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DIFFUSION OF BORON IN COBALT SINTERS

DYFUZJA BORU W SPIEKACH KOBALTU

The paper describes the process of diffusion taking place at the surface of sinters produced from Co Extrafine powder after saturation with boron. Boronizing was performed at a temperature of 950 °C for 6 and 12 hours by applying B_4C powder as a depositing source, $NH_4Cl + NaF$ as an activator and Al_2O_3 as an inert filler.

The study involved determining the diffusion coefficient, which required analyzing the microstructure and thickness of the layers and the process time. The images obtained with a Leica DM-4000 optical microscope revealed a two-phase structure of the boride layers. The presence of the two phases, i.e. CoB and Co_2B, was confirmed by X-ray diffraction (XRD).

A model of diffusion of boron atoms into the cobalt substrate was developed assuming the reaction diffusion mechanism. This model was used to calculate the diffusion coefficient. It required taking account of the interatomic potentials of boron and cobalt. The calculation results were compared with the experimental data concerning the diffusion of boron in other materials.

Keywords: diffusion, sinter, cobalt, boronizing

W pracy przedstawiono wyniki badań procesu dyfuzji w warstwach powierzchniowych uzyskanych w wyniku nasycenia borem spieków otrzymanych z proszku kobaltu gatunku Co Extrafine. Warstwy otrzymano przy zastosowaniu proszkowej metody borowania opartej na wykorzystaniu mieszaniny o składzie: B_4C jako składnik podstawowy stanowiący źródło boru, $(NH_4Cl + NaF)$ aktywator i Al_2O_3 jako wypełniacz. Zachowane były następujące parametry procesu: temperatura 950°C, czas 6 h i 12 h.

Badania obejmowały wyznaczenie współczynnika dyfuzji w oparciu o strukturę, grubość uzyskanych i czas nasycenia warstw. Obserwacji naniesionych warstw dokonano za pomocą mikroskopu optycznego Leica DM-4000. Zdjęcia ujawniły dwufazową strukturę warstw borkowych. Badania rentgenowskie potwierdziły występowanie faz o składzie: CoB i Co_2B.

Zbudowano model dyfuzji atomów boru w strukturze kobaltu zakładając dyfuzję reaktywną. Obliczono współczynnik dyfuzji w oparciu o model atomowy dyfuzji wykorzystując potencjały oddziaływań pomiędzy atomami boru i kobaltu. Otrzymane wyniki porównano z danymi doświadczalnymi dyfuzji boru w innych materiałach.

1. Introduction

Boronizing is becoming increasingly common in industry because it greatly contributes to an increase in the durability of mechanical components. Characterized by very high abrasion resistance, boronized elements are particularly suitable when lubrication is poor or when no lubrication is allowed.

The first research project on boron diffusion was undertaken at the Kraków University of Science and Technology (AGH,) Poland, by Prof. I. Feszczenko-Czopiwski. He investigated the cementation of iron, nickel, cobalt and special-purpose steels with boron and beryllium, which was described in his doctoral thesis in 1927 [1]. The research on diffusion has been continued by Prof. K. Przybyłowicz, whose studies have focused on grain-boundary diffusion. Under his academic supervision, B. Kastner conducted a thorough analysis of boronizing with a focus on boron diffusion [2].

This thermo-chemical diffusion process causes that hardness as well as resistance to corrosion in water-soluble acids, salts and bases improve considerably. In the case of water-soluble organic and non-organic (HCl, H_2SO_4, H_3PO_4, HF) acids, the corrosion resistance increases 15 times. These properties make boronizing an important industrial process [3,4].

As can be seen from the Co-B phase diagram (Figure 1), the change between the cobalt allotropic forms $\varepsilon \rightarrow \alpha$ occurs at a temperature of approximately 417°C [5,6,7], while the melting point and the Curie temperature of cobalt are 1495°C and 1121°C, respectively. The hexagonal lattice of the ε-allotrope changes into the face-centred cubic lattice of the α-allotrope. CoB is a compound containing 15.5% of boron by mass. In Co_2B and Co_3B, the content of boron is 8.4% and 7.8%, respectively.

