Effects of Boride Former Elements on Recovery and Recrystallization of Reverse-transformed Austenite in Fe–19%Ni Alloy

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Effects of various boride former elements (Ta, W, Nb, Ti, Mo) and/or B on recovery and recrystallization of reverse-transformed austenite were examined in carbon-free Fe–19mass%Ni alloys. The combined addition of Nb and B was found to be the most effective in suppressing them; the recrystallization temperature of the reverse-transformed austenite rose up to 1 200 K which is ~ 100 K higher than that of alloys with single addition of boride former element or B. TEM observation of extraction replicas indicated that the retardation of recovery and recrystallization was due to very fine precipitates of Nb-boride. It was made clear from the theoretical analysis on the solubility product of several MB₂-type borides (M = Cr, Mn, Nb, Ti, Mo) that NbB₂ was the most stable over a wide range of temperature (773–1 173 K). This may be the reason why recovery and recrystallization do not occur up to the highest temperature in case of the combined addition of Nb and B.

KEY WORDS: Fe–19%Ni alloys; solution treatment; boride; reverse-transformed austenite; recovery; recrystallization.

1. Introduction

When microstructure is controlled through the ferrite transformation, the structure after the transformation is largely influenced by the grain size and the dislocation density in the prior austenite (γ). Normalizing of steel is known as a heat treatment for obtaining fine ferrite (α) structure by reducing the prior grain size of γ and increasing the number of nucleation site of α during subsequent transformation. Control rolling for manufacturing pipes for pipeline is also understood to be a process aiming at the fine α structure by suppressing recovery and recrystallization of γ during hot rolling by the precipitation of Nb-carbonitrides and by inducing the subsequent transformation from small grain-sized γ with high dislocation density. Similar effect has been used in the so-called ausforming, in which γ with high dislocation density is forced to transform into martensite (α'). Thus, the utilization of dislocations in the prior γ as the nucleation sites during the ferrite transformation is essential in microstructural control for obtaining fine transformed α structure.

Some of the present authors have reported the following results on 18% Ni maraging steels^{1–3)}: (1) Addition of a small amount of B (0.001–0.003%)

produces a fine dispersion of borides, and the dispersion suppresses recovery and recrystallization of γ formed by the shear-type reverse transformation. As a result, one can fairly easily obtain the reverse-transformed but still unrecrystallized γ . (2) The dislocation density in γ is very high because it contains both dislocation existed originally in the martensite (α') and those introduced later during the reverse transformation. Therefore, the solution treatment in γ region below recrystallization temperature subsequently induces α' transformation from γ with very high dislocation density, bringing about strengthening and toughening effects similar to those of ausforming only by a heat treatment, that is without deformation.

In the B added 18% Ni maraging steels, the suppression of recovery and recrystallization is caused by a dispersion of M₃B₂-type borides,⁴⁾ where M is Mo or Ti that also contributes to age hardening of this alloy. For effective suppression of recovery and recrystallization, borides are required to be finely dispersed and thermally stable. From this criterion, however, it is not necessarily clear whether Mo or Ti is the most suitable alloying element. Further, to the authors' knowledge, no systematic works have been carried out concerning the effect of boride former elements other than Mo and Ti

on recovery and recrystallization of reverse-transformed γ of extra low carbon steels.

This paper reports the effects of several boride former elements on recovery and/or recrystallization in reverse-transformed γ of an extra low carbon Fe–19%Ni alloy. This alloy was used as a model material of maraging steels, and it should be noticed that this alloy also undergoes the shear-type reverse transformation as the 18% Ni maraging steels.

2. Experimental Procedure

About 10 mm thick materials examined in the present work were produced by vacuum melting and casting, hot forging and hot rolling. Their chemical compositions are given in **Table 1**. The base composition of the alloys is Fe–19%Ni, and the alloys can be divided into three groups: single addition of a boride former element, single addition of B and combined addition of them. Ta, W, Nb, Ti and Mo were selected as boride former elements, since high melting-point borides are formed in their binary system with B. The initially designed content of alloying element was 0.1 mol% for boride former element and 0.05 mol% for B.

