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X-RAY MICROANALYSIS OF Fe(B,C)-BASED SOLID SOLUTIONS

The structure and properties of FeB-based solid solutions of Fe–B–C alloys cooled within the range of crystallization rates from 10 to 10³ K/s are investigated. The solubility of Mn, Cr, V, Ti, Si, Al, Ni, Cu, Mo, or Nb in Fe(B,C) phase is estimated using X-ray microanalysis. The crystallization of this phase is established to proceed either from the liquid or under peritectic reaction depending on alloying element added. The existence of two polymorphic modifications of iron monoboride with transition temperature at about 1398 K is confirmed. The elements which additions allow increasing hardness and decreasing brittleness of Fe(B,C)-based solid solutions are determined. The change of the structure and properties of the phase caused by the increase in a cooling rate up to 10³ K/s is described. The brittleness of Fe(B,C) crystals lowers with decreasing quantity of the electrons taking part in the electron exchange and weakening “boron-boron” and “metal-boron” bonds of the phase crystal lattice while the iron atoms are substituted by the atoms of alloying elements.

Keywords: iron monoboride, alloying elements, solid solutions, dendrite parameters, electron structure, microhardness, brittleness.

Исследуются структура и свойства твердых растворов на основе борида FeB в сплавах Fe–B–C, закристаллизованных в интервале скоростей охлаждения 10–10³ К/с. Растворимость Mn, Cr, V, Ti, Si, Al, Ni, Cu, Mo или Nb в фазе Fe(B,C) определяется с использованием рентгеноспектрального микроанализа. Установлено, что в зависимости от состава легирующих добавок кристаллизация этой фазы может протекать как непосредственно из жидкости, так и по перитектической реакции. Подтверждается существование двух полиморфных модификаций моноборида железа с температурой перехода 1398 К. Определяются элементы, введение которых позволяет увеличить твердость и уменьшить хрупкость твердых растворов на основе моноборида железа. Описывается изменение структуры и свойств фаз, вызванное увеличением скорости охлаждения до 10³ К/с. Показано, что снижение хрупкости твердых растворов на основе Fe(B,C) при замещении атомов железа атомами легирующих элементов связано с уменьшением количества электронов, участвующих в электронном обмене, и ослаблением связей «бор–бор» и «металл–бор» в кристаллической решетке фазы.

Ключевые слова: моноборид железа, легирующие элементы, твердые растворы, дендритные параметры, электронное строение, микротвердость, хрупкость.

Досліджуються структура та властивості твердих розчинів на основі бориди FeB у сплавах Fe–B–C, закристалізованих в інтервалі швидкостей охолодження 10–10³ К/с. Розчинність Mn, Cr, V, Ti, Si, Al, Ni, Cu, Mo або Nb у фазі Fe(B,C) визначається із застосуванням методу рентгеноспектрального мікроаналізу. Встановлено, що залежно від складу легуючих домішок кристалізація цієї фази може відбуватися як безпосередньо з рідини, так і за перитектичною реакцією. Підтверджується існування двох поліморфних модифікацій моноборида заліза з температурою переходу 1398 К. Визначаються елементи, додавання яких дозволяє збільшити твердість і зменшити крихкість твердих розчинів на основі моноборида заліза. Надається опис зміни структури та властивостей фаз, спричинену збільшенням швидкості охолодження до 10³ К/с. Показано, що зниження крихкості твердих розчинів на основі Fe(B,C) у разі заміщення атомів заліза атомами легуючих елементів пов'язане зі зменшенням кількості електронів, що беруть участь в електронному обміні, та послабленням зв'язків «бор–бор» і «метал–бор» у кристалічній ґратці фази.

Ключові слова: моноборид заліза, легуючі елементи, тверді розчини, дендритні параметри, електронна будова, микротвердість, крихкість.

Introduction

Fe–B–C alloys for industrial applications can be successfully utilized since the alloys have sufficient thermal stability to resist oxidation, corrosion, abrasive wear at elevated temperatures [1, 2]. Strengthening is accomplished through structure stabilization by Fe(B,C) crystals appearing in the high boron iron alloys. However, under impact loads these alloys become inadequate because of their low resistance to cracking. It results in the loss of the valuable properties and severely limits the high temperature characteristics of the alloys restricting their use in critical applications. Recent results have indicated that the alloying of the Fe(B,C) crystals not only influences their morphology, but also significantly reduces their brittleness [3–6]. To obtain a high-quality coatings based on Fe–B–C alloys with good comprehensive mechanical properties, it is important to be aware of their microstructure. X-ray microanalysis is one of the main methods of studying crystal structure. Since only a few studies have been carried out and are in some aspects contradictory, especially in the alloyed Fe–B–C system, experiments were initiated to determine the effect of alloying elements on the structure and the properties of Fe(B,C)-based solid solutions.

Experimental procedure and results

The chemical composition of Fe–B–C alloys, determined by chemical and spectral analyses, has been within the composition region 10–14 wt. pct. B, 0.1–1.2 wt. pct. C, 0–5 wt. pct. M (where M – one of the following elements: Mn, Cr, V, Ