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Distribution equilibria of iron and nickel in two phase fields of the Fe–Ni–B system

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The crystallographic characteristics and the equilibrium ratios for solid solutions containing 33 and 50 at% boron which belong to the Fe–Ni–B system are described. The study was carried out on samples obtained by diffusion at 1073 K, of mixtures of the elements in powder form. It was possible to confirm the existence of a complete solid solution between the compounds Fe_2B and Ni_2B. On the other hand, there are two solid solutions containing 50 at% boron: one is derived from the compound FeB in which up to 70% of the iron atoms can be substituted by nickel, the other derives from the boride NiB and extends as far as the component $(Ni_{0.85}Fe_{0.15})B$. Curves were obtained indicating the variation of lattice parameters and volume of the respective elementary cells with composition for these solid solutions. The different insertion of nickel in the borides was also quantified and the relative limit distribution coefficient was evaluated. Its value is consistent with those calculated on analogous borides of transition elements at the same temperature.

1. Introduction

The results reported in this paper fit into a series of systematic research projects aiming to define the equilibrium relations between the phases which appear in ternary systems including boron and transition metals. The knowledge obtainable from a precise definition of the Fe–Ni–B state diagram provides a valuable contribution to the development of cast irons and steels alloyed to boron, and to the characterization of the borided surface layers obtained on iron–nickel alloys and austenitic stainless steels [1, 2].

As early as 1966, Kaneko *et al.* [3] ascertained the presence of a complete series of components included between the isomorphous tetragonal compounds Ni_2B and Fe_2B (G.S. D_{4h}^{18}–I4/mcm). Shortly afterwards Monnier *et al.* [4] reached the same conclusion. Moreover they reported the variation of the cell parameters (with the composition) calculated on samples obtained at 1123 K (850° C). In particular, the value of a_0 decreases progressively, although not linearly, with the increase in the number of iron atoms substituted by nickel atoms, in accordance with the relative dimensions of the two types of metallic atoms. On the other hand, c_0 varies only slightly and its trend, with composition, shows a minimum at 45 at% nickel, related to the sum of the metallic atoms. Starting from this last paper, Stadelmaier and Pollock [5] traced the ternary phase diagram Fe–Ni–B limiting it to a non-metal content of between 0 and 33 at%, confirming the existence at 1073 K (800° C) of a one-phase field between the two extreme borides Fe_2B and Ni_2B.

Today the information in the literature is still not exhaustive with regard to the compounds FeB and NiB, to the possibility of the formation of (Fe, Ni)B type crystals and to the variation of their cell parameters with composition. When deciding the aims of this research we proposed not only to define the zone of the above-mentioned phase diagram between 33 and 50 at% non-metal, but also to quantify, in particular, the differentiated distribution of the metallic atoms among the phases with a different boron content present in them.

It is known that in ternary samples containing (M′, M″)B and $(M', M'')_2B$ type crystals (M′, M″ = chromium, manganese, iron, cobat) the transition element with the lower atomic number is preferentially inserted in the phase richest in the non-metal [6–9]. If, in the isothermal sections of the relative ternary equilibrium diagrams, the points corresponding to the composition of the two components in equilibrium with each other are joined together, segments are obtained which belong to sloping straight lines all lying on the same side in relation to the vertex corresponding to 100% boron.

In order to represent the phenomenon of differentiated distribution better, Hagg and Kiessling [10] proposed, for analogous systems, to report on a graph the atomic fractions of a single element in borides in equilibrium with each other. The locus of points having co-ordinates $x_{M'}^{(M',M'')B}$ and $x_{M'}^{(M',M'')_2B}$ is a curve which moves further away from the diagonal of the diagram the greater the preferential insertion of the metal M′ in one of the two borides is.

This phenomenon can then be quantified on the basis of the "distribution ratio" value, calculated by means of the following formula:

$$\alpha_{M'} = \frac{x_{M'}^{(M',M'')B}}{x_{M'}^{(M',M'')_2B}}$$

which is valid assuming that the metal M′ is inserted

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TABLE I Composition (in wt %) of the two-phase alloys examined

Sample no.	Fe ±0.1	Ni ±0.1	B ±0.3
1	81.9	6.3	11.7
2	76.3	12.3	11.5
3	68.9	18.9	12.0
4	61.2	27.6	11.3
5	52.2	36.6	11.0
6	45.3	43.1	11.8
7	34.9	53.5	11.6
8	25.8	63.2	11.1
9	17.3	71.3	11.8

to a greater extent in the boride $(M', M'')_2B$. The value of the above-mentioned parameter decreases and tends to become constant for very dilute solid solutions, that can be considered almost ideal within this range. It is thus possible to obtain, by extrapolation, the limit distribution ratio characteristic of every pair of transition elements.

2. Operative methods

The samples used in this research were obtained from reduced Merck iron (Fe = 99.5 wt %), Merck nickel (Ni = 99.5 wt %) and Research O.I.C.C. boron (B = 99.98 wt%). The particle-size analysis of the three raw materials ranged from 10 to 20 μm.

After mixing thoroughly in a mortar, cylindrical tablets of 10 mm diameter were formed by means of pressing at 200 MPa. Then the samples, each of 5 g in weight, were closed in evacuated silica glass tubes and heated to a temperature of 1073 K (800° C) for times from 4 to 20 h.

Measurement of the lattice constants of one-phase solids (accuracy ± 0.2 pm) was carried out roentgenographically using radiation $\text{Fe}K\alpha_1 (\lambda = 193.60\,\text{pm})$. The results enabled us to trace the graphs reporting the variation in value of each cell parameter with composition. Of the components present in the two-phase samples, the dimensions of the respective elementary cells were measured first by means of an X-ray diffractometer, then the compositions were deduced using the relative graphs previously described.

After heating, every solid sample was subjected to atomic absorption analysis in order to determine the exact percentage of the constituents. The composition of two-phase samples is shown in Table I.

3. Discussion of the results

This research was conducted on samples heated to 1073 K (800° C) in order to avoid the formation of liquid. It must be remembered that the binary diagram Ni–B available in the literature [11] reports eutectic temperatures close to 1290 K (precisely 1018° C), where the boron content is between 33 and 50 at %.

3.1. (Fe, Ni)$_2$B phase

We were able to confirm the existence of a complete solid solution included between the isomorphic compounds Fe_2B and Ni_2B. Fig. 1 shows the variation of the cell parameters and volume, with composition, for the $(Fe, Ni)_2B$ phase. The shape of the trend is in accordance with what Monnier *et al.* [4] observed previously on samples heated to 1123 K (850° C).

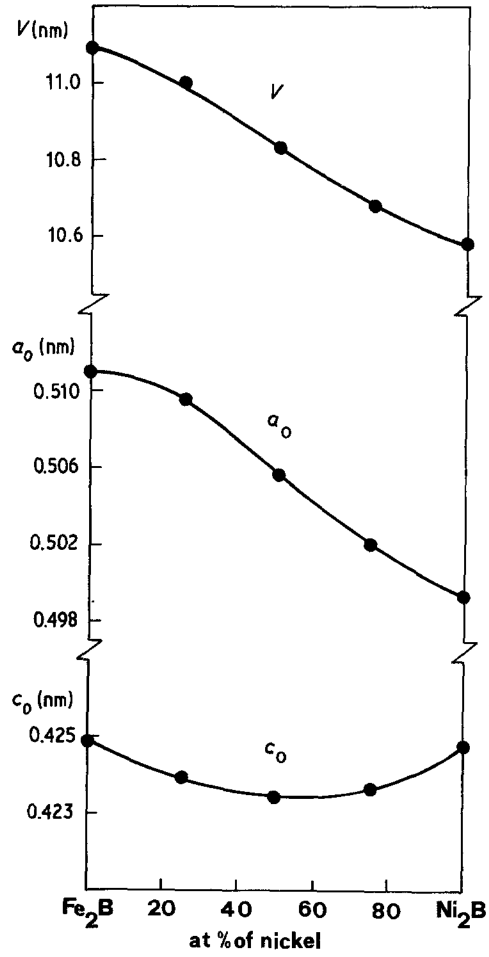

Figure 1 Variation of the cell parameters and volume with composition for the $(Fe, Ni)_2B$ phase.