In the first place, all the samples were solution treated at 1473 K for 4 ks to cancel production history and to dissolve borides into the γ matrix. Samples after the

solution treatment will be called “starting materials” in the present paper. These samples were then subjected to solution treatment at lower temperatures between 923 and 1173 K for 4 ks at an interval of 25 K. They were quenched into water after each heat treatment. As in previous experiment,^{3,5)} a chloride salt bath and an alumina fluidizing bed were used for the high temperature solution treatment and for solution treatment at lower temperatures, respectively.

On all the samples, microstructure after each heat treatment was examined by optical microscopy to find out the recrystallization temperature of the reverse-transformed γ . Change in Vickers hardness (load: 10 kgf) during isochronal and isothermal annealing was measured to know the behavior of recovery and recrystallization. Dispersion state of precipitates was inspected with TEM using an extraction replica technique and their chemical compositions were analysed with EDS.

3. Experimental Results

Figures 1(a) to 1(c) shows the microstructural change of the base alloy, Fe–19%Ni, with the temperature of solution treatment. In the starting materials (a), grain boundaries of coarse prior γ can clearly be seen. After solution treatment at 923 K (b), one can still find grain boundaries of prior γ ; the recrystallization has not yet

Table 1. Chemical composition in mass% of the alloys employed. (mass%)

	Ni	Ta	W	Nb	Ti	Mo	B	C	N	P	S
Base	19.2	—	—	—	0.03	—	—	0.002	0.0022	0.002	0.0007
+ Ta	20.4	0.32	—	—	0.03	—	—	0.001	0.0020	0.001	0.0007
+ W	18.9	—	0.29	—	0.03	—	—	0.003	0.0019	0.002	0.0010
+ Nb	19.0	—	—	0.15	0.03	—	—	0.002	0.0025	0.002	0.0009
+ Ti	18.9	—	—	—	0.11	—	—	0.002	0.0017	0.002	0.0010
+ Mo	19.3	—	—	—	0.04	0.15	—	0.001	0.0022	0.002	0.0010
+ B	19.0	—	—	—	0.02	—	0.0076	0.003	0.0022	0.002	0.0007
+ B + Ta	19.1	0.25	—	—	0.02	—	0.0120	0.002	0.0021	0.001	0.0007
+ B + W	18.9	—	0.29	—	0.02	—	0.0080	0.002	0.0019	0.002	0.0007
+ B + Nb	18.9	—	—	0.15	0.02	—	0.0072	0.002	0.0017	0.002	0.0007
+ B + Ti	18.8	—	—	—	0.12	—	0.0055	0.001	0.0018	0.002	0.0010
+ B + Mo	19.0	—	—	—	0.04	0.15	0.0090	0.002	0.0025	0.002	0.0009

Si, Mn: <0.006 Al: <0.03

Fig. 1. Optical micrographs of Fe–19%Ni base alloy.

(a) 1473 K, 4 ks → WQ

(b) 1473 K, 4 ks → WQ + 923 K, 4 ks → WQ

(c) 1473 K, 4 ks → WQ + 1023 K, 4 ks → WQ

Fig. 2. Optical micrographs of Fe-19%Ni alloys.

- (a) Fe-19Ni-Nb; 1473 K, 4 ks → WQ
 (b) Fe-19Ni-Nb; 1473 K, 4 ks → WQ + 973 K, 4 ks → WQ
 (c) Fe-19Ni-Nb; 1473 K, 4 ks → WQ + 1073 K, 4 ks → WQ
 (d) Fe-19Ni-Nb-B; 1473 K, 4 ks → WQ
 (e) Fe-19Ni-Nb-B; 1473 K, 4 ks → WQ + 1123 K, 4 ks → WQ
 (f) Fe-19Ni-Nb-B; 1473 K, 4 ks → WQ + 1173 K, 4 ks → WQ

occurred. After solution treatment at 1023 K (c), however, the grain size is rather small. No trace of coarse prior γ grains can be seen, indicating the completion of recrystallization at this temperature.

