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Effect of boron on the ductility of ordered Ni–Ni_4Mo alloys

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Boron was identified to have a beneficial effect on the room temperature ductility of ordered Ni–Ni_4Mo alloys. An addition of 0.01 to 0.03 wt % boron to hypostoichiometric alloys was found to increase the tensile ductility from about 5% to 30% in the ordered state produced by exposure at 600 to 800 °C, of the annealed material. The boron effect was, however, found to diminish with exposure time at a given temperature and not to be maintained at elevated temperatures. The beneficial effect of boron on room temperature ductility was also found to be considerably less pronounced in stoichiometric Ni_4Mo alloy. Both electron energy loss spectroscopy and Auger electron spectroscopy techniques revealed no preferential segregation of boron to grain boundaries. Experimental results suggested that boron decelerates the kinetics of heterogeneous grain boundary ordering which leads to an improvement in ductility.

1. Introduction

Among the important factors which limit the structural applications of ordered alloys and intermetallic compounds is their relatively poor ductility [1]. For example, polycrystalline Ni–Mo alloys are known to be intergranularly embrittled by long-range ordering to Ni_4Mo after short-term exposure at 600 to 800 °C [2–7].

Generally, two approaches have been identified to improve the ductility of ordered alloys and intermetallic compounds depending on the mechanism responsible for the embrittlement, namely: (a) macroalloying, and (b) microalloying. Macroalloying is employed in cases where the embrittlement is associated with the crystal structure of the ordered phase. For example, the crystal structure of Co_3V could be changed from hexagonal (low ductility) into cubic (high ductility) by substituting Ni and Fe for Co [8]. Microalloying is utilized when the embrittlement is related to a grain boundary effect, e.g. weak cohesion. It has been demonstrated that small additions of B to polycrystalline Ni_3Al significantly improves its ductility [9–11]. In this case, the beneficial effect of B on ductility is correlated with its segregation to grain boundaries which improves their cohesion and promotes plastic flow alongside grain boundaries due to a disordering effect [12, 13].

Similar to the case of Ni_3Al, a single crystal of Ni_4Mo is highly ductile [14]. Unlike the case of Ni_3Al [9, 10, 15], a discontinuous grain boundary ordering reaction has, however, been identified as a source of embrittling polycrystalline Ni–Ni_4Mo alloys [2, 7]. Although the ordered structure of Ni_4Mo ($D1_a$ superlattice) deforms readily by twinning and maintains a relatively high ductility, discontinuous ordering is found to create Mo-depleted zones alongside grain boundaries where plastic deformation becomes highly localized and, thus, intergranular embrittlement is promoted [2]. Consequently, it might be expected that the microalloying approach could be useful in improving the ductility of Ni–Ni_4Mo alloys.

It was the objective of this investigation to determine the effect of B additions on the ductility of hypostoichiometric and stoichiometric Ni_4Mo alloys.

2. Experimental procedure

Six hypostoichiometric alloys nominally containing 27 wt % Mo and 0 to 0.03 wt % B and two stoichiometric alloys (Ni_4Mo composition) containing 0 and 0.01 wt % B were investigated. All alloys were prepared by vacuum melting and then processed into 1 mm thick sheets. Table I summarizes their chemical compositions. Test specimens were solution heat treated at 1065 °C for 15 min and then water quenched. To induce long-range ordering to Ni_4Mo, annealed specimens were exposed for up to 1000 h at temperatures in the range of 650 to 815 °C.

Mechanical properties were determined from room and elevated temperature tensile tests and surface hardness measurements. All tensile tests were performed on specimens having a gauge length of 50.8 mm. Fractography was conducted in a scanning electron microscope (SEM).