3.2. (Fe, Ni)B phase derived from FeB boride

One should not expect the existence of a single one-phase field between the two compounds FeB and NiB, both orthorhombic, but which have different space groups: the first V_h^{16}–Pbnm, the second V_h^{17}–Cmcm [12]. In the first phase the substitution of iron by nickel reches 70 at % at 1073 K (800° C).

Fig. 2 shows the variation of a_0 with composition. This follows Vegard's law only for quantities of nickel greater than 40 at %. Where there are high percentages of iron we measured values systematically higher than those theoretically to be expected: as a result, in this part the a_0/composition curve is markedly concave towards the bottom.

In accordance with the different dimensions of the metallic atoms and with Vegard's law, b_0 varies in a way inversely proportional to the percentage of nickel atoms as far as the solid of formula $(Fe_{0.60}Ni_{0.40})B$. For the samples richest in this metal, however, it was found that there is an increase in b_0 directly proportional the percentage of atoms substituted.

The c_0 increases with the progressive iron–nickel substitution. This trend is, however, more marked for components included between the compounds FeB and $(Fe_{0.60}Ni_{0.40})B$ compared with solids richest in nickel.

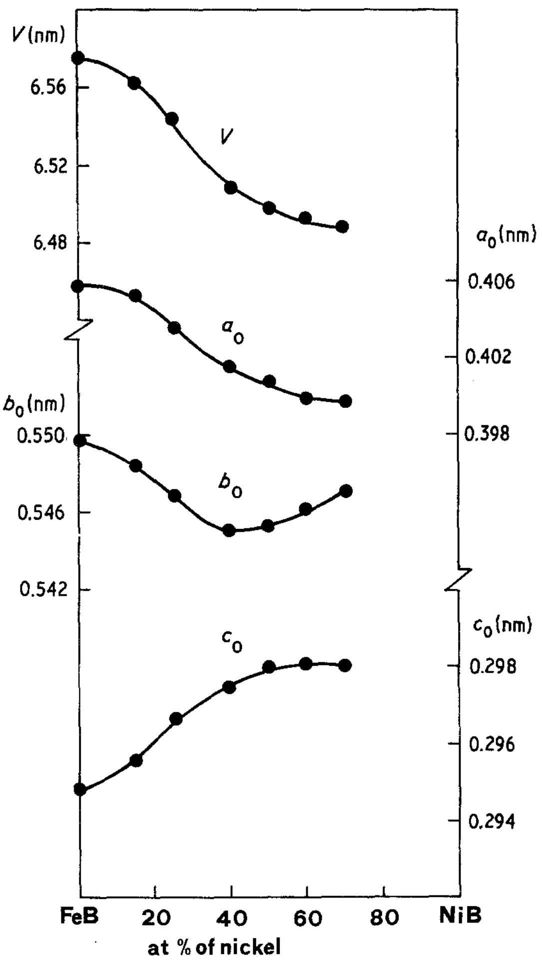

Figure 2 Variation of the cell parameters and volume with composition for the (Fe, Ni)B phase.

In order to correlate more correctly the variation in size of the crystal lattice with composition, the same figure shows the values of the elementary cell volume for the components of the solid solution (Fe, Ni)B used in this research. In accordance with the different atomic radii of the two diadochal metals we observe that the above-mentioned volume decreases with the progressive substitution of nickel. The tendency towards lattice contraction is less marked for solids containing more than 40 at % nickel.

To justify the presence of a singular point in the lattice parameters/composition graphs at an iron–nickel substitution equal to 40 at %, we can refer to the structure of compound FeB described by Kiessling [13]. The zig-zag chains of which the boron atoms are part and which extend indefinitely through the crystal, could explain the particular variation of the cell dimensions when the substitution of metalic atoms occurs in the area of the positions 4c which these atoms occupy. Also in solid solutions derived from the compound Fe_2B, which presents analogous chains of boron atoms, other authors [4, 14] observed a singular point in the lattice parameter/composition graphs when the substitution Fe–M (M = nickel, manganese) occurs.

3.3. (Ni, Fe)B phase derived from NiB boride

Unlike what happens in the compound FeB, in the boride NiB, metallic atom substitution occurs to a limited extent: samples containing more than 15 at % iron (compared with the sum Fe + Ni) were found to be heterogeneous on roentgenographic analysis. The variation of the lattice parameters b_0 and c_0 with composition, calculated on powder spectra, is very small and consequently not higher than measurement errors. On the other hand, we can affirm that the parameter a_0 increases as a result of the progressive substitution of nickel atoms with iron, passing from 293.1 pm for the compound NiB to 294.5 pm for the component $(Ni_{0.85}Fe_{0.15})B$. This is in accordance with the greater dimensions of iron atoms compared with those of nickel.

3.4. Differentiated distribution

Fig. 3 represents the portion included between 33 and 50 at % of the nonmetal of the Fe–Ni–B phase diagram. In this figure we joined with thin segments the points indicating the composition of the components in equilibrium with each other contained in two-phase samples and belonging to the solid solutions (Fe, Ni)B and $(Fe, Ni)_2B$. As a result of the differentiated distribution of the metallic atoms, these segments lie on straight lines, all situated on the same side compared with the vertex representing 100% boron.

In Fig. 4 on the x and y co-ordinates, respectively, the atomic fractions of nickel (compared with the total of metallic atoms) in the phases (Fe, Ni)B and $(Fe, Ni)_2B$ are shown. For ease of interpretation, we have inserted the diagonal of the diagram with a thin line. Because of the inequality in distribution, the representative points which we obtained on the samples are a long way from the diagonal.

It is possible to quantify the preferential distribution (see Fig. 5) by plotting, against the average atomic fraction of nickel in the two borides, the α_{Ni} distribution ratio, defined as the quotient between the atomic fractions of this element in the above-mentioned phases. This ratio, which tends towards one for high nickel concentrations, decreases until it assumes an almost constant value obtainable by extrapolation of those values calculated for

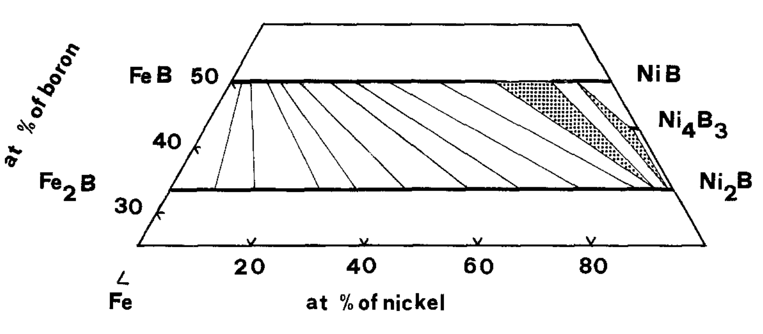

Figure 3 Portion of Fe–Ni–B phase diagram included between 33 and 50 at % boron (1073 K).

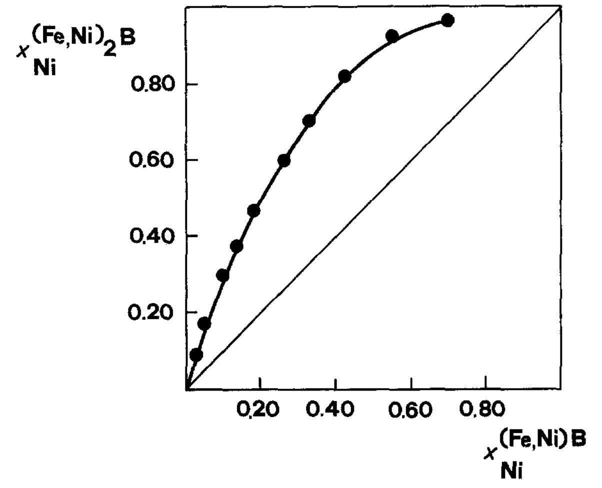

Figure 4 Relation between the atomic fractions of nickel in the phases (Fe, Ni)B and (Fe, Ni)$_2$B.

