

STRUCTURAL TRANSFORMATIONS IN $\text{Co}_{87}\text{B}_{13}$ AND $\text{Ni}_{87}\text{B}_{13}$ ALLOYS DURING BALL MILLING AND INFLUENCE OF STACKING FAULTS IN FCC Co ON AMORPHOUS PHASE FORMATION

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Abstract. A solid state interaction in $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ mixtures by high energy ball milling was studied. The methods of XRD and DTA calorimetry analyses were used. It has been established that the formation of Co (B) and Ni (B) solid solutions takes place on the base of fcc structure of both metals. The interaction of B with Co develops in accordance to $\text{Co}_{\text{hcp}} \rightarrow \text{Co}_{\text{fcc}}$ transformation. Fcc solid solutions Co (B) and Ni (B) can be characterized as interstitial solutions or as mixed-type solutions of substitution-interstition. During prolonged milling of Co (B), stacking faults in its lattice are formed, concentration of which goes up to 12.5%. The probability of stacking faults formation in Ni (B) is one order lower. The high defectiveness of Co (B) promotes the amorphous phase formation and the full transformation of $\text{Co}_{87}\text{B}_{13}$ alloy into amorphous state is observed after 4200 min of milling. Crystallization of amorphous alloy during heating takes place at temperature above 490 °C, and herewith fcc supersaturated solid solution Co (B) is formed again and the cobalt boride excretion is not observed. Co (B) fcc solid solution formed as a result of mechanical alloying (MA) has decomposed with the Co_2B (C16) tetragonal phase formation at temperature above 560 °C.

1. INTRODUCTION

The synthesis of Co-B alloys by mechanical alloying (MA) acquires specific peculiarities connected with polymorphic conversion of Co under the deformation. The Co powder usually consists of mixtures of high temperature fcc and low temperature hcp modifications. Under deformation action the transition $\text{Co}_{\text{fcc}} \leftrightarrow \text{Co}_{\text{hcp}}$ is reversible due to the stacking faults formed in each structure.

The structural transition of $\text{Co}_{\text{fcc}} \leftrightarrow \text{Co}_{\text{hcp}}$ by milling is described in [1-3]. The results of the solid state reaction of Co with B were published in [4-6]. As a result of high-energy milling of Co-B mixtures containing from 20 to 50 at.% of B one can be observed a formation of amorphous-crystalline or

amorphous alloys [4,5]. Moreover, only $\text{Co}_{80}\text{B}_{20}$ and $\text{Co}_{67}\text{B}_{33}$ alloys were fully amorphous. The amorphous alloy was obtained for $\text{Co}_{89}\text{B}_{11}$ composition, but after milling prolongation the crystallization was observed [6]. The publications show that the Co-B alloys exerts a tendency to amorphization by deformation action. The reversible phase transition in Co as well as a big radius of B atom ($r_{\text{B}} = 0.086$ nm [7]), that is considerably exceeding the radius of octahedral interstice in Co fcc (0.064 nm), complicates the chemical interaction of Co with B by means of a simple mechanism. Therefore the defects of Co crystalline structure can play certain role in the formation of intermediate metastable phases during MA.

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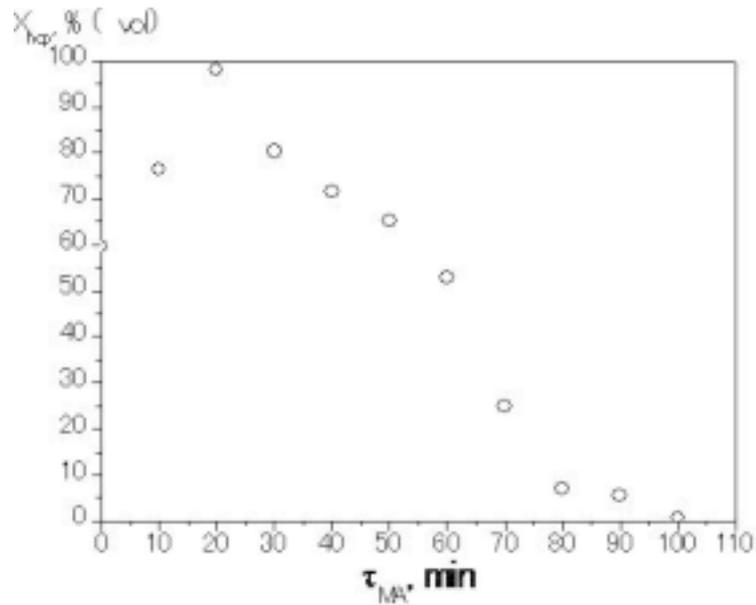


Fig. 1. Dependence of Co hcp content on the duration of milling time.

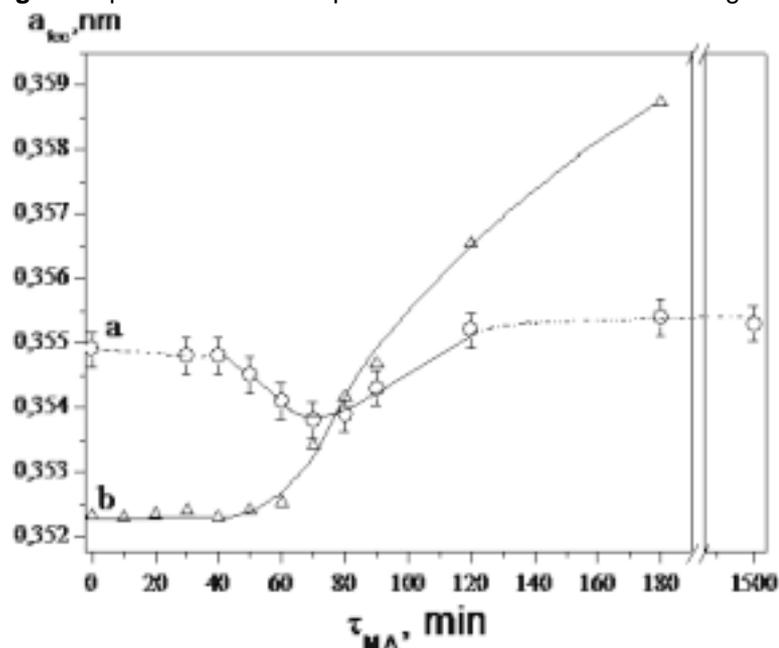


Fig. 2. Lattice parameters of Co(B) (a) and Ni(B) (b) solid solutions as a function of milling time.

The aim of this work was to study the solid state interaction of Co and Ni with B during high energy ball milling of $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ mixtures. The stacking faults in fcc lattice of Co(B) solid solution were measured and their influence on amorphization process of $\text{Co}_{87}\text{B}_{13}$ alloy was showed.

2. EXPERIMENTAL PROCEDURES

The powders of Co and Ni with a purity of 99.96%, the particle size of 40-70 μm and crystalline B (99.99%) with a particle size $\sim 10 \mu\text{m}$ were used. The mixtures of $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ composition were subjected to milling. The milling of $\text{Ni}_{87}\text{B}_{13}$