Transmission electron microscopy (TEM), SEM and light optical metallography were utilized for microstructural characterization. Both electron energy loss spectroscopy (EELS) and Auger electron spectroscopy were employed for qualitative microchemical analysis to determine the distribution of B

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TABLE I Chemical compositions of the alloys investigated (wt %)

Ni	Mo	B	Fe	Cr
Hypostoichiometric alloys				
Balance	26.88	—	< 0.1	< 0.1
Balance	26.85	0.009	< 0.1	< 0.1
Balance	26.95	0.014	< 0.1	< 0.1
Balance	27.00	0.019	< 0.1	< 0.1
Balance	26.84	0.022	< 0.1	< 0.1
Balance	27.06	0.027	< 0.1	< 0.1
Stoichiometric alloys				
Balance	29.12	—	< 0.1	< 0.1
Balance	29.05	0.009	< 0.1	< 0.1

throughout the grain structure. Selected specimens were *in situ* fractured in a scanning Auger microprobe and the chemical compositions of freshly exposed grain boundaries were analysed with particular emphasis on B. Also, the B content of the matrix was analysed by sputtering a 40 nm thick layer. Thin foils for TEM and EELS were prepared by the jet polishing technique in a solution consisting of 30% nitric acid in methanol kept at about − 20 °C. All foils were examined at 200 kV.

3. Results and discussion

3.1. Effect of boron on room temperature ductility of hypostoichiometric alloys

Fig. 1 illustrates the effect of B content on the room temperature hardness and tensile properties of the hypostoichiometric alloy nominally containing 27 wt % Mo after 24 h of exposure at 760 °C. It is observed that regardless of the B content, the same level of order strengthening is achieved as revealed by hardness and yield strength measurements. In contrast, the tensile ductility can be seen to increase from about 5% in the absence of B to 30% with an addition of 0.01% B. As the B content was increased from 0.01% to 0.03%, the tensile ductility remained nearly unchanged. Associated with this effect was a change in the tensile fracture mode from predominantly intergranular (0% B) into transgranular (0.01 to 0.03% B) as shown in the example of Fig. 2.

As pointed out earlier, Ni–Mo alloys are severely embrittled after short-term exposure at temperatures in the range of 600–800 °C. An addition of 0.01% B was found to maintain a high ductility level after 24 h exposure in the above range as demonstrated in Fig. 3.

The above results demonstrated the beneficial effect of B on the room tensile ductility of hypostoichiometric Ni_4Mo alloys similar to the case of Ni_3Al [9–11].

3.2. Limitations of the beneficial effect of boron on ductility

Despite the beneficial effect of B described above, its usefulness in ductilizing ordered Ni–Mo alloys is found to be restricted by the following limitations.

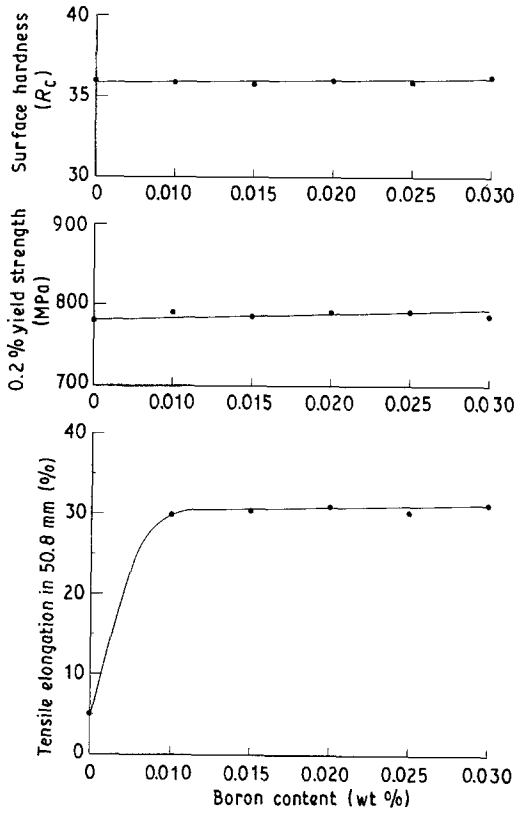

Figure 1 Effect of boron content on the room temperature hardness and tensile properties of a Ni–27Mo alloy ordered to Ni_4Mo (exposed 24 h at 760 °C)

First, the beneficial effect of B on room temperature ductility of hypostoichiometric alloys was observed to diminish with exposure time at a given temperature as shown in Fig. 4. Secondly, at the exact stoichiometric Ni_4Mo composition, i.e. Ni–29.1% Mo, the effect of B on room temperature ductility was much less pronounced in comparison with the hypostoichiometric alloys as illustrated in Fig. 5. This behaviour is similar to that found in the case of Ni_3Al [10]. Thirdly, the observed effect of B on room temperature ductility was not realized at elevated temperatures as demonstrated in Fig. 6.