Figure 2 shows microstructural change in two kinds of alloys: the alloy of single addition of Nb (Figs. 2(a) to 2(c)) and the one with combined addition of Nb and B (Figs. 2(d) to 2(f)). In the former alloy, grain boundaries of coarse prior γ are seen in the starting material (a) and after solution treatment at 973 K (b). The alloy is still in the unrecrystallized state after heating up to 973 K. During solution treatment at 1073 K (c), however, the alloy is considered to have recrystallized since no evidence of grain boundaries of prior γ can be found. In the latter alloy, grain boundaries of coarse prior γ are found in the starting material (d) and after heating at 1123 K (e), at which the former alloy has already recrystallized. Further, even after the solution treatment at 1173 K (f), grain boundaries of prior γ could be seen in some areas of the sample (as indicated by an arrow), suggesting that the alloy has recrystallized only partially, not in the whole volume.

Effects of the addition of boride former element and/or B on the recrystallization temperature of the reverse-transformed γ , determined from the microstructural observation, are summarized in Table 2. The sign ○

Table 2. Recrystallization temperature of various Fe-19%Ni alloys.

	923 K	973 K	1023 K	1073 K	1123 K	1173 K
Base	○	◐	●	—	—	—
+B	—	○	◐	●	—	—
+W	—	○	◐	●	—	—
+Ti	—	○	◐	●	—	—
+Mo	—	○	◐	●	—	—
+Ta	—	○	◐	●	—	—
+Nb	—	○	◐	●	—	—
+B+W	—	—	○	◐	●	—
+B+Ti	—	—	—	○	◐	●
+B+Mo	—	—	—	○	◐	●
+B+Ta	—	—	—	—	○	◐
+B+Nb	—	—	—	—	○	◐

- : Unrecrystallization
 ◐: Partial recrystallization
 ●: Full recrystallization

indicates the unrecrystallized state, ● the completion state of recrystallization and ◐ the intermediate state of partial recrystallization. The followings can be perceived from the table. The recrystallization is completed at 1023 K in the Fe-19%Ni base alloy. The addition of either boride former element or B certainly raises the recrystallization temperature, but the amount of its

Fig. 3. Transmission electron micrographs of extraction replicas taken from (a) Fe-19Ni-B and (b) Fe-19Ni-Nb-B alloys austenitized at 1223 K for 4 ks.

increase ΔT is rather small ($\Delta T = \sim 50$ K). In contrast with the single addition, the combined addition of both boride former element and B raises the recrystallization temperature more notably. The raising effect is the largest in Nb and Ta ($\Delta T > 150$ K), followed by Mo and Ti ($\Delta T = \sim 150$ K). The effect of W is the smallest ($\Delta T = \sim 100$ K) among boride former elements examined.

The reason for the increase in recrystallization temperature is considered below, taking Nb as an typical example of boride former element. It may be reasonable to consider that the recrystallization is retarded by the solute drag effects⁶⁾ due to Nb and/or by the inhibition of dislocation motion due to the dispersion of some kind of precipitates such as Nb-carbides, Nb-carbonitrides, (Nb, B) complexes or Nb-borides. In the alloy of single addition of Nb after water-quenching from 1223 K*, no precipitates could be observed with TEM, denying the possibility of Nb-carbides and Nb-carbonitrides. Further, since the single addition of Nb results in only a small increase in the recrystallization temperature (see Table 2), the above fact indicates a rather small contribution through the solute drag effects due to Nb. In the alloys with single addition of B and with combined addition of Nb and B, on the other hand, precipitates were certainly observed after the same heat treatment (Figs. 3(a) and 3(b), respectively). They can be seen black spots in the figure. Smaller precipitates are distributed more uniformly in a finer scale in the latter alloy than in the former one. Results of EDS analysis of precipitates are given in Fig. 4. As can be seen from the figure, large precipitates in the former alloy contains a large amount of Fe and Ni (a), and may be Fe- and/or Ni-borides. In the latter alloy, on the other hand, the intensity peak of Nb can be detected and is higher compared to those of Fe and Ni (b), indicating that the precipitate in this alloy is some phase consisting mainly of Nb and B, (Nb, B) complexes or Nb-borides. Here, we would like to insist the precipitates to be Nb-borides, not (Nb, B) complexes, from the following facts: Although (Nb, B) complexes have been reported to form mainly on grain boundaries

Fig. 4. Results of EDS analysis of precipitates observed in Fig. 3. Energy peaks corresponding to Cu come from the mesh holder of carbon replica.

due to strain-induced segregation in B added Nb-treated HSLA steels⁷⁾ after high temperature deformation, the present precipitates are uniformly dispersed within grains, not on grain boundaries, as seen in Fig. 3(b) and the samples have not been largely strained even though they have been subjected locally to some deformation during reverse transformation to γ .

At the present stage of investigation, unfortunately, we do not have any definite evidence that the precipitates are Nb-borides. Nevertheless, it may be safe to assert that the large increase in recrystallization temperature in the latter alloy originates from the fine dispersion of precipitate particles through the inhibition of dislocation motion and rearrangement by them; whether they are (Nb, B) complexes or Nb-borides seems not to be a critical point in discussing the mechanism of recrystallization retardation.

4. Discussion

The characteristics of (boride former element, B) complexes are not known and their thermodynamic data are not available at present. In the following, therefore, we will continue our discussion on the assumption that the precipitates formed by the combined addition of boride former element and B are borides. As will be shown later, the results of discussion do not contradict our insistence that the precipitates in Fig. 3(b) are Nb-borides.

* This temperature of solution treatment was chosen to be higher than the recrystallization temperature (see Table 2), to coarsen precipitates if they exist.

4.1. Effect of Boride Former Elements on Recovery Behavior

As was made clear in the previous section, the increase in recrystallization temperature of reverse-transformed γ was the most notable in case of the combined addition of Nb or Ta with B. Further, it was suggested from TEM and EDS analysis that its increase is related to the hindering effect of fine dispersion of boride-precipitates on dislocation motion and rearrangement. The suppression of recrystallization is generally considered to follow the retardation of recovery. However, the recovery behavior can not be clarified by optical microscopy, though it is suitable to decide whether the recrystallization has occurred or not. Here, the hardness measurement was used to evaluate the degree of recovery in reverse-transformed γ .

Hardness was measured using a high-temperature Vickers hardness tester under a load of 10 kgf. Since the creep strain arising during indenting can not be neglected at high temperatures and the amount of strain differs at different temperatures, measurement was made at a constant temperature, 623 K (higher than the Md point), after holding samples at a prescribed heating temperature (923–1173 K) for 1 ks. The alloys examined are the base

alloy, the B added alloy and those with combined addition of Mo, Ti or Nb with B. **Figure 5** shows the change in hardness during isochronal annealing for 1 ks. The temperature above which rapid softening occurs, presumably due to the initiation of recrystallization, is different from alloy to alloy: ~ 1020 K in the base alloy and the B added one, ~ 1070 K in the alloys of combined addition of Mo or Ti with B and ~ 1130 K in the one with combined addition of Nb and B. Unfortunately, however, a gradual decrease in hardness due to recovery can not be discerned clearly in the isochronal annealing, so that the hardness change was measured during isothermal annealing at 973 K (Fig. 6) to examine this precedent phenomenon, recovery.

As seen in Fig. 6, hardness of the samples is almost equal immediately after heated up to 973 K, since they are all in the unrecrystallized state. With an increase in holding time, softening occurs from the beginning in the base alloy and in the B added one. However, no significant reduction of hardness does not occur until 100 s in the alloys with combined addition of Mo or Ti with B, and until 1 ks in the Nb and B added alloy. These facts certainly imply that the rate of recovery is reduced by the combined addition of boride former element and

Fig. 5.

Change in Vickers hardness during isochronal annealing. Measurement was made at 623 K on the samples heated at the prescribed temperature (923–1173 K) for 1 ks and then cooled down to 623 K.

Fig. 6.

Change in Vickers hardness of the starting materials during isothermal annealing at 973 K.