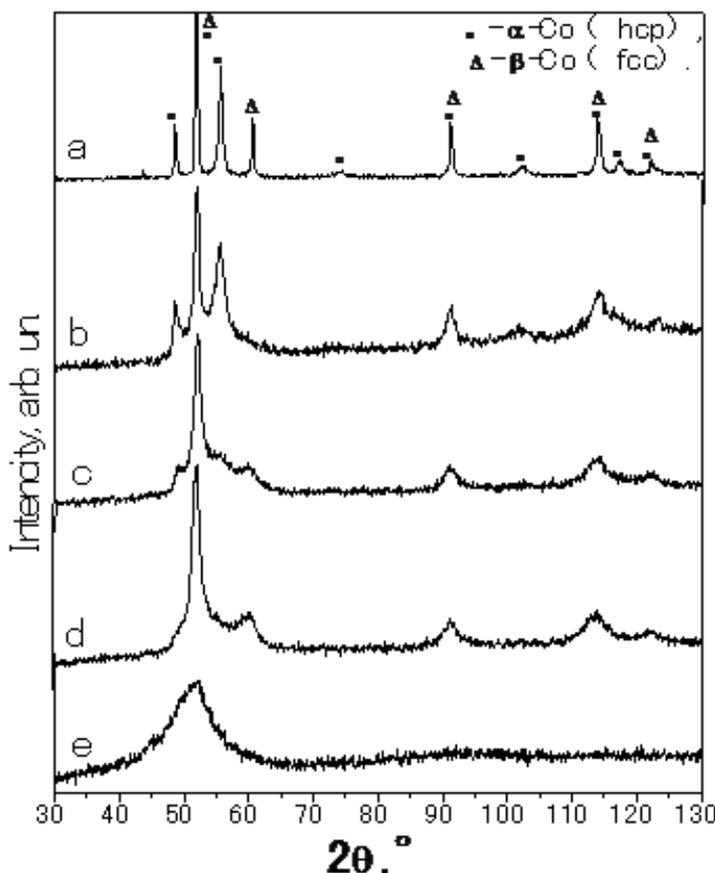


Fig. 3. XRD patterns of $\text{Co}_{87}\text{B}_{13}$ after different milling time: a- initial powder; b- 20 min; c – 70 min; d- 180 min; e- 4200 min.

mixture was carried out in order to compare the resulting structures in this alloy to the ones in $\text{Co}_{87}\text{B}_{13}$. In this case fcc Ni interacts with B and in this system the metal does not exhibit a polymorphous transformation. The syntheses was carried out in a planetary ball mill MAPF-2M in water-cooling steal containers with steel balls in the argon atmosphere. The ratio of balls mass to powder mass was 6:1. The products of milling were studied by XRD analysis (diffractometer HCG, $\text{CoK}\alpha$ -radiation) and differential thermal analysis (DTA Setaram – 1000).

The stacking faults probability expressed in percents ($P_{\text{st.f.}}$) characterizes the number of wrong alternations of (111) planes in the (110) dimension. For fcc lattice this leads to the shift of diffraction maximums which is defined by Fourier coefficients. The shift of (220) and (311) lines of Co_{fcc} were measured according to the shift coefficients stated

in [8]. The concentration of stacking faults $P_{\text{st.f.}}$ (%) was defined with a help of the expression:

$$\left(\frac{d_{311}}{d_{220}} \right)^{\text{st.f.}} = \frac{\left(\sqrt{h^2 + k^2 + l^2} \right)_{(311)}}{\left(\sqrt{h^2 + k^2 + l^2} \right)_{(220)}} \cdot \frac{1 + k_{(220)}\alpha}{1 + k_{(311)}\alpha},$$

k – Fourier coefficients ($k_{(220)} = +0.0345$; $k_{(311)} = -0.0125$); $P_{\text{st.f.}} = \alpha \times 100$ %.

The experimental error at determination of the shift lines of Co(B) was corrected by means of the measurement of the same lines position of the internal standard that was the powder of annealed copper. The DTA curves were recorded in the 200-800 °C temperature range with a heating speed of 40 °/ min. The annealed samples were analyzed by XRD method.