It was possible to correlate the above observations with an effect of B on the kinetics of heterogeneous grain boundary ordering as described below.

3.3. On the mechanism of ductility improvement by boron addition

It is known that B segregates to various crystal defects such as dislocations, stacking faults, antiphase boundaries, twin boundaries and both low- and high-angle grain boundaries. Although in the case of Ni_3Al, the beneficial effect of B on ductility is correlated with its segregation to grain boundaries [9, 13], this was not found to be the case for Ni–Ni_4Mo alloys as demonstrated below.

Electron energy loss spectra derived from the matrix and grain boundary zones of the alloys containing 0.01 to 0.03 wt % B were found to be indistinguishable. A representative example is given in Fig. 7 for the Ni–27Mo–0.03B alloy after 24 h exposure at 760 °C. It

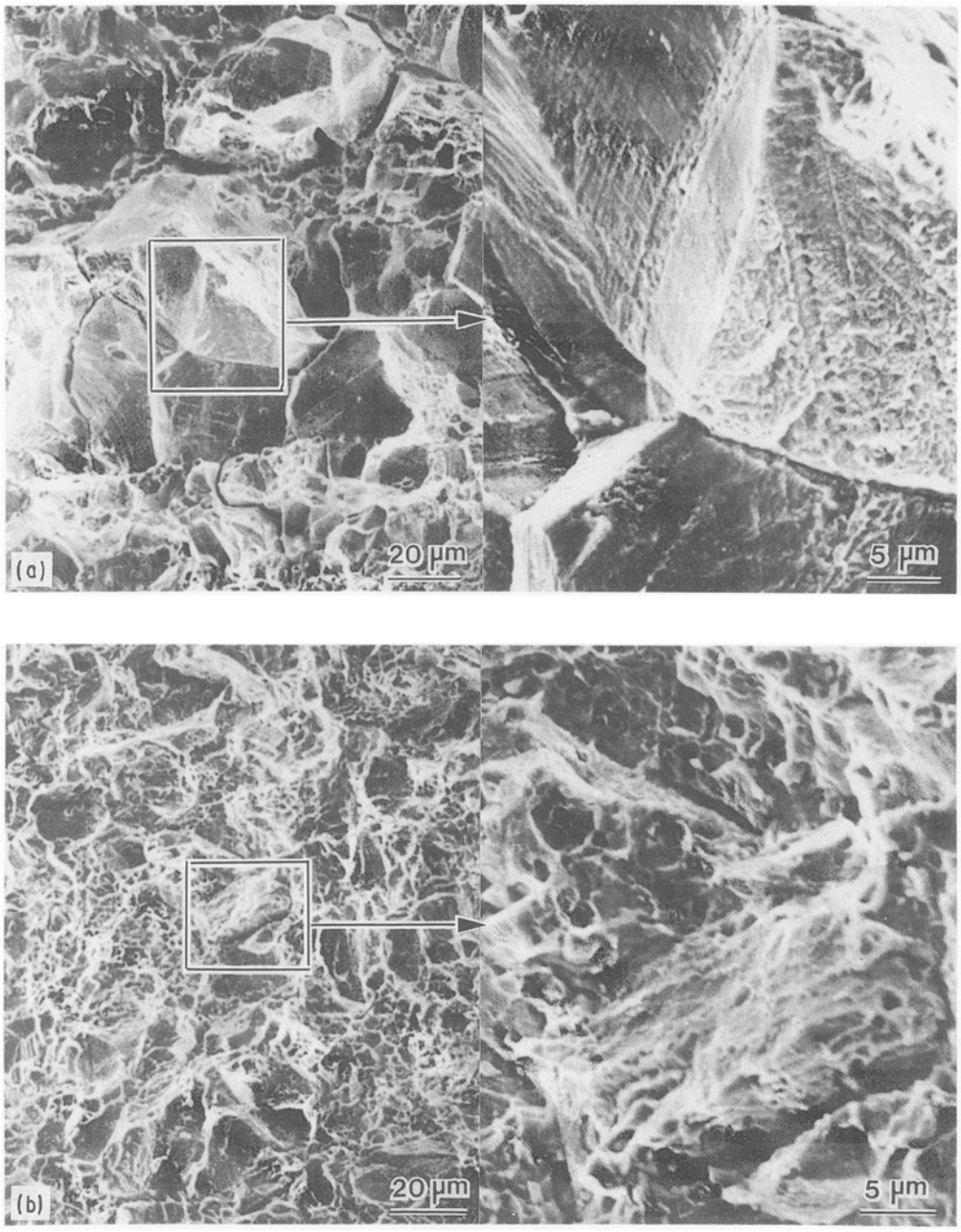

Figure 2 Secondary electron SEM micrographs illustrating the effect of boron on the tensile fracture mode of a Ni–27Mo alloy ordered to Ni_4Mo (exposed for 24 h at 760 °C). (a) Ni–27Mo alloy (predominantly intergranular mode). (b) Ni–27Mo–0.01B alloy (predominantly transgranular mode).

is noted that no B *K*-edge peak is observed at the corresponding energy of 188 eV. Even if the B concentration at a grain boundary is below the detecting limit of the technique (~ 0.05 wt %), it could be concluded that B showed no tendency for preferential segregation to grain boundaries. Occasionally the tensile fracture of the B containing alloys exhibited a small proportion of an intergranular mode as shown in Fig. 2b. Auger spectra