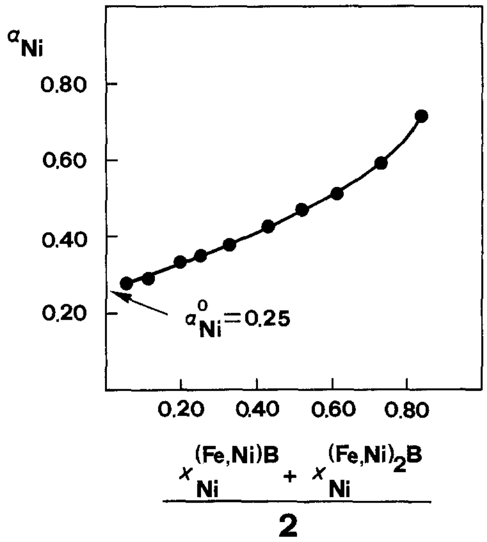

Figure 5 Variation of the distribution ratio with the mean atomic fraction of nickel (1073 K).

components richest in iron. In the case under study, the limit distribution ratio of nickel (α_{Ni}^0) was found to be 0.25, which conforms with what was found in previous papers [15].

4. Conclusions

On the basis of the results obtained in this research, the following conclusions can be drawn:

1. The existence of a complete solid solution, of which the isomorphic compounds Fe_2B and Ni_2B constitute the extreme components, is confirmed. The cell parameter variations which we observed are consistent with the different dimensions of the diadochal atoms and are in agreement with those found in the literature.

2. Nickel can substitute iron in the compound FeB up to 70 at %; this causes the contraction of the elementary cell of the iron boride. The presence of a singular point in the lattice parameter/composition graphs is due to the particular arrangement of the boron atoms forming direct chains parallel to the z-axis of the crystal lattice.

3. The solubility of iron in the compound NiB is slight: the one-phase field extends as far as the composition component $(Ni_{0.85}Fe_{0.15})B$. The cell deformation, resulting from nickel–iron substitution, is negligible: only the a_0 parameter varies appreciably.

4. In the area of the Fe–Ni–B phase diagram included between 33 and 50 at % non-metal, there is a large three-phase field in which the components $(Fe_{0.30}Ni_{0.70})B$ and $(Ni_{0.85}Fe_{0.15})B$ are in equilibrium with each other. The third solid consists of the compound $(Fe_{0.03}Ni_{0.97})_2B$ which is part of the complete solid solution included between the borides Fe_2B and Ni_2B.

5. Nickel is present in different concentrations in components of type (Fe, Ni)B and (Fe, Ni)$_2$B in equilibrium with each other. To be more precise, it inserts itself preferentially, compared with iron, in the boride containing less boron, similar to what was found with other transition metals with atomic number between 24 and 28. This behaviour can be justified by recalling the hypothesis previously advanced as regards the stability of the M–X bond (M = transition metal; X = hydrogen, boron, carbon, nitrogen) [16]. The value of α_{Ni}^0 is consistent with those obtained at the same temperature in the course of previous studies carried out on systems M′–M″–B (M′, M″ = chromium, manganese, iron, cobalt). However, we were not able to calculate the corresponding value of α_{Fe}^0 because of the limited extension of the solid solution (Ni, Fe)B, which gives rise to a variation in the lattice parameters which is not exactly quantifiable. In addition, the presence of a phase derived from the intermediate compound Ni_4B_3 prevents equilibrium between those components richest in nickel, belonging to the two solid solutions (Fe, Ni)$_2$B and (Ni, Fe)B, whose distribution coefficients could reach in value α_{Fe}^0.

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