GRAIN BOUNDARY SEGREGATION OF BORON IN NICKEL AND EFFECT OF MOLYBDENUM ADDITIONS①

Chu Youyi②, Ji Ping③, Tang Li③, Ke Jun(T.Ko)④

University of Science and Technology Beij ing, Beij ing 100083, China

ABSTRACT

By means of particle tracking autoradiography it has been found that there exists a strong tendency of equilibrium grain boundary segregation of B in Ni with binding energy of 18 ± 2 kJ / mol. In Ni–Mo–B alloys the segregation is alleviated. For additions of 0.5% and 3% Mo the grain boundary binding energies of B decrease to 14 ± 1 kJ / mol and 13 ± 1 kJ / mol respectively.

Key words: grain boundary, segregation, autoradiography

1 INTROUDUCTION

It is well known that trace additions of B in Ni-based superalloys make significant improvement of creep strength and ductility and increase the service life of the alloys at high temperature[1]. The mechanism of this effect is rather complex and depends on its composition and working conditions. In general, it has been suggested that this is attributed to the B segregation at grain boundaries. The strength of grain boundaries can be enhanced by B segregation through the following ways: 1) increment of the grain boundary coherency, 2) inhibition of grain boundary diffusion, 3) reduction of the harmful effect of impurities (O, S etc.) at grain boundaries, 4) improvement of the distribution and morphology of grain boundary precipitates[1–5].

However, few studies on grain boundary segregation of B in Ni and Ni-based super alloys have been reported. By secondary mass spectrometry, Walsh and Kear[6] found B segregation and constituents at grain boundaries in a low carbon Udiment 700 superalloy doped with 0.03%B. Suto and Sato[7] analyzing the results of internal friction of Ni and Ni–B alloys supposed that significant B segregation may exist at Ni grain boundaries. It has been shown that particle tracking autoradiography (PTA) is a powerful method for detection of the micro-distribution of B in materials[8]. Through this method Jandeska[9] measured the binding energy of B at austenite grain boundaries in a low carbon steel with 7 ppm B. In our previous works [10,11] equilibrium and nonequi librium segregations of B at austenite grain boundaries in Fe–30%Ni–B alloys were systematically studied. In order to explore the mechanism of the advantageous effect of B in Ni-based

①Manusocript Received April 2,1991.

②Professor, Academician; ③MSc; ④Professor

superalloys for long service at high temperature, the equilibrium grain boundary segregation of B in Ni and the effect of Mo additions, which is one of the common alloying elements in Ni-based superalloys, have been studied by PTA in the present work.

2 EXPERIMENTAL ALLOYS AND HEAT TREATMENT

Ni–B and Ni–Mo–B alloys were prepared with pure electrolytic Ni in a 10kg vacuum induction furnace. For deoxidation and fixation of nitrogen, 0.01%Mg and 0.008%Ti were added before the end of the melting, followed by additions of 0.5% and 3%Mo and a certain amount of Ni–B master alloy to obtain an expected content of 20ppm B in tested alloys. One 5kg ingot was produced for each heat. After homogenization at 1050℃ for 4h, the ingots were forged into 12mm diameter bars. Analyzed results of Mo and B contents of tested alloys sampled on the bars are given in Table 1. Contents of C, Mg, Ti and Co in the alloys are less than 0.01%. Then the forged bars were machined into 10mm diameter specimens, 10mm long for Ni–B alloy and 5mm long for Ni–0.5Mo–B and Ni–3Mo–B alloys.

Table 1 Mo and B contents of tested alloys (wt.%)

No	Alloy	Mo	B
1	Ni–B	/	0.0020
2	Ni–0.5Mo–B	0.46	0.0018
3	Ni–3Mo–B	2.83	0.0016

In order to obtain the same big grain size, complete dissolution of B precipitates and homogenous B distribution, specimens were first heated to a high temperature of 1,050℃ for 0.5h, followed by furnace cooling to 1,000, 900, 800, 700, 600, 500 and 400℃, each held for 0.5h, to set up the equilibrium segregation of B at grain boundaries and then rapidly quenched into ice brine to keep the segregation down to room temperature.