derived from a freshly exposed grain boundary and the underlying matrix after sputtering a 40 nm thick layer revealed no preferential B segregation to grain boundaries as shown in Fig. 8 which is consistent with the result of EELS analysis shown in Fig. 7.

The above results suggested that B segregation to grain boundaries could be excluded as a possible mechanism for the observed improvement in ductility. It was, however, possible to correlate the influence of B on ductility with an effect on the kinetics of heterogeneous grain boundary ordering as described below.

It is known that long-range ordering to Ni_4Mo occurs homogeneously in the matrix and heterogeneously at grain boundaries by a discontinuous mechanism [2, 3, 5, 7, 16]. Associated with the later mechanism is strain-induced or self-generated recrystallization [16]. Both the grain structure in the annealed condition and ordered microstructure in the matrix were found to be similar for all the alloys investigated regardless of the B content. An example is given in Fig. 9. Since the order-induced strengthening can be expected to be primarily determined by matrix ordering, the above result is consistent with the hardness and yield strength data of Fig. 1. After a given exposure time, however, both the frequency of observing discontinuous grain boundary ordering and the size of the resulting lamellar structure appeared to be

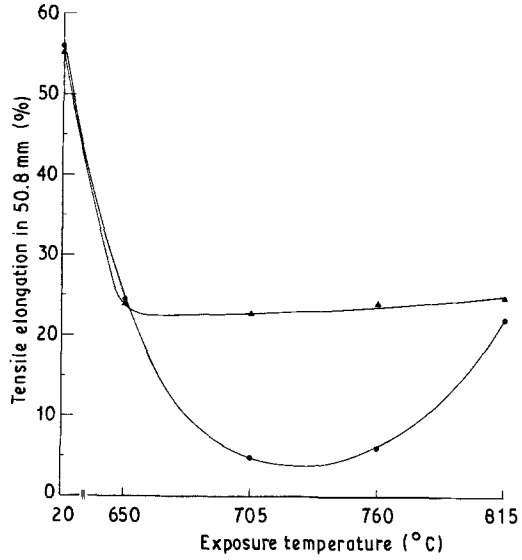

Figure 3 Comparative effects of 0.01 wt % B addition to a Ni–27Mo alloy on the room temperature tensile ductility following 24 h exposure at the indicated temperatures. (● Ni–27Mo, ▲ Ni–27Mo–0.01B).