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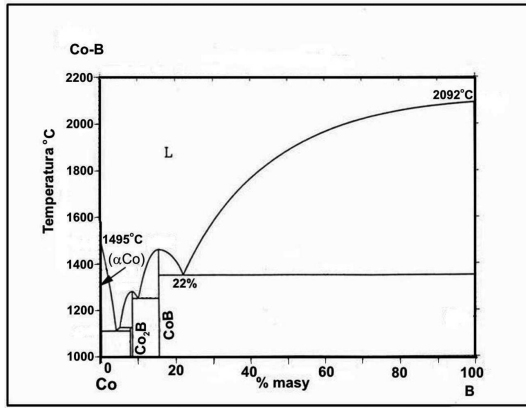
Fig. 1. Phase diagram of Co-B alloys [5]

2. Methodology

The analysis was conducted for sinters produced from Co Extrafine powders. The layers were formed by boronizing from a mixture of B_4C, which acted as a depositing source, NH_4Cl + NaF, used as an activator, and Al_2O_3, having the function of an inert filler. The experiments were performed at a temperature of 950°C for 6 h and 12 h. The structure and thickness of the boronized layers were determined through observation under a Leica DM-4000 optical microscope.

The samples were cut using a low speed diamond disc saw. Then inclusions and metallographic microsections were prepared. The microstructures were observed at a magnification of 1000x using a Leica DM-4000 optical microscope (Figure 2).
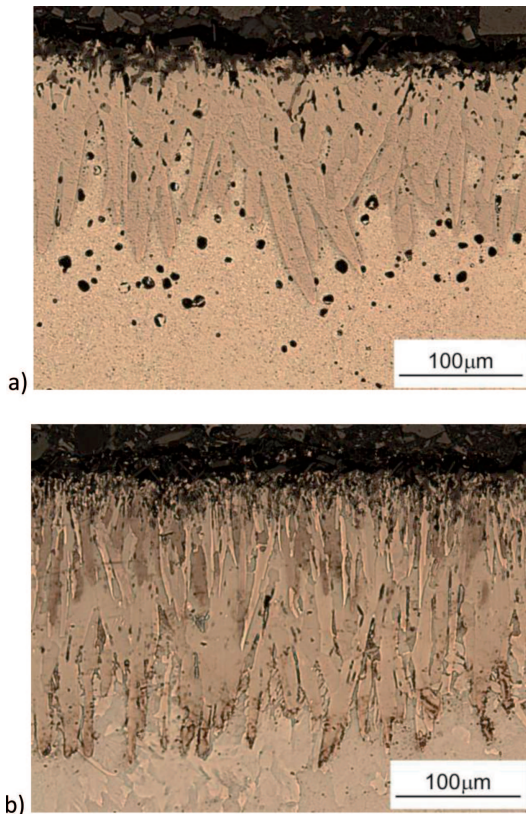
The phase analysis of the boride layers forming on the Co sinters was conducted by X-ray diffraction, using a Brücker D-8 Advance diffractometer. A diffractogram of a cobalt sample boronized by applying a mixture containing 25% of B_4C is shown in Figure 3. The phase analysis confirmed the occurrence of two phases: CoB and Co_2B.

Before determining the relationship between the diffusion depth and the boronizing time, it was essential to define the thickness of the layer. The task was difficult because the boron atoms diffused in the cobalt matrix forming a tooth-like structure.

The thickness of the boride layer can be assessed in several different ways [8], which require establishing the tooth length ranges for the valleys and peaks of the boride structure separately.

The experiment involved determining the average lengths of the clear boride 'teeth' (Figures 2a and 2b). The thickness of the layer was also assessed by measuring the longest 'teeth' and neglecting one clearly a typical tooth in Figure 3a (in the centre). The results are shown in Table 1. The average thickness of the layers obtained in 6 h and 12 h was 153.3 μm and 226.7 μm, respectively.