B, especially by the addition of Nb and B.

Retardation of the recovery process mentioned above may be ascribed to the hindering effect of fine dispersion of borides on dislocation motion and rearrangement.⁴⁾ We would like to assert here that the retardation of recovery leads to the suppression of recrystallization and further to the increase in recrystallization temperature of the reverse-transformed γ .

4.2. Relation between Solubility Product of Borides and Recrystallization Temperature

If the above origin of the increase in recrystallization temperature is correct, the boride precipitates effective to its increase must be (1) fine in size, (2) abundant in number and (3) stable thermally. Conditions (1) and (2) could be realized by increasing the degree of supersaturation of the boride former element and B and further by increasing the number of nucleation site of precipitates through the increase in dislocation density. For the condition (3), a boride former element with small diffusivity would be desirable. In view of practical heat-treatment processes of the present alloys, characteristics required for the borides are that they dissolve into the reverse-transformed γ matrix during heating around 1473 K and that they precipitate at a temperature below its recrystallization temperature. The optimum contents of boride former element (M) and B and the resultant quantity of precipitates could be expected from the evaluation of solubility product of borides. Although the stoichiometric compositions of borides formed in the alloys examined are unclear at present, the existence of at least 3 types of boride⁸⁾ has been confirmed: MB_2 , M_2B and M_3B_2 . Among high melting-point borides formed in an M and B binary system, the solubility product of MB_2 -type boride was evaluated here for $M = \text{Cr, Mn, Nb, Ti and Mo}$,* since thermodynamic data for them are available at present. In practical calculation, a simplification was made using the interstitial-type regular solution model⁹⁾ for the free energy (G) of a quaternary system Fe-X1-X2-B and the chemical potential (μ) of each element.

In an A-B binary system, the equilibrium between α phase (the primary solution of A) and θ phase (AmBn) at a given temperature is expressed by a common tangential line on to the free energy curves of both phases. Their equilibrium composition can be obtained by solving the following equation,

$$(m+n)G\theta = m\mu_A\alpha + n\mu_B\alpha \quad \text{.....(1)}$$

where $G\theta$ is the free energy of θ phase per mol, and $\mu_A\alpha$ and $\mu_B\alpha$ are the chemical potentials of A and B in α , respectively. Here, we consider the solubility of MB_2 -type boride in the austenite γ . Assuming that Fe is substantially insoluble into the MB_2 -type boride, the condition for equilibrium between MB_2 and γ can be expressed by

$$3G_{MB_2} = \mu_M + 2\mu_B \quad \text{.....(2)}$$

Using approximate equations for the interstitial-type

regular solution model and some simplification, the following expression can be obtained for the solubility product of MB_2 -type boride:

$$(X_M)(X_B)^2 = \exp\left[\frac{\{\Delta G_{MB_2} - 2(G_B\gamma - G_B + \Omega_{FeB}) - X_{Fe}\Omega_{FeM} - X_{X_2}(\Omega_{MX_2} - \Omega_{FeX_2})\}}{RT}\right] \quad \text{.....(3)}$$

where $\Omega_{X_iX_j}$ is the interaction parameter of X_i and X_j atom. The derivation of Eq. (3) is given in the Appendix in detail.

As an example, the solubility product $(X_{Nb})(X_B)^2$ in case of $M = \text{Nb}$ at 1273 K is evaluated from Eq. (3) to be 1.22×10^{-11} by substituting parameters reported hitherto: $\Delta G_{NbB_2} = -59\,000 \text{ cal/mol}$,¹⁰⁾ $G_B\gamma - G_B + \Omega_{FeB} = 6\,900 \text{ cal/mol}$,¹¹⁾ $\Omega_{NbNi} = -21\,600 \text{ cal/mol}$,¹²⁾ $\Omega_{FeNb} = -7\,140 \text{ cal/mol}$,¹³⁾ $\Omega_{FeNi} = -1\,900 \text{ cal/mol}$,¹³⁾ $X_{Ni} = 0.19$ and $X_{Fe} = 0.80$. To the authors' knowledge, however, data of Ω_{MX_2} have not been reported in the literature except for $M = \text{Nb}$. In practice, therefore, the solubility product was estimated using Eq. (4) in which the fourth term in the bracket in Eq. (3) was omitted.