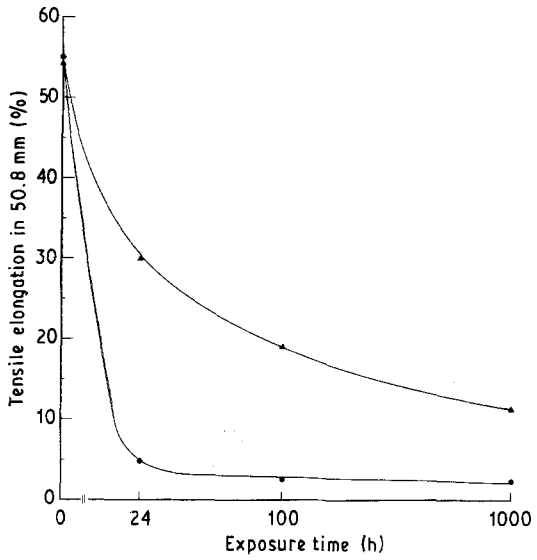

Figure 4 Comparative effects of 0.01 wt % B addition to a Ni–27Mo alloy on the room temperature tensile ductility as a function of exposure time at 760 °C. (● Ni–27Mo, ▲ Ni–27Mo–0.01B).

sensitive functions of the B content. In the presence of B, the size of the lamellar structure resulting from discontinuous ordering was observed to be comparatively finer as illustrated in the example of Fig. 10. Also, the frequency of observing discontinuous grain boundary ordering was notably less in the presence of B.

An earlier investigation revealed that Ni–Ni_4Mo alloys can be embrittled by heterogeneous grain boundary ordering [2]. Combining this with the above observations could lead to the conclusion that B reduces the lattice strain energy available to induce recrystallization, e.g. by segregation to stacking faults, transformation twins, antiphase boundaries and dislocations. It is noted that the above planar defects

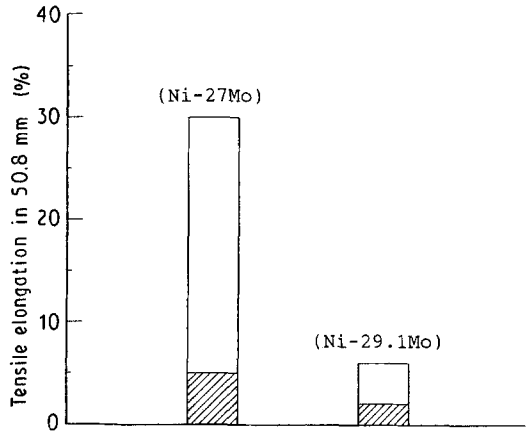

Figure 5 Comparative effects of 0.01B addition on the room temperature tensile ductilities of hypostoichiometric (Ni–27Mo) and stoichiometric (Ni–29.1Mo) alloys ordered to Ni_4Mo (exposed 24 h at 760 °C). (□ 0.01% B, ▨ 0% B).

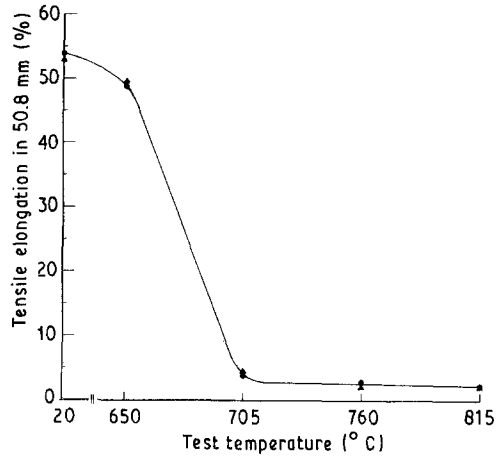

Figure 6 Comparative effects of 0.01B addition to a Ni–27Mo alloy on the elevated temperature tensile ductility (specimens exposed 24 h at the indicated temperatures prior to testing). (● Ni–27Mo, ▲ Ni–27Mo–0.01B).