The values suggest that there exists a parabolic relationship between the layer thickness x and the boronizing time t [9,10]

$$x^2 = k \cdot t \qquad (1)$$

TABLE 1

Thickness of the boride layers

Measurement method	Thickness of boride layer after 6h, x_1 [μm]	Thickness of boride layer after 12h, x_2 [μm]	Layer ratio x_1 / x_2
Average tooth length	145.7	223.0	0.653
Maximum tooth length	160.9	230.4	0.698

Fig. 2. Microstructure of the layers boronized for 6 h (a) and 12 h (b). No etching
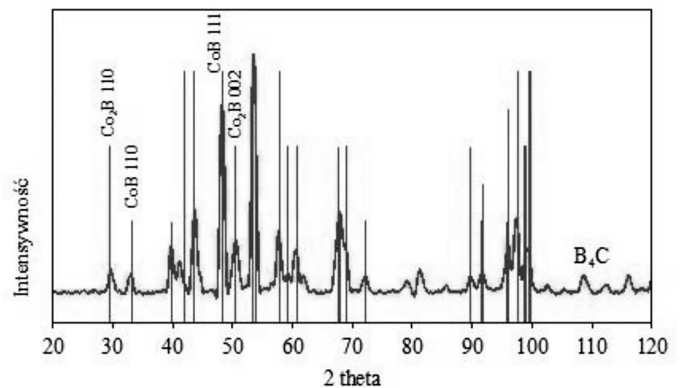

Fig. 3. Diffractogram of the boronized layer

where: k– the constant of proportionality. Both values in the layer ratio column (Table 1) are close to the value obtained by applying the parabolic law, which is equal to 0.707.

This relationship and the clear phase boundary between the boride layer and the matrix were used to assume that the boron diffusion was of the reaction type and the atoms of boron diffused from the sinter surface to the phase boundary. Additionally, it was suggested that the diffusion into the depth of the sample occurred through the Co_2B phase, which contains less boron. These assumptions were used to develop a model of diffusion, which will be discussed in the next section.

Prof. Karol Przybyłowicz and B. Kastner conducted model studies, which involved carbonizing a boronized specimen with a mixture containing carbon C^{14} atoms [4,11]. They analyzed the distribution of C^{14} in the layer of boronized steel at a depth of 50 μm from the surface. The study showed non-uniformed cellular distribution of labeled carbon atoms, which indicated that the process of carbon diffusion occurred along boride grain boundaries. As boron and carbon do not dissolve in borides, we can assume that their mechanisms of diffusion are identical. The model of diffusion of boron atoms along boride grain boundaries will be presented below.

3. Model of Diffusion of Boron in Cobalt

3.1. Macroscopic model

The diffusion process is governed by Fick's first and second laws of diffusion [8,12]. The diffusion is analyzed from a macroscopic point of view; it may refer to any state of matter. If we assume that the diffusion of boron in cobalt is of the reaction type [4,12], then Fick's first law defines the flux of diffusing particles:

$$J = -D\nabla c \qquad (2)$$

where: D – diffusion coefficient, and ∇c – boron concentration gradient.

For a one-dimensional case, the gradient of concentration of boron atoms ∇c in the surface layer with the thickness x can be described using a simple formula

$$\nabla c = \frac{c - c_0}{x} \qquad (3)$$

where: c – concentration of atoms in the matrix at the depth x, and c_0 – concentration of atoms on the surface. Assuming that the concentration in the matrix near the boride front is negligibly small (like in the case of Fe [4]) and substituting (3) into (2), we get

$$J = D\frac{c_0}{x} \qquad (4)$$

The flux of diffusing particles J can be defined as the number of migrating particles per unit surface area in unit time

$$\frac{dn}{dt} = D\frac{c_0}{x} \qquad (5)$$

where: n – number of migrating additive atoms per unit surface area. The quantity dn and the growth in the thickness of the boride layer are proportional to each other

