Mechanical behavior and crystallization features of amorphous alloys based on cobalt and iron after annealing

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Abstract. The sequence of structural transformations of amorphous alloys Fe53.3Ni26.5B20.2 and Co28.2Fe38.9Cr15.4Si0.3B17.2 during heat treatment in a wide temperature range was studied by transmission electron microscopy and differential scanning calorimetry. The response of mechanical properties (plasticity, hardness, crack resistance) during transition from an amorphous to a crystalline state was investigated. The nature of discovered embrittlement phenomenon and plasticizing effect in amorphous alloys during annealing was discussed.

1. Introduction
The satisfactory plasticity, good soft magnetic characteristics, high values of hardness, tensile strength prompt practitioners to look for the possibility of using amorphous alloys (AA) with disordered structure, characterized by short-range order in the arrangement of atoms, as constructional materials or as components for composites. However, for widespread use, there are limitations regarding the ranges and conditions of their thermal stability [1, 2]. The intense processes of structural relaxation and crystallization occur in AA at the temperature rises.

The aim of this work is a detailed study of structure changes and mechanical properties of AA based on cobalt and iron after annealing.

2. Materials and techniques
The Co28.2Fe38.9Cr15.4Si0.3B17.2 and Fe53.3Ni26.5B20.2 (at.%) AA in the form of ribbon 25 μm thick were obtained by melt spinning. AA were subjected to vacuum isothermal annealing for 10 minutes in a furnace in the temperature range T_an = 100-800°C. Differential scanning calorimetry (DSC) was performed at a rate of 10°C/min using SETSYS Evolution-1750 module analyzer (SETARAM Instrumentation).

The amorphous and crystalline phases in the alloys were identified by transmission electron microscopy (TEM) with JEM 1400 microscope (JEOL). The tensile curves were shooting by electromechanical universal testing machine (INSTRON-5565) at a speed of 0.1 mm/min.

The plasticity of AA was estimated by U-method during bending deformation. The sample of AA was placed between two parallel planes of the special device. In condition of approaching of parallel planes with a constant speed, the plasticity ε was determined by the formula:

$$\varepsilon = h / (D - h)$$  \hspace{1cm} (1)
where \( h \) is thickness of the sample; \( D \) – distance between planes at moment of the sample destruction. Temperature of transition in the brittle state \( (T_f) \) was estimated as average temperature from \( T_{an1} \) and \( T_{an2} \), where \( T_{an1} \) is the largest annealing temperature, at which \( \varepsilon = 1 \), \( T_{an2} \) is the lowest fixed temperature of annealing, at which was observed a sharp abatement of plasticity \( (\varepsilon << 1) \).

The microhardness of AA samples was measured by indentation with a Vickers pyramid using MHT-3M microhardness tester (LOMO). \( K_{ic} \) values were calculated by the formula:

\[
K_{ic} = A(E/HV)^{1/2} P/C^{1/2}
\]

where \( A = 0.016 \) is the calibration coefficient of proportionality for thin ribbons of amorphous alloys; \( E \) is Young’s modulus measured by dynamic indentation methods; \( HV \) is Vickers microhardness; \( P \) is the critical load for the appearance of radial cracks in the process of local loading of samples of amorphous alloys; \( C \) is the average length of cracks [3, 4].

3. Results and discussion

According to DSC data, the AA differ substantially in crystallization behavior. In particular, the crystallization of Fe\(_{53.3}\)Ni\(_{26.5}\)B\(_{20.2}\) alloy occurs in two stages, namely, at \( T_{x1} = 434^\circ C, T_{x2} = 453^\circ C \). The crystallization of Co\(_{28.2}\)Fe\(_{38.9}\)Cr\(_{15.4}\)Si\(_{0.3}\)B\(_{17.2}\) alloy is long and includes three stages at temperatures \( T_{x1} = 483^\circ C, T_{x2} = 588^\circ C, T_{x3} = 660^\circ C \) (Figure 1).

![Figure 1](image_url) DSC curves for AA: Fe\(_{53.3}\)Ni\(_{26.5}\)B\(_{20.2}\) (1) and Co\(_{28.2}\)Fe\(_{38.9}\)Cr\(_{15.4}\)Si\(_{0.3}\)B\(_{17.2}\) (2).

The mechanical properties of the alloys are also different from each other. Based on the studies on tension and indentation of the initial AA ribbon samples at room temperature, the values of their mechanical characteristics were established (Table 1):

| Alloy               | \( \sigma_T \), GPa | \( E \), GPa | \( HV \), GPa |
|---------------------|----------------------|-------------|--------------|
| Fe\(_{53.3}\)Ni\(_{26.5}\)B\(_{20.2}\) | 2.74                 | 181         | 8.5          |
| Co\(_{28.2}\)Fe\(_{38.9}\)Cr\(_{15.4}\)Si\(_{0.3}\)B\(_{17.2}\) | 2.94                 | 239         | 9.1          |

A study of the mechanical behavior of each AA after heat treatment was carried out (Figure 2). Based on the graphs presented in Figure 2a, both AA suffer temper embrittlement: \( T_{f1} \approx 363^\circ C \) for Fe\(_{53.3}\)Ni\(_{26.5}\)B\(_{20.2}\), \( T_{f2} \approx 388^\circ C \) for Co\(_{28.2}\)Fe\(_{38.9}\)Cr\(_{15.4}\)Si\(_{0.3}\)B\(_{17.2}\). In comparison with the DSC (Figure 1), it can be seen that the alloys become embrittled in the process of structural relaxation at temperatures below \( T_x \). The loss of plasticity of the AA Fe-Ni-B system occurs in one step, in contrast to the AA Co-Fe-Cr-Si-B system, in which two stages of decline are established with a slight increase in the \( \varepsilon_f \) parameter in the pre-crystallization temperature range from 400°C to 450°C (Figure 2a). The difference between the alloys with respect to the course of the \( \varepsilon_f \) dependences is associated with
different quenching rates during their preparation: a higher rate (for Fe\textsubscript{53.3}Ni\textsubscript{26.5}B\textsubscript{20.2}) leads to a one-stage decrease in plasticity, and a lower one (for Co\textsubscript{28.2}Fe\textsubscript{38.9}Cr\textsubscript{15.4}Si\textsubscript{0.3}B\textsubscript{17.2}) – to the two stages of decline $\varepsilon_f$.

Figure 2. The effect of heat treatment on the value of plasticity $\varepsilon_f$ (a) and microhardness $HV$ (b) of AA: 1 – Fe\textsubscript{53.3}Ni\textsubscript{26.5}B\textsubscript{20.2}; 2 – Co\textsubscript{28.2}Fe\textsubscript{38.9}Cr\textsubscript{15.4}Si\textsubscript{0.3}B\textsubscript{17.2}.

The nature of embrittlement for AA is rather complex and is associated with a number of reasons. First, non-metal atoms make a significant contribution to the embrittlement process. These atoms, due to their ability to quickly diffuse during annealing, can form aggregation that cause local stresses at the boundary with the amorphous matrix. This process stimulates a decrease in the plasticity of segregation areas.

Secondly, those elements that make up the basis of AA are also important. It is known that crystalline transition metals with a BCC lattice are more prone to embrittlement than metals with a FCC lattice. In the AA, the coordination number $Z \approx 12$, which corresponds to FCC/HCP structures. During aging caused by annealing, a short-range order changes, and, accordingly, $Z$ of AA changes to $Z$ of the crystalline element (in our case, for both alloys, one of the first precipitated $\alpha$-Fe phases with a BCC lattice of $Z = 8$). Thus, in the course of establishing the order characterizing the BCC lattice, internal stresses in the AA can arise, reinforcing the visco-brittle transition during heat treatment.

In addition, there is experimental evidence that the direction of magnetization varies from transverse to longitudinal in annealed (brittle) AA ribbons [5-7]. An increase in tensile stress can be associated with positive magnetostriction values in volume. In this regard, the temper embrittlement of Fe-Ni-B AA can be explained if we assume the presence of BCC-type regions with local short-range order included in the amorphous Fe-Ni-based matrix with an Invar effect. This matrix has a small thermal expansion, while ordered areas have a thermal expansion similar to BCC-Fe. Such a difference in thermal expansion can lead to thermal stresses in the AA during cooling after annealing. AA will lose plasticity when the thermal stress becomes higher than the critical fracture stress.

Thus, the key factor for embrittlement of amorphous ribbons after heat treatment is, apparently, stresses caused by the structural, compositional, or magnetic form of inhomogeneity. AA based on Fe without the Invar effect are structurally more homogeneous and, therefore, more resistant to thermal embrittlement.

The microhardness changes are nonmonotonic for both alloys (Figure 2b). $HV$ behavior is similar up to 300°C, i.e. a decrease in this characteristic by 9-10% relative to the initial values is observed. Above 300°C, an increase $HV$ for Fe\textsubscript{53.3}Ni\textsubscript{26.5}B\textsubscript{20.2} alloy is observed up to complete crystallization. For Co\textsubscript{28.2}Fe\textsubscript{38.9}Cr\textsubscript{15.4}Si\textsubscript{0.3}B\textsubscript{17.2} alloy, a further increase in temperature leads to two $HV$ maxima (the first peak at 400°C, the second at 600°C), and the softening stages correspond to intervals above 400°C to 500°C and over 600°C to 700°C.
The sequence of structural transformations in AA after heat treatment is presented in Table 2 on the basis of detailed studies by TEM (Figures 3 and 4).

Table 2. Phase transformations of AA after annealing.

| Alloy         | Temperature range | Phase composition                  |
|---------------|-------------------|-------------------------------------|
|               | 23°C ≤ T < 450°C  | A’                                  |
| Co_{28.2}Fe_{38.9}Cr_{15.4}Si_{0.3}B_{17.2} | 450°C ≤ T < 500°C | A+α-Fe                              |
|               | 500°C ≤ T < 525°C | A+α-Fe+α-Co                         |
|               | 525°C ≤ T ≤ 700°C | α-Fe+α-Co+β-Co+Co_{2}B+Fe_{2}B       |
|               | 23°C ≤ T ≤ 425°C  | A                                   |
| Fe_{53.3}Ni_{26.5}B_{20.2} | 425°C < T < 440°C | A+α-Fe                              |
|               | 440°C ≤ T < 450°C | A+α-Fe+γ-Fe                         |
|               | 450°C ≤ T ≤ 500°C | α-Fe+γ-Fe+Fe_{2}B+FeB               |

* A – amorphous phase.

Figure 3. Selected area electron diffraction (SAED) patterns and TEM images of structure AA Co_{28.2}Fe_{38.9}Cr_{15.4}Si_{0.3}B_{17.2} after annealing:
a – 350°C, dark field;
b – 450°C, dark field, α-Fe;
c – 500°C, dark field, α-Co;
d – 550°C, dark field, borides;
e – 650°C, bright field.
Figure 4. SAED patterns and dark-field TEM images of structure AA Fe$_{53.3}$Ni$_{26.5}$B$_{20.2}$ after annealing:

a – 250°C;
b – 425°C;
c – 440°C, α-Fe (200) and γ-Fe (111), correspondingly;
d – 450°C, borides;
e – 500°C, γ-Fe (111) and borides, correspondingly.

Co$_{28.2}$Fe$_{38.9}$Cr$_{15.4}$Si$_{0.3}$B$_{17.2}$ alloy remains amorphous up to 450°C (Figure 3a). Then, the first signs of crystallization in the amorphous matrix – α-Fe nanocrystals with a characteristic size of 5 to 25 nm were discovered (Figure 3b). In addition to the α-Fe crystalline phase, during annealing at 500°C α-Co (Figure 3c) with a nanocrystal size of 5-40 nm is also segregated. Extended sections of borides Co$_2$B, Fe$_2$B, as well as β-Co are observed in the structure over 525°C and AA completely turned into a nanocrystalline state (Figure 3d). The noticeable increase in the grain size of the alloy is discovered in the temperature range from 600°C to 650°C (Figure 3e).