$$(X_M)(X_B)^2 = \exp\left[\frac{\{\Delta G_{MB_2} - 2(G_B\gamma - G_B + \Omega_{FeB}) - X_{Fe}\Omega_{FeM}\}}{RT}\right] \quad \text{.....(4)}$$

It may be seen from comparison of $(X_{Nb})(X_B)^2$ values obtained from Eq. (3) (1.22×10^{-11}) and Eq. (4) (see Fig. 7) that the omission of the term regarding Ω_{MX_2} does not make a large difference in the solubility product.

Logarithm of the solubility product for $M = \text{Cr, Mn, Nb, Ti and Mo}$ is given in Fig. 7 as a function of the reciprocal of temperature. For alloying elements examined in the present work, it decreases in the order of Mo, Ti and Nb at a given temperature. This order agrees with the order of recovery retardation estimated by the high-temperature hardness measurement (see Fig. 6). When both boride former element and B have all

Fig. 7. Calculated solubility product of MB_2 -type boride in Fe-M-B ternary system, as a function of the reciprocal of temperature.

* M was selected from among transition elements belonging to the IV through VII family in the periodic table.

dissolved into the γ matrix, the solubility product should be $(0.001)(0.0005)^2 = 2.5 \times 10^{-10}$. Further, when it becomes larger than this value above a certain temperature, the corresponding boride could not remain thermally stable any more above that temperature; they would dissolve into the matrix. Judging from such a point of view, the notable dissolution into the matrix is considered to occur only above ~ 1500 K in case of NbB_2 and TiB_2 , while it begins at a much lower temperature, ~ 1000 K, for MoB_2 (see Fig. 7). Recovery and subsequent recrystallization will certainly be accelerated by the dissolution of boride.

From the experimental results and analysis mentioned before, we would like to conclude that microalloying of the elements, which dissolve into the reverse-transformed γ matrix during the high temperature heat treatment (1473 K for 4ks) and then precipitate as fine boride particles at lower temperatures during solution treatment in the unrecrystallized region of γ , is effective in suppressing the recovery and subsequent recrystallization and hence in raising the recrystallization temperature. Within the extent of the present work, the combination of Nb and B was concluded to be the most effective. Further, the validity of the above analysis may be supported by a fact that the MB_2 -type boride has the highest melting point at least in the Nb-B and Ti-B binary systems, though there exist other types of boride in these systems.

5. Summary

Effects of boride former elements (Ta, W, Nb, Ti and Mo) and B on the behavior of recovery and recrystallization of reverse-transformed austenite were studied using Fe-19mass%Ni alloys added with 0.1 mol% of one of the above metallic elements and/or 0.05 mol% of B, singly or in combination. Main results are summarized as follows.

Single addition of either boride former element or B raised the recrystallization temperature, but its increase was only ~ 50 K at most. In case of the combined addition of both boride former element and B, on the other hand, its increase came up to more than 100 K. Further, at least within the extent of the present experiment, the combination of Nb and B was the most effective for its increase.

Combined addition of boride former element and B also retards the recovery process that occurs prior to recrystallization. This may be ascribed to the hindering effect of fine dispersion of boride precipitates on dislocation motion and rearrangement. The most notable recovery retardation and the highest recrystallization temperature observed in case of the combined addition of Nb and B may be due to a fact that, because of the smallest value of its solubility product, fine precipitates of Nb-boride (probably NbB_2) still remain even at high temperatures in the unrecrystallized region of γ .

From a viewpoint of practical heat treatment of Fe-19mass%Ni alloy, Nb and B are concluded to be the best selection as microalloying elements for strengthening and toughening the alloy by the solution treatment in

the unrecrystallized region.

