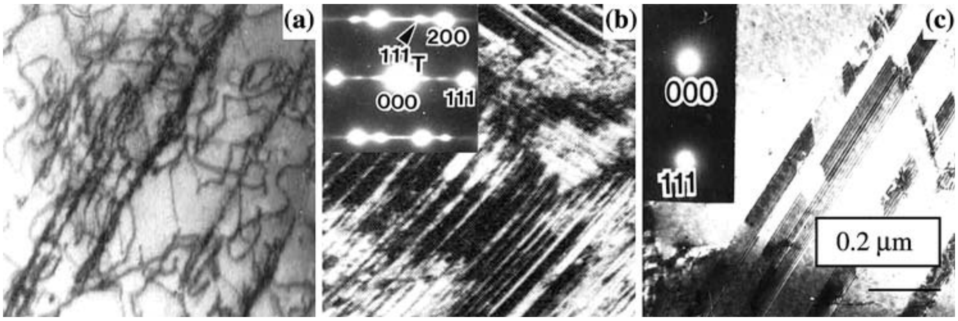


Fig. 4 Bright-field TEM images illustrating the effect of long-range ordering to Ni_4Mo on the deformation substructure (**a**) Annealed (3% strain). (**b**) Exposed for 24 h at 700 °C (15% strain) (**c**) Exposed for 1,000 h at 700 °C (2% strain; fractured specimen)

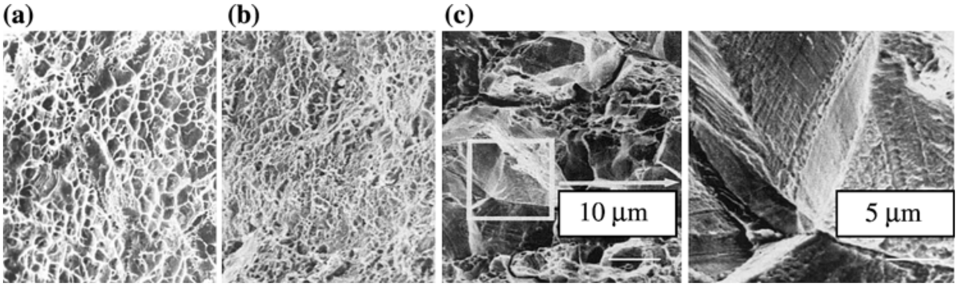


Fig. 5 Secondary electron SEM images illustrating the effect of long-range ordering to Ni_4Mo on the morphology of tensile fracture surfaces. (**a**) Annealed. (**b**) Exposed for 24 h at 700 °C. (**c**) Exposed for 1,000 h at 700 °C

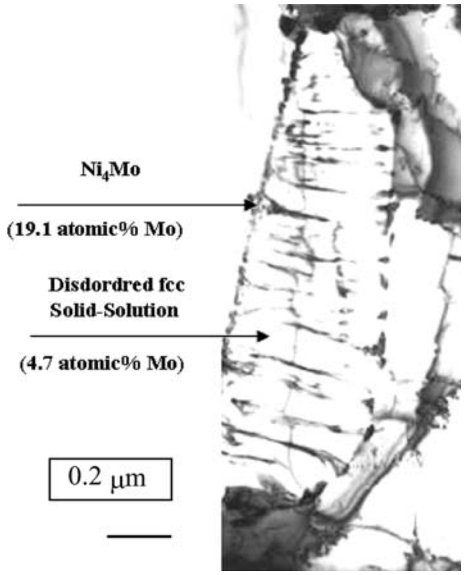


Fig. 6 Bright-field STEM image showing lamellar grain boundary structure of Ni_4Mo after 1,000 h of exposure at 700 °C; also shown is the Mo concentration alternating lamellae as derived from microchemical analysis

a Mo-depleted solid–solution. This could also explain the substantial increase in corrosion rate as demonstrated in Fig. 7. In the annealed condition and after matrix ordering, corrosion was predominantly of the uniform or general type (Fig. 7a). However, after the onset of the discontinuous grain boundary reaction, most of the metal wastage appeared to be due to intergranular attack as shown in Fig. 7b.

In conclusion, the present study had demonstrated that long-range atomic order may not necessarily degrade the mechanical strength and corrosion resistance of certain alloy systems. Conversely, it may even have some beneficial effects on properties particularly mechanical strength. However, property degradation may result from the specific morphology produced by localized ordering in the vicinity of grain boundaries as shown in this study. Therefore, it may prove viable to use single crystals of ordered alloys in certain applications and/or identify means for modifying the structure of grain boundaries to suppress the undesirable discontinuous ordering reaction.

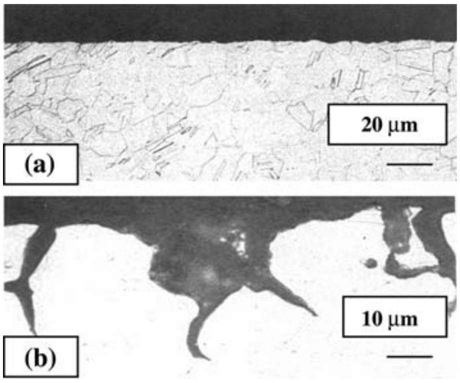


Fig. 7 Light optical micrographs along cross-sections of corrosion tested specimens. (**a**) annealed. (**b**) exposed for 1,000 h at 700 °C

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