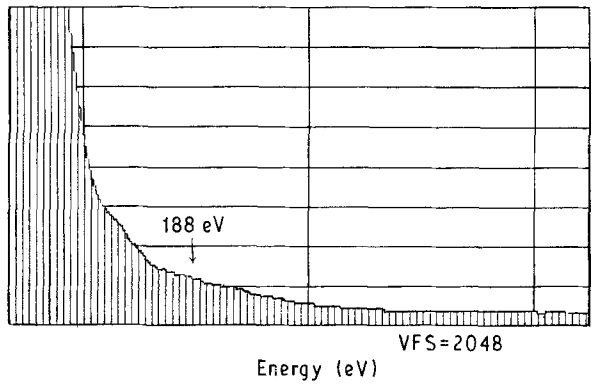

Figure 7 An EELS spectrum derived from Ni–27Mo–0.03 alloy ordered to Ni_4Mo (exposed 24 h at 760 °C). The spectrum is representative of both a grain boundary and the matrix. No B *K*-edge peak is observed at the corresponding energy of 188 eV.

result from the ordering reaction [3]. Consequently, the kinetics of heterogeneous ordering at a given exposure temperature become more sluggish. This is consistent with the observation that the beneficial

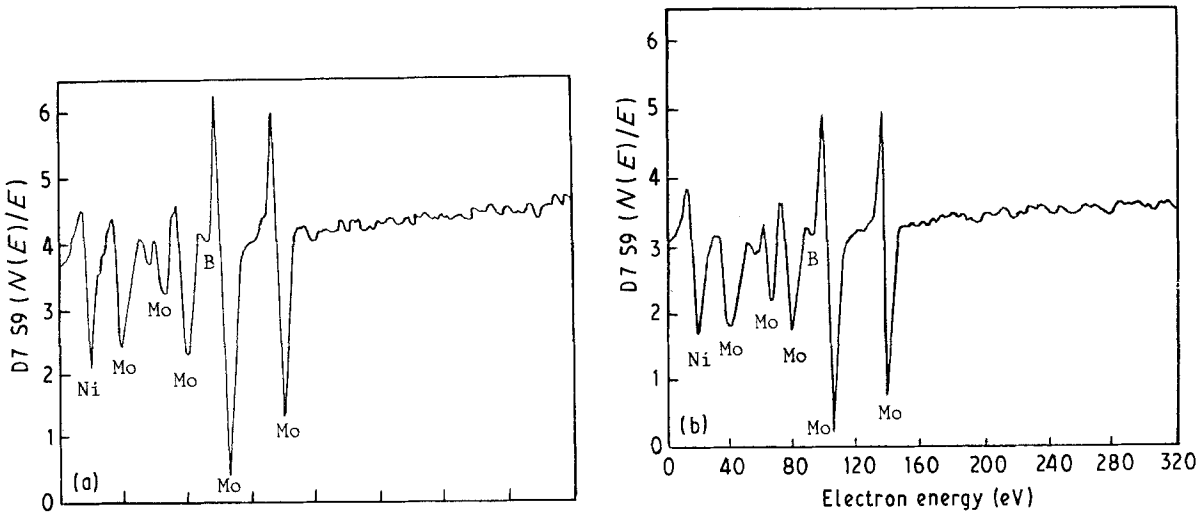

Figure 8 Auger analysis of a grain boundary and the matrix of Ni–27Mo–0.03B alloy ordered to Ni_4Mo (exposed 24 h at 760 °C). (a) Auger spectrum derived from a freshly exposed grain boundary. (b) Auger spectrum derived from the same region of (a) after sputtering a 40 nm thick layer to reveal the underlying matrix.