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Appendix

The right hand side of the Eq. (2) can be derived by introduction of respective chemical potentials.

$$\begin{aligned} \mu_M + 2\mu_B = & {}^\circ G_M + 2(1 - X_M - X_{X_2})G_B^{\text{Fe}} + 2X_M\Delta G_B^M \\ & + 2X_{X_2}\Delta G_B^{X_2} + (1 - 4X_M - X_{X_2})\Omega_{\text{FeM}} - 3X_{X_2}\Omega_{\text{FeX}_2} \\ & + X_{X_2}\Omega_{\text{MX}_2} + 2X_M L_{\text{FeM}}^B + 2X_{X_2} L_{\text{FeX}_2}^B \dots\dots\dots (\text{A-1}) \end{aligned}$$

where $L_{X_i X_j}^B$ is the interaction coefficient of X_i and X_j atom when B atom occupies the sub-lattice, G_B^{Fe} is the free energy when B atom occupies all the sub-lattice point in Fe-B solid solution, and ΔG_B^M and $\Delta G_B^{X_2}$ the free energy of B atom in dilute solution. Furthermore by assuming that the interaction parameters are not affected by the presence of B, namely $G_{\text{FeM}} = L_{\text{FeM}}^B$, $\Omega_{\text{FeX}_2} = L_{\text{FeX}_2}^B$, Eq. (A-1) is expressed as follows.

$$\begin{aligned} \mu_M + 2\mu_B = & {}^\circ G_M + 2(1 - X_M - X_{X_2})G_B^{\text{Fe}} + 2X_M\Delta G_B^M \\ & + 2X_{X_2}\Delta G_B^{X_2} + (1 - 2X_M - X_{X_2})\Omega_{\text{FeM}} \\ & - X_{X_2}(\Omega_{\text{FeX}_2} - \Omega_{\text{MX}_2}) + RT \ln(X_M)(X_B)^2 \dots (\text{A-2}) \end{aligned}$$

Since the terms ΔG_B^M and $\Delta G_B^{X_2}$ represent free energies of B in a dilute solution, if the interaction is free from Fe, M, and X_2 , the underlined terms in Eq. (A-2) will be

$$\begin{aligned} 2(1 - X_M - X_{X_2})G_B^{\text{Fe}} + 2X_M\Delta G_B^M + 2X_{X_2}\Delta G_B^{X_2} \\ = 2(G_B^\gamma - G_B + \Omega_{\text{FeB}}) \dots\dots\dots (\text{A-3}) \end{aligned}$$

(In ternary systems this represents substitution to free energy of B) where G_B^γ is the free energy of B in γ . Therefore the free energy for formation of MB_2 , ΔG_{MB_2} , will be expressed in the following equation in terms of Eqs. (A-2) and (A-3).

$$\begin{aligned} \Delta G_{\text{MB}_2} = & 3G_{\text{MB}_2} - (G_M + 2G_B) \\ = & 2(G_B^\gamma - G_B + \Omega_{\text{FeB}}) + (1 - 2X_M - X_{X_2})\Omega_{\text{FeM}} \\ & - X_{X_2}(\Omega_{\text{FeX}_2} - \Omega_{\text{MX}_2}) + RT \ln(X_M)(X_B)^2 \dots\dots (\text{A-4}) \end{aligned}$$

and results in

$$\begin{aligned}
 (X_M)(X_B)^2 = \exp[\{ \Delta G_{MB_2} - 2(G_B \gamma - G_B + \Omega_{FeB}) \\
 - (1 - 2X_M - X_{X_2})\Omega_{FeM} \\
 - X_{X_2}(\Omega_{MX_2} - \Omega_{FeX_2}) \} / RT] \quad \dots\dots (A-5)
 \end{aligned}$$

$$\begin{aligned}
 (X_M)(X_B)^2 = \exp[\{ \Delta G_{MB_2} - 2(G_B \gamma - G_B + \Omega_{FeB}) - X_{Fe}\Omega_{FeM} \\
 - X_{X_2}(\Omega_{MX_2} - \Omega_{FeX_2}) \} / RT] \quad \dots\dots\dots (3)
 \end{aligned}$$

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where, if $X_M \ll X_{X_2} + X_{Fe} \cong 1$, Eq. (A-5) is