3 PARTICLE TRACKING AUTORADIOGRAPHY (PTA)

3.1 *Principle*

There are about 19.8 at.% isotope ^{10}B contained in natural B. Under the irradiation of thermal neutrons the nuclear fission reaction $^{10}B+^{1}n\rightarrow{}^{4}\alpha+{}^{7}Li$ takes place. The reaction products shoot into the detector film closely adhered to the specimen surface causing damage along its tracks which will be revealed as pits after etching. The density of etching pits per area (ρ) is proportional to the B concentration at the corresponding area (c) and the integrating flux of the thermal neutron irradiation (Φ), that is:

$$\rho = AC\Phi \qquad (1)$$

where A is an experimental constant. It has been estimated that for PTA, the sensitivity to B content is about 1ppm and the resolution of B spatial distribution is about 2μm[8].

Usually, measurement of the area fraction of etching pits (S) is more convenient for quantitative analysis. Assuming α as area of one etching pit, we have:

$$S = \alpha\rho = \alpha\Phi AC \qquad (2)$$

Using the following equation, the overlapping effect of etching pits can be corrected:

$$S = -\ln(1-S') \qquad (3)$$

where S′ is the apparent area fraction of etching pits experimentally measured.

3.2 *Procedure*

After heat treatment each specimen was line cut in the middle, mounted and metal lographically polished. A CA detector film was closely glued by acetone onto the surface of

the specimen, baked at 120℃ for 12h and irradiated by thermal neutrons in a nuclear reactor with integrating flux of 2×10^{13} neutrons / cm^2. After decay for about two weeks the film was removed, etched by 7.5mol NaOH aqueous solution plus potassium per manganate 5g / 100ml for about 14 min to obtain etching pits with size around 1μm, rinsed with 50% HCl solution and cleaned by water. Then the film sputtered by Cr to improve the contrast was examined under microscope and quantitatively measured by a Cambridge Q–900 Image Analyzer.

4 GRAIN BOUNDARY SEGREGATION OF B IN Ni AND EFFECT OF Mo ADDITIONS

Our previous work[10, 11] have shown that there exist equilibrium and nonequilibrium segregation of B at austenite grain boundaries. The former sets up during holding at high temperature and the latter occurs during cooling at adequate rate. In consideration of the fact that Ni-based superalloys are subjected to long service of work at high temperature, the present study focuses on equilibrium grain boundary segregation. By means of PTA, the grain boundary segregation of B was observed after isothermal holding at different temperatures in Ni–B, Ni–0.5Mo–B and Ni–3Mo–B alloys. Some typical experimental results are given in Figs.1 and 2 which show the temperature dependence of equilibrium grain boundary segregation. At high temperature, the grain boundary segregation of B was hard to be found. With decreasing temperature, the segregation intensified and the grain boundaries revealed by dense etching pits appeared as discontinuous bands up to complete networks. As temperature further decreased, besides segregation there was obvious B constituents precipitated at grain boundaries and the etching pits within grain were reduced correspondingly. All three tested alloys had this same tendency, but at the same temperature the segregation in the free Mo alloy was stronger than that in Mo bearing alloys. For Ni–B alloys, grain boundaries began to be revealed as complete networks by PTA at 800℃, and grain boundary precipitates were easy to become coarse at low temperature.

The equilibrium grain boundary segregation of solute follows the Mclean relation[12]:

$$C_B = C_G \cdot e^{Q/RT} \tag{4}$$

$$\ln(C_B / G_G) = Q / RT \tag{5}$$

where C_B and C_G are concentrations of solute at grain boundaries and within grain respectively, and Q is the grain boundary binding energy of solute. It is recognized that equilibrium segregation always concentrates in a narrow region with assumed width as δ. By means of PTA, the segregated grain boundaries are revealed as etching pit hands broadened to the width of ω, in which the etching pit density is determined by the equation:

$$\rho_B = A\Phi[\delta C_B + (\omega - \delta)C_G / \omega \tag{6}$$

The etching pit density within grain is:

$$\rho_G = A\Phi C_G$$

Thus

$$\rho_B / \rho_G = [\delta(C_B / C_G - 1) / \omega] + 1$$

when $C_B >> C_G$,

$$C_B / C_G = \omega(\rho_B / \rho_G - 1) / \delta \tag{7}$$

substituting Eq.(7) into Eq.(5), we find:

$$\ln(\rho_B / \rho_G - 1) = Q / RT - \ln\omega / \delta \tag{8}$$

With image analyzer, taking the width of the measured area as $\omega = 3.92\mu$m, the area

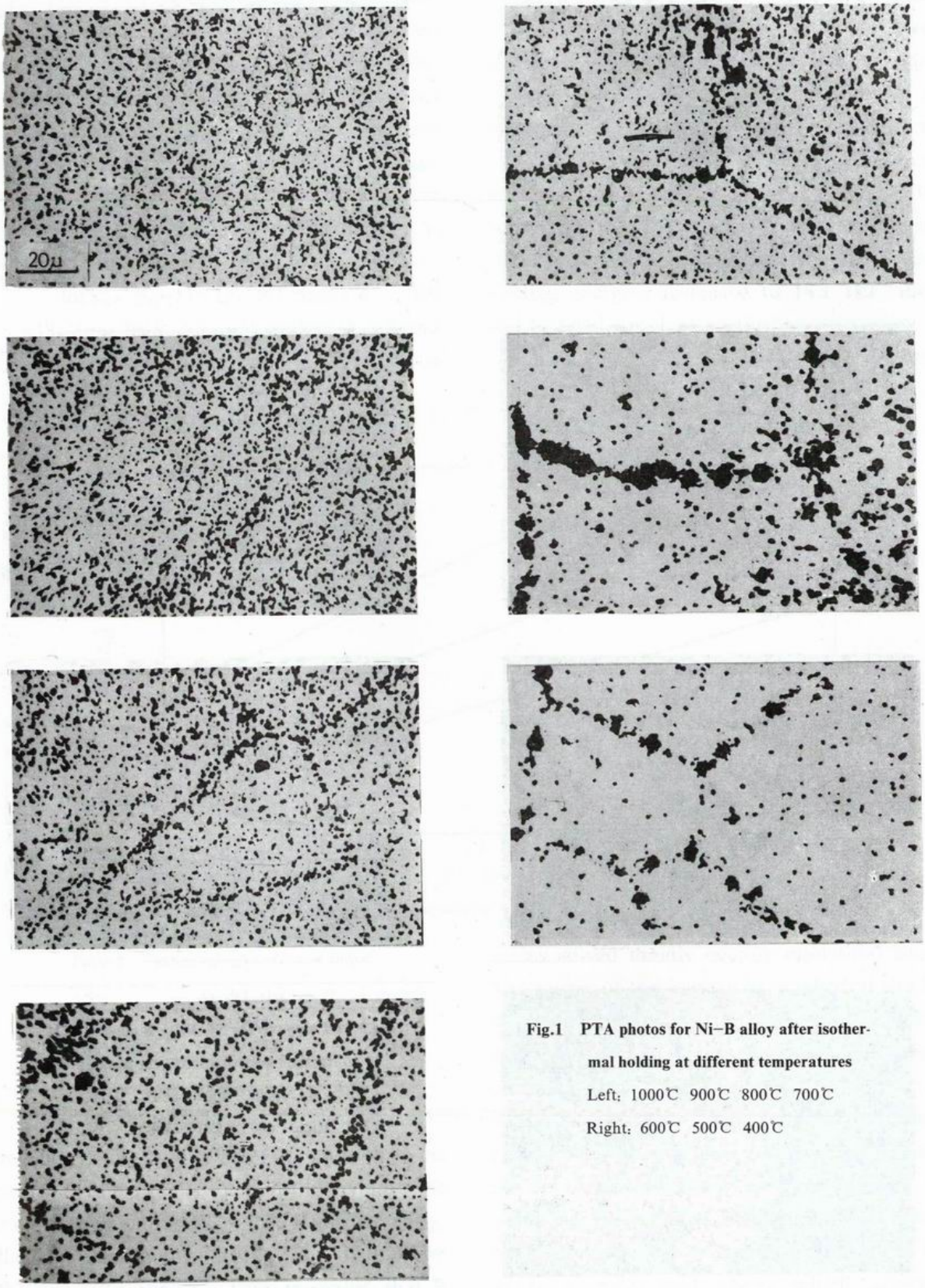

Fig.1 PTA photos for Ni–B alloy after isothermal holding at different temperatures