$$dx = K \cdot dn \qquad (6)$$

where: K – constant with a dimension of m^3 which expresses the volume occupied by one atom of boron. Substituting (6)

into (5) and integrating, we obtain a well-known parabolic law [4]

$$x^2 = 2KDc_0t \qquad (7)$$

If we assume that the gradient of boron concentration in the boride structure (Co_2B) does not occur, as is the case of Fe [4], then the following relation will be satisfied

$$K \cdot c_0 = 1 \qquad (8)$$

Then, Equation (7) can be used to independently calculate the diffusion coefficient D. The values of the diffusion coefficient obtained for the data presented in Table 1 are given in Table 2.

TABLE 2

Diffusion coefficient

Calculation method	Diffusion coefficient calculated after 6 h [mm^2/s]	Diffusion coefficient calculated after 12 h [mm^2/s]
From average tooth length	$4.91 \cdot 10^{-7}$	$5.75 \cdot 10^{-7}$
From longest tooth length	$5.99 \cdot 10^{-7}$	$6.14 \cdot 10^{-7}$

From the above table, the average value of the diffusion coefficient is $5.70 \cdot 10^{-7} \, mm^2$/s.

There is very little experimental data concerning boron diffusion in the literature [4,13]. In particular, there is no information on boron diffusion in cobalt. The comparison of boron diffusion in cobalt with boron diffusion in iron alloys is discussed in the subsection on the Atomic Model of Diffusion (Table 5).

3.2. Cobalt structure

Since the atoms of boron diffuse into the face-centred cubic structure of cobalt, it was crucial to analyze the cobalt matrix properties. The lattice constant of the elementary cell, a, is 0.3544 nm [8], whereas the distance between two neighbouring atoms, a_1, is 0.2506 nm. The structure contains two types of voids: tetrahedral and octahedral, as shown in Table 3.

Analyzing the radii of cobalt and boron atoms as well as the radii of both types of voids [14], we can conclude that the diffusion through octahedral voids is more probable. There are four octahedral voids in each elementary cell of the face-centred cubic system (A1). Around each void there are six node atoms arranged on the sphere with the radius $R = \frac{a}{2}$. In the neighbourhood of each octahedral void at the distance $\frac{a}{\sqrt{2}}$, there are 12 other octahedral voids.

TABLE 3

Parameters of the voids in the A1 cobalt structure

Void type	Sphere radius	Distance between Voids
Tetrahedral	$\frac{1}{4}\sqrt{3}a$	$\frac{1}{2}a$
	0.1532 nm	0.1769 nm
Octahedral	$\frac{1}{2}a$	$\frac{1}{2}\sqrt{2}a$
	0.1768 nm	0.2501 nm

3.3. Atomic interactions in the cobalt structure

The diffusion was analyzed using the potentials of the interactions between the cobalt and boron atoms discussed in Ref. [15]. The energy of atomic interactions dependent on the distance r (Fig. 4) was described by the following polynomial equation

$$\phi(r) = a_1 (r - b_1)^4 + a_2 (r - b_2)^2 + a_3 \tag{9}$$

where a and b are coefficients given in Table 4. All the values presented in this table and in the next sections of this paper were determined in the SI system units, i.e. *nN*, *aJ* and *nm*, instead of traditionally used eV and A [15]. The unit *aJ* (atto-joul) is well-suited to describe the energy at the atomic level because its value is close to that of eV, i.e. 1 aJ = 0.1601 eV.