During the controlled heating of the rapidly quenched alloy Fe$_{53.3}$Ni$_{26.5}$B$_{20.2}$, it was found that its structure is amorphous up to 425°C (Figure 4a). However, it should be noted that as the annealing temperature approaches 425°C, changes in the amorphous matrix are noticeable in TEM-images. The structure becomes less homogeneous, there is some “layering” (Figure 4b). As in the case of Co$_{28.2}$Fe$_{38.9}$Cr$_{15.4}$Si$_{0.3}$B$_{17.2}$ alloy, the Fe$_{53.3}$Ni$_{26.5}$B$_{20.2}$ alloy crystallizes by the primary crystallization mechanism. The first crystalline phase detected at 430°C is α-Fe with a BCC lattice, and then γ-Fe nanocrystals with a FCC lattice were also detected (Figure 4c). Particles of α phase have a size from 30 to 120 nm and a cubic shape with distinct faces oriented along the {100} crystallographic planes in the early stages of crystallization. In turn, particles of the γ-phase, which have the same sizes, are characterized by approximately equiaxial shape. Above 450°C, FeB, Fe$_2$B borides appear in the structure (Figures 4d and 4e) and the alloy turned into completely crystalline state. The proportion of borides increases markedly at $T_{\text{ann}} \geq 500°C$ (Figure 4e).

Until recently, there was a general opinion regarding the plasticity behavior of amorphous-nanocrystalline and fully nanocrystalline alloys, that if high strength could still be obtained, then
plasticity at the smallest sizes of nanocrystals or grains was always zero. The problem of giving plasticity to AA and composites based on them has been discussed for a long time [8, 9]. Currently, evidence has appeared that demonstrates in these materials both good strength and satisfactory plasticity [4, 10, 11]. This is a consequence of more advanced production technologies and the use of additional, and sometimes combined subsequent effects on materials.

Studies of AA after heat treatment showed that a plasticizing effect is inherent in them – an increase in the $K_{1c}$ parameter in the temperature ranges from 425°C to 445°C for Fe 53.3Ni26.5B20.2 and from 425°C to 485°C for Co 28.2Fe38.9Cr15.4Si0.3B17.2 (Figure 5). The subsequent decrease in crack resistance with increasing temperature is due to the appearance of borides in the structure (Table 2, Figures 3d and 4d), which have an active embrittlement effect on both alloys.

![Figure 5. Temperature dependence of crack resistance $K_{1c}$ of AA:](image)

$1$ – Fe 53.3Ni26.5B20.2; $2$ – Co 28.2Fe38.9Cr15.4Si0.3B17.2.

The discovered plasticizing effect is, apparently, stipulated by the efficient retardation of quasi-brittle cracks arising and growing in an amorphous matrix as a result of application of an external load. Possible retardation mechanisms that govern the propagation of cracks in various materials were analyzed in monograph [12]. However, the theoretical and experimental studies of this situation yield a basis to suggest a new unusual retardation mechanism governing the development of quasi-brittle cracks in the amorphous-nanocrystalline state. [4]. The movement of the crack can end in the region of the nanoparticle. It turns out to be an insurmountable barrier for crack propagation. It is established that crack retardation occurs, most probably, not at the interphase boundary between a nanocrystal and an amorphous matrix (in our case, both phases have close values of Young’s moduli) but in the vicinity of a nanoparticle, while approaching it. This is associated with the fact that, around each nanoparticle, an atmosphere is formed consisting of boron and silicon atoms (abundantly presented in an amorphous alloy but weakly dissolved in the nanocrystalline phase). The Young modulus of this atmosphere considerably exceeds that of the amorphous matrix in which a quasi-brittle crack propagates. This, obviously, should lead to the retardation effect or complete braking of crack.

**Acknowledgments**

The authors are grateful to their colleagues Chueva Tatiana, Umnova Nadezhda (Baikov Institute of Metallurgy and Materials Science, RAS, Russia) and Pluzhnikova Tatyana (Derzhavin Tambov State University, Russia) for long-term fruitful cooperation. The reported study was funded by Russian Foundation for Basic Research, project No. 20-08-00341 "A".

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