Left: 1000℃ 900℃ 800℃ 700℃

Right: 600℃ 500℃ 400℃

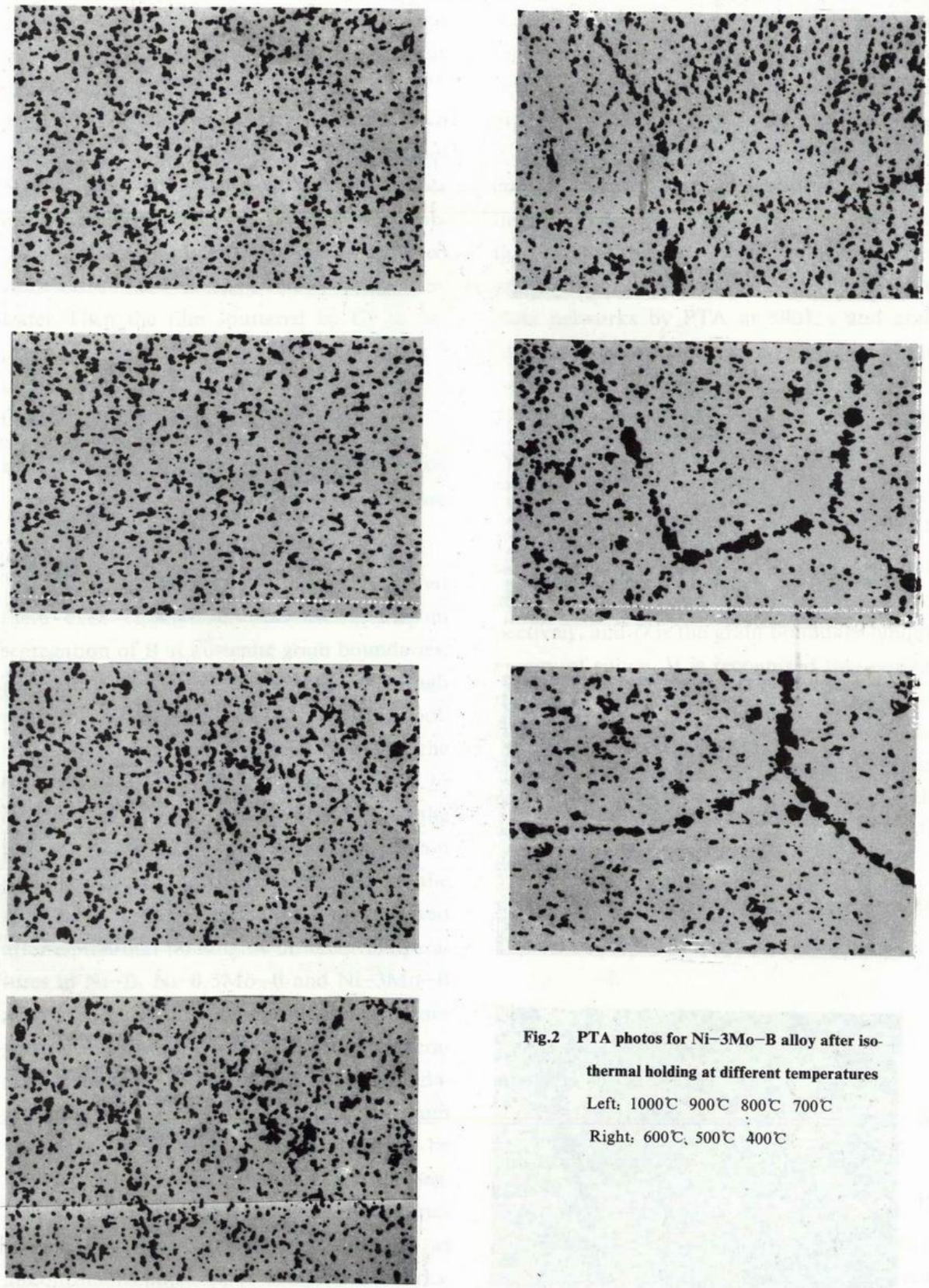

Fig.2 PTA photos for Ni–3Mo–B alloy after isothermal holding at different temperatures

Left: 1000℃ 900℃ 800℃ 700℃

Right: 600℃、500℃ 400℃

fractions of etching pits along grain boundaries (S_B) and within grain (S_G) were measured from the temperature at which grain boundaries began to be revealed as complete networks up to the temperature at which too many grain boundary precipitates occurred. The average of results from 10 grain boundaries were taken in each specimen. Substituting $S_B / S_G = \rho_B / \rho_G$ in Eq.(8), we have:

$$\ln(S_B / S_G - 1) = Q / RT - \ln\omega / \delta \qquad (9)$$

Plotting $\ln(S_B / S_G - 1)$ against $1 / T$ and fitting the experimental points with least square method as shown in Fig. 3, the grain boundary binding energies of B for the tested alloys we obtained are listed in Table 2. The experimental results show that there exists a strong tendency of grain boundary segregation of B in Ni which follows Mclean's relation with binding energy of 18± 2kJ / mol. In Ni–Mo–B alloys the segregation was alleviated. For additions of 0.5% or 3%Mo the binding energies decreased to 14± 1kJ / mol and 13 ± 1kJ / mol, respectively.

In the view of distortion energy, B with atomic radius $R_B = 0.097$nm is difficult to be resolved interstitially or substitutely into Ni with atomic radius $R_{Ni} = 0.1246$nm. Recently, the experimental results of B diffusion in Ni by the present authors[13] have indicated that B atoms solved mainly occupy interstitial sites. The raduis of the interstitial octahedral site in fcc Ni is estimated as $0.414R_{Ni} = 0.05158$nm, which is too small for the entrance of a B atom causing severe distortion in the lattice. It is reasonable that the grain boundary binding energy of B depends on the difference between the distortion energies caused by setting a B atom in grain and in grain boundaries. It is the high distortion energy caused by a B atom in grain as mentioned above which arouses