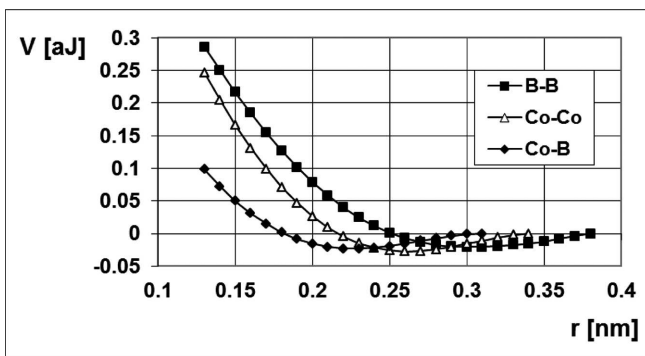Fig. 4. The interatomic potentials

TABLE 4

Parameters of the interaction potentials

Atoms	a_1 [aJ/nm^4]	a_2 [aJ/nm^2]	a_3 [aJ]	b_1 [nm]	b_2 [nm]
Co-Co	-205.2	18.49	-0.0215	-0.1827	-0.2508
Co-B	-175.7	15.83	-0.0184	-0.1477	-0.2158
B-B	-140.5	12.66	-0.0147	-0.2118	-0.2858

The interatomic force was calculated as a derivative of potential (9). When six atoms of cobalt act on one atom of boron in an octahedral void, the interaction force is specified with the force constant $k = 30$ nN/nm. If we take account of the mass of a boron atom $A_B = 10.81$ AU [7], which gives the SI mass m = $1.806 \cdot 10^{-26}$ kg, then we can obtain the frequency of vibrations of the boron atoms in the lattice: $\nu = 6.5 \cdot 10^{12} s^{-1}$.

In the calculations, we took into consideration the change in the lattice constant a caused by the change in the sample composition after saturation with boron. The change in the lattice constant was calculated from the density of the cobalt and boron mixture. Reference [15] provides the relationship between this density and the molar fraction of boron. This assumption suggests that the lattice constant for the Co_2B structure increases to a new value a' = a· 1.037.

3.4. Atomic model of diffusion

If we assume random motion or 'jumping' of boron atoms in the cobalt structure, the expression for the diffusion coefficient [12,13,16] has the following form

$$D = \frac{1}{6} f z \alpha^2 \omega \tag{10}$$

where f is the correlation coefficient dependent on the crystalline structure and the diffusion mechanism. For a face-centred cubic system, the coefficient is close to one [12,16]; in these considerations, it will be equal to one. The parameter z refers to the number of sites where a boron atom may jump; in this model, z is equal to 12. In other words, it is equal to the number of neighbouring octahedral voids. The parameter α is the distance that an atom covers moving from one site to another. In the case of the diffusion of boron in cobalt, the distance is equal to the distance between the octahedral voids (Table 3). On the other hand, ω is the frequency of jumps between two equilibrium sites and is defined by the following equation [12,13]

$$\omega = \nu \exp\left(-\frac{E_A}{kT}\right) \tag{11}$$

where: ν – frequency of atomic vibrations at equilibrium sites, E_A – energy barrier at the transition from one equilibrium site to another, k – Boltzmann constant (equal to $1.38 \cdot 10^{-5}$ aJ/K), and T – absolute temperature.

The transition of the additive atom from one void to another requires overcoming the potential barrier. While boron atoms move, they come across a barrier with a height of 0.198 aJ at the half length of the jump. Considering the number of sites where a boron atom can jump, we can calculate the diffusion coefficient using the following formula based on Equation (10)

$$D = 0.872 \frac{mm^2}{s} \exp\left(-\frac{0.198 aJ}{kT}\right) \tag{12}$$

which, for the process temperature $T = 1223$ K (950°C), gives the value of the diffusion coefficient $D = 7.01 \cdot 10^{-6} mm^2$/s. The calculated value is significantly higher than the average value of the diffusion coefficient from Table 2. The correlation with the experimental data can be improved if we take into account the average concentration of boron in the Co_2B phase. Half of the octahedral voids are occupied by boron atoms, which suggests that the number of sites decreases, i.e. $z = 6$. Moreover, near the saddle point there are an average of two atoms of boron which also act on the jumping atom. Each atom of boron increases the potential barrier by another 0.032 aJ. Then, the diffusion coefficient can be calculated using the following formula

$$D = 0.436 \frac{mm^2}{s} \exp\left(-\frac{0.262 aJ}{kT}\right) \tag{13}$$

The diffusion coefficient is $7.89 \cdot 10^{-8}$ mm^2/s for the temperature of the boronizing process. The diffusion depth in the time t can be calculated from the following equation

$$x = \sqrt{2Dt} \tag{14}$$

For the diffusion coefficient (13) and the time $t = 6$h, the diffusion depth was 62 μm. If we assume that there is one boron atom located close to the saddle point, then we have the formula

$$D = 0.436 \frac{mm^2}{s} \exp\left(-\frac{0.230 aJ}{kT}\right) \tag{15}$$

the diffusion coefficient D is $5.26 \cdot 10^{-7}$ mm²/s and the diffusion depth is 151 μm. The latter quantity of diffusion depth is well correlated with the experimental results, where the length of a boron tooth was 153 μm for time 6 h.

4. Diffusion of boron in other materials

Experimental data concerning diffusion of boron is not frequently found in the literature [4,13]. The diffusion parameters determined in this study, i.e. the frequency factor (D_0) and the activation energy (E_A), were compared with the data obtained by other authors (see Table 5). The results obtained by different researchers may differ considerably [2].

TABLE 5

Diffusion parameters

Material	D_0 [mm²/s]	E_A [aJ]	Temperature range	Reference
Co sinter	0.436	0.262	over 417°C	This paper
Fe-γ	0.20	0.146	over 1000°C	[2]
Iron	0.239	0.187	1100-1250 K	[2]
C45 steel	0.763	0.210	1100-1250 K	[2]
Fe -α	0.230	0.131		[13]
Molybdenum	6.96	0.310	1373-1473 K	[13]

The data presented here focuses on boron diffusion in cobalt sinters. As there is no literature on the subject, i.e. boron diffusion in sintered materials, the model parameters of diffusion obtained in this study were compared with the data relating to the diffusion of boron in solid materials, e.g. iron and steel (Table 5). Basically, the parameters of diffusion such as the frequency factor and the activation energy are not much different from the parameters of diffusion of boron in iron alloys obtained by other researchers (Table 5).

5. Model of boride grain boundary diffusion

Inside the tooth-like layer of borides, the boron diffusion occurs along the boride grain boundaries [11]. It is vital to determine a probable structure of the boride boundaries in order to analyze the diffusion in this area. As there is no appropriate data available, the diffusion process needs to be analyzed assuming that the boundaries have an amorphous structure. In such a case, the radial distributions of the structure parameters at different concentrations of Co and B are known [15].

From the radial distribution function (RDF) for the B-Co pair [15] it is clear that the sphere of Co atoms surrounding a B atom has a radius of approx. 0.2 nm (a maximum of the RDF), and the average number of Co atoms over the sphere is nine. The frequency of vibrations of the boron atom in the centre of the cobalt atom sphere, which was calculated using the Co-B potential, is

$$\nu \approx 2 \cdot 10^{12} s^{-1}. \qquad (16)$$

If the radius of a void is greater than 0.05nm, then the void may play a role in the vacancy diffusion of boron [15]. The average number of voids in the neighborhood of a B atom is 0.12, 0.15 and 0.43 for the amorphous mixture of $Co_{90}B_{10}$, $Co_{81.5}B_{18.5}$ and $Co_{70}B_{30}$, respectively [15]. A mixture with the highest content of boron is similar to the composition of Co_2B and the number of voids is 0.43. For the CoB boride, the number of adjacent voids should be even larger. The closest sufficiently large voids into which a B atom may migrate are located at a average distance of 0.3 nm (the RDF for the Co-B pair assumes the zero value) [15].

It is difficult to determine the regular distribution of nine Co atoms over the sphere. The distance between atoms resulting from the RDF for a Co-Co pair is 0.25 nm on average and it ranges from 0.2 nm to 0.3 nm. The simplest approximation is the jump of a boron atom from one void to another over a saddle formed temporarily by three or four Co atoms (Fig. 5).
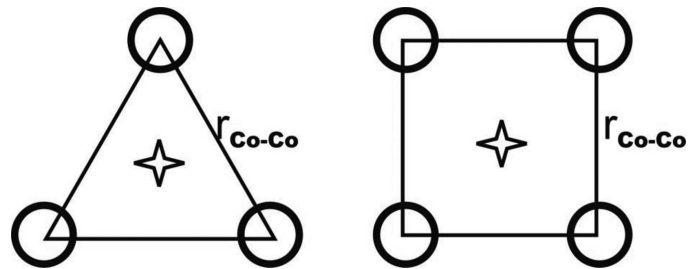

Fig. 5. Triangular and square saddle points for the jump of a boron atom, circle – a Co atom, cross – the saddle point, **r** – the average distance between the Co atoms

The difference in the potential energy resulting from the arrangement of the nine Co atoms in the centre of the sphere and at the triangular or square saddle point gives

$$V_{3Co} = 0.314\,aJ \text{ and } V_{4Co} = 0.068aJ, \text{respectively.} \qquad (17)$$

The value of V_{3Co} contributes to a definitely low value of the coefficient of diffusion and is not taken into consideration. It is assumed that the number of the adjacent voids is z = 0.43 and the length of the jump from one void to another is at least 0.3 nm, according to the RDF function [15]. Thus, from formula (10) the coefficient of diffusion D for the other case (square saddle) is

$$D_g = 0.014\frac{mm^2}{s} \exp\left(-\frac{0.068aJ}{kT}\right) \qquad (18)$$

At T = 1223 K, the coefficient of diffusion is $D = 2.4 \cdot 10^{-4}$mm²/s. To obtain effective diffusion in the volume of the surface layer, it is necessary to normalize the coefficient of diffusion to the form of an effective coefficient of volumetric diffusion. For this purpose, we can use the formula proposed by Jarzębski [10], where an effective coefficient of diffusion is expressed by the coefficient of diffusion along the grain boundaries

$$D_{ef} = \sqrt{\frac{\delta}{d}}D_g \qquad (19)$$

where δ is the boundary thickness, and d is the average diameter of a grain. If we assume the average diameter of the grain to be 10 μm [11], and the boundary thickness of an order of 1 nm, then the effective coefficient of diffusion is about 100 times lower than the coefficient of diffusion along the grain boundaries. Thus we have $D_{ef} = 2.4 \cdot 10^{-6}$mm²/s at

T = 1223 K. This value gives a depth of diffusion of 322 μm after 6 h. The value of the coefficient of diffusion and the depth of reactive diffusion are qualitatively consistent with the experimental results.

A migration of a B atom from one void to another over a saddle formed by three Co atoms (Fig. 5) may also result in more rapid diffusion. If the adjacent boron atoms have an effect on the height of the potential barrier, there may be a decrease in the barrier potential, as is the case of octahedral void, and then an increase in the value of the coefficient of diffusion. Additionally, if the distances between Co atoms in the triangular system are greater (up to 0.3 nm), then the value of the coefficient of diffusion increases. However, accurate analysis of the diffusion process requires developing a numerical model of the grain boundary of borides and performing a computer simulation of diffusion.

6. Conclusions

It was found that the cobalt sinter samples produced from Co Extrafine powder had a boride layer with a characteristic tooth-like structure. The metallographic analysis showed that the pre-determined parameters, i.e. time and temperature, contributed to the formation of two-phase layers of cobalt borides, i.e. Co_2B and CoB.

In this study, the coefficient of diffusion of boron in cobalt sinter was calculated using an atomic model of reactive diffusion. The diffusion parameters (Table 5) give a boronizing depth comparable to the experimental data.

To obtain more accurate data concerning the diffusion process, it is necessary to conduct further experiments in wider temperature and time ranges. It is vital that computer simulations be performed at the atomic level using the molecular dynamics or the Monte-Carlo methods.

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