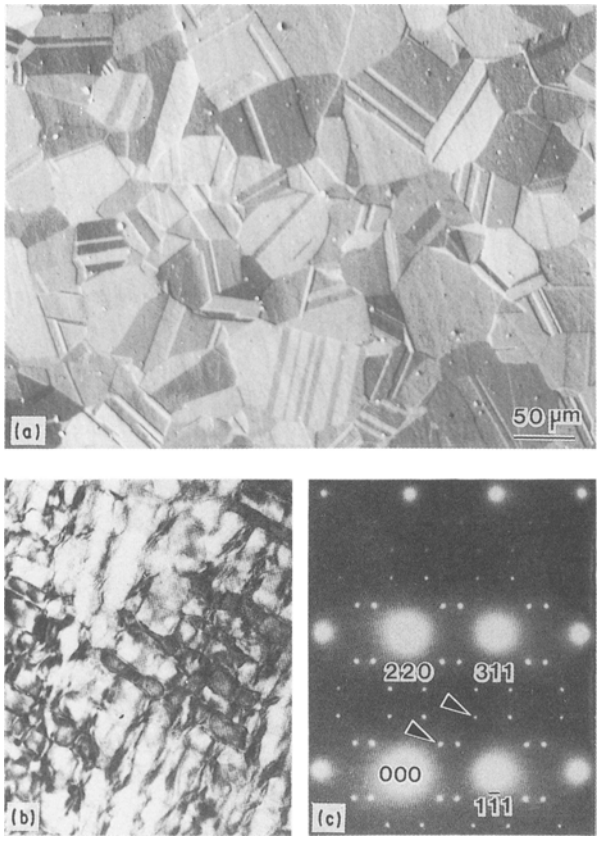

Figure 9 Representative microstructures of the alloys investigated. (a) Secondary electron SEM image illustrating a typical grain structure in the annealed condition (1065 °C/15 min/water quenching). (b) Bright-field TEM image illustrating ordered domains of Ni_4Mo in the matrix formed after 24 h exposure at 760 °C. (c) Selected-area electron diffraction pattern corresponding to the image of (a) in $[\bar{1}\,1\,2]$ orientation. Characteristic reflections of the $D1_a$ superlattice of Ni_4Mo are observed at 1/5 ⟨420⟩ positions as indicated by the arrows.

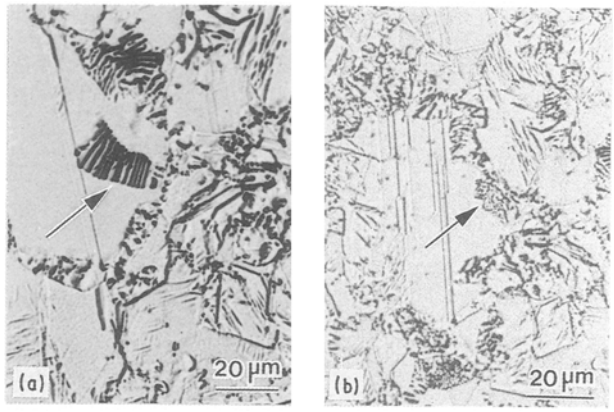

Figure 10 Light optical micrographs illustrating the effect of boron on heterogeneous grain boundary ordering after 100 h exposure at 760 °C. The resulting lamellar structure is indicated by the arrows. (a) Ni–27Mo alloy (coarse lamellar structure). (b) Ni–27Mo–0.01B (fine lamellar structure).

effect of B diminishes with exposure time at a given temperature as shown in Fig. 4. As the Mo concentration is increased and the stoichiometric composition is approached, the strain energy available to induce grain boundary migration and, thus, heterogeneous ordering becomes larger. The fraction of strain energy reduced by B addition can be expected to be comparatively less. Accordingly, the beneficial effect of B on ductility at the stoichiometric composition can be expected to become less pronounced as observed (Fig. 5). At elevated temperatures, the growth kinetics of heterogeneously nucleated ordered domains and the associated strain-induced recrystallization can be expected to be accelerated in the presence of stress which may explain the absence of a B effect as shown in Fig. 6.

4. Conclusions

An addition of 0.01 to 0.03 wt % boron was found to significantly improve the room temperature tensile ductility of hypostoichiometric Ni_4Mo alloys exposed at temperatures in the range of 600 to 800 °C. In the presence of boron, the tensile ductility was observed to increase from about 5% to 30% after short-term exposure and tensile fracture mode changed from predominantly intergranular into transgranular. The

beneficial effect of boron was, however, observed to diminish after extended exposure at a given temperature. At elevated temperatures, boron had no effect on ductility. Also, for a stoichiometric Ni_4Mo alloy, the boron effect on room temperature ductility was much less pronounced as compared to hypostoichiometric alloys. Boron showed no tendency for preferential segregation to grain boundaries. Experimental results indicated, however, that boron tends to decelerate the kinetics of heterogeneous grain boundary ordering which had the effect of improving the ductility particularly at room temperature.

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