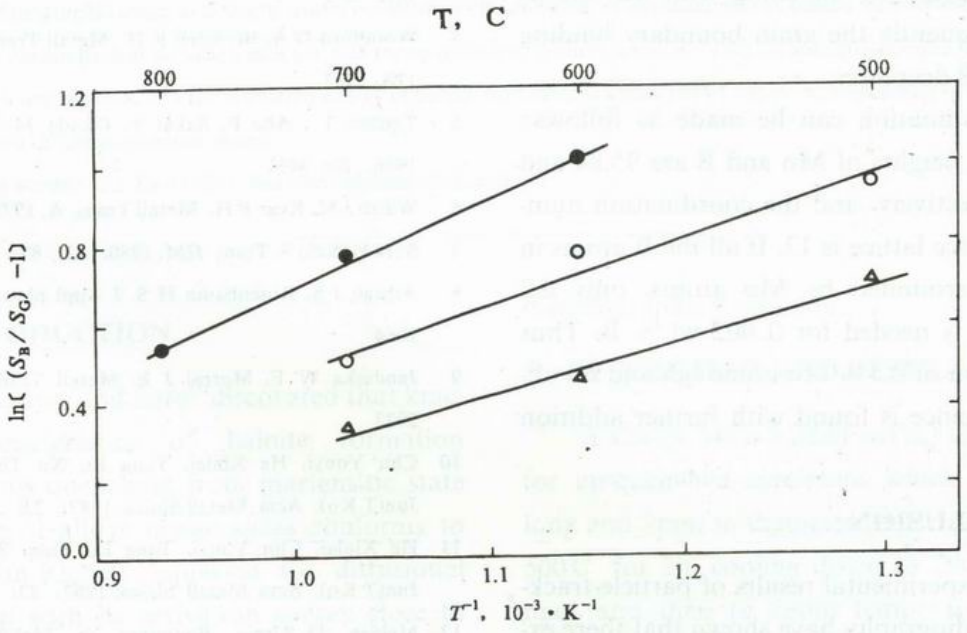

Fig.3 Temperature dependence of grain boundary segregation of B for Ni–B, Ni–0.5Mo–B and Ni–3Mo–B alloy

Table 2 Binding energies of tested alloys

Alloy	Q+δQ (kJ / *mol*)	δ_Q / Q
Ni–B	18 ± 2	11%
Ni–0.5Mo–B	14 ± 1	8.8%
Ni–3Mo–B	13 ± 1	9.7%

* δQ is the standard error.

strong B segregation to grain boundaries. Mo with atomic radius R_{Mo} = 0.1326 nm, much larger than that of Ni, substitutively resolves in Ni and gives rise to high distortion energy too. But if a big Mo atom matches with a small B atom, the size of this couple $R_{Mo}+ R_B$ = 0.2332nm is approximately equal to the size of two Ni atoms: $2R_{Ni}$ = 0.2492nm. This will lead to reduced distortion energy, which is expected to be much smaller than that caused by B and Mo atoms separately in the Ni lattice. Thus in Ni–Mo–B alloys B atoms will be stabilized in grain by matching with Mo atoms and consequently the grain boundary binding energy of B decreases.

An estimation can be made as follows: the atoms weights of Mo and B are 95.84 and 10.81 respectively, and the coordination number of the fcc lattice is 12. If all the B atoms in Ni are surrounded by Mo atoms, only 0.2 wt.% Mo is needed for 0.002 wt.% B. Thus the addition of 0.5% Mo is enough and no obvious influence is found with further addition of 3% Mo.

5 CONCLUSION

The experimental results of particle-tracking autoradiography have shown that there exists a strong tendency of grain boundary segregation of B in Ni which follows the Mclean's relation for equilibrium grain boundary segregation with binding energy of 18 ± 2kJ / mol. In Ni–Mo–B alloys the segregation is alleviated. With the addition of 0.5% and 3% Mo the grain boundary binding energies of B decrease to 14 ± 1kJ / mol and 13 ± 1kJ / mol, respectively.

REFERENCES

1 Holt R T, Wallace W. Inter Met. Rev. March 1976, 1

2 Garosshen T J, Tillman T D, McCarthy G P. Metall Trans. A. 1987. 18A: 69

3 Floreen S, Davidson J M. Metall Trans. A. 1983, 14A: 895

4 Woodford D A, Bricknell R H. Metall Trans. A. 1981, 12A: 1467

5 Tanabe T , Abe F, Sakai Y, Okada M. Trans 1S1J. 1986, 26: 968

6 Walsh J M, Kear B H. Metall Trans. A. 1975, 6A: 226

7 Suto H, Sato S. Trans JIM. 1980, 21: 83

8 Armijo J S, Rosenbaum H S. J Appl phys. 1967, 38: 2064

9 Jandeska W F, Morral J E. Metall Trans. 1972, 3: 2933

10 Chu Youyi, He Xinlai, Tang Li, Xu Tingdong, Ke Jun(T.Ko). Acta Metall Sinica. 1987, 23: A169

11 He Xinlai, Chu Youyi, Tang Li, Zhou Zhenxin, Ke Jun(T.Ko). Acta Metall Sinica. 1987, 23: A291

12 Mclean D. Grain Boundary in Metals. Oxford: Clarendon Press, 1957

13 Chu Yonyi, Ji Ping, Ke Jun (T. Ko). Acta Metall Sinica. 1991, 27: B303