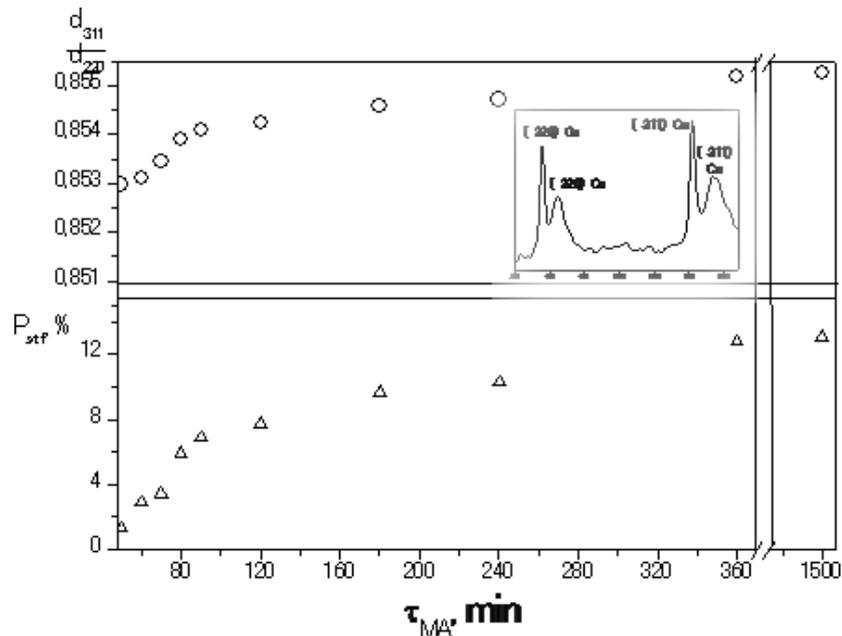


Fig. 4. Change of stacking faults probability in Co(B) solid solution v.s. milling time.

3. RESULTS AND DISCUSSION

The structural transformations during milling of $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ mixtures can be observed on XRD patterns. Both modifications of Co were present in the ratio of $\text{Co}_{\text{hcp}} : \text{Co}_{\text{fcc}} = 60:40$ (%) in the initial powder (Fig. 1). However, when the milling is continued, a reverse transition takes place $\text{Co}_{\text{hcp}} \rightarrow \text{Co}_{\text{fcc}}$ and after 180 min of MA the sample contained only Co_{fcc} .

The lattice parameters of Co_{hcp} do not change during MA and are $a=0.2503$ nm, $c=0.4082$ nm, $c/a=1.63$. This proves that B does not dissolve in hcp lattice of Co. At the same time, as shown on Fig. 2, the lattice parameter of fcc phase changes non-monotonic. It decreases first, then increases and finally has a stable value in wide range of milling time (from 120 to 1500 min). The change of the lattice parameters of fcc phase shows that the interaction of Co with B proceeds by the formation of Co(B) solid solution. Various alterations of a parameter during MA caused to different displacement of B atoms in Co_{fcc} lattice. At the initial stage a substitutional solid solution is formed. At the next stage the interstitial or mixed type solid solutions can be formed [8]. Prolonged milling of fcc Co(B) results in the formation of an amorphous phase.

After 4200 min of MA the diffractogram of the specimen showed a wide halo in the range of $2\theta = 30-65^\circ$ and it is similar to XRD pattern of amorphous phase (Fig. 3).

During milling of $\text{Ni}_{87}\text{B}_{13}$ mixture interaction between Ni and B proceeds by a simplified mechanism as the structure of Ni does not change during deformation. The lattice parameter of Ni began to increase after 60 min of MA. One can assume that B is transitioned to amorphous state at first stage of milling and then migrates actively into the Ni lattice forming interstitial solid solutions.

The substructure characteristics – the domain size D and mean square microdeformation $\langle \epsilon^2 \rangle^{1/2}$ for fcc phases of the $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ alloys changed identically during MA. Nanosize phases are formed already after 60 min of MA. Value of D has reached approximately 7 nm and did not change any further. Microdeformation of fcc nanocrystalline phases equals $\sim 1\%$ and it is twice higher than the one in lattice of the initial Co and Ni. The amorphous phase formation in $\text{Co}_{87}\text{B}_{13}$ at prolonged milling is caused probably with increase of the stacking faults concentration.

As seen in Fig. 4, the concentration of stacking faults in Co_{fcc} ($P_{st.f}$) progressively increased at the

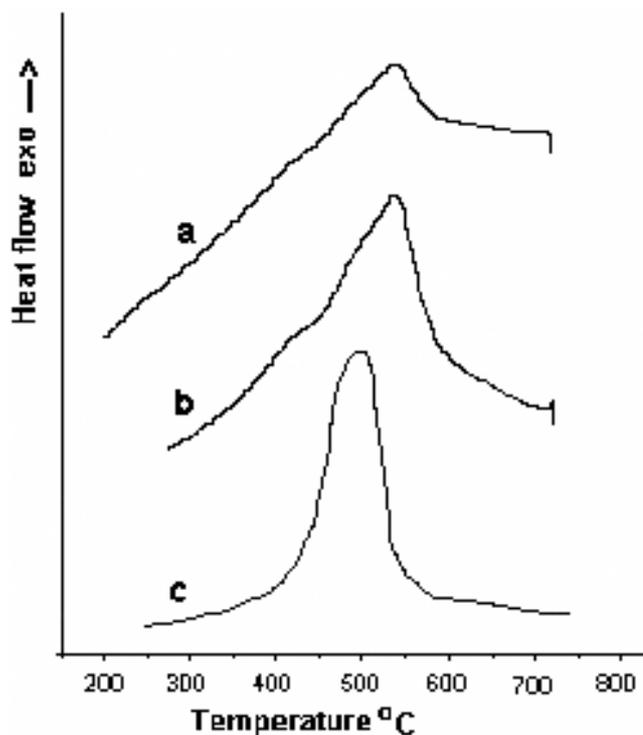


Fig. 5. DTA curves of $\text{Co}_{87}\text{B}_{13}$ after different milling time: a- 70 min; b- 360 min; c – 4200 min. (40 °/min).

prolongation of milling from 70 to 1500 min and reached about 12.5%. Such a high stacking faults probability is explained by $\text{Co}_{\text{fcc}} \leftrightarrow \text{Co}_{\text{hcp}}$ transition. The stabilization of high temperature fcc modification of Co is promoted by the dissolving of B in the Co lattice. Due to the fact that the dissolved component is able to localize close to stacking fault, it can lead to the formation of B-B links. In the case of critical concentration of such defects and inhomogeneous local areas in the Co(B) lattice, the solid solution becomes nonstable. As a result a boride phase or amorphous phase enriched with boron can be formed from solid solution. The formation of amorphous alloy after 4200 min of MA can be observed in our case. Under deformation action the stacking faults can be also formed in Ni(B) but their concentration is low and does not exceed 0.3-0.5%.

The presence of exothermic peak of crystallization on the DTA curves indicates the formation of amorphous phase during long milling of fcc Co(B) solid solution (Fig. 5). The T_p of crystallization peak on DTA curve of an amorphous alloy is ~ 495 °C.

According to XRD only fcc Co(B) is detected after heating up to 720 °C. Two overlapping exothermic peaks on the DTA curves can be observed after 70 min and 360 min of MA. The peak with $T_p \sim 560$ °C is caused by segregation of Co_2B (C16) from Co(B) solid solution. The first weak exothermic peak on DTA curves (Figs. 5a and 5b) corresponds to crystallization of an amorphous phase existing also in the alloys. The fcc Co(B) formed during crystallization of fully amorphous alloy is stable up to temperature above 800 °C.

4. CONCLUSIONS

- The solid state reaction by MA of $\text{Co}_{87}\text{B}_{13}$ and $\text{Ni}_{87}\text{B}_{13}$ resulted in dissolution of B in fcc Co and Ni. The supersaturated solid solutions are interstitial or substitutional-interstitial mixed type.
- The continuous milling of fcc solid solution Co(B) is accompanied by the increasing of concentration of the stacking faults, promoting the amorphization of the alloy.

- $\text{Co}_{87}\text{B}_{13}$ amorphous alloy crystallization results in fcc Co(B) solid solution formation.
- The tetragonal Co_2B (C16) boride is segregated from the supersaturated fcc solid solution Co(B) after heating at temperature above 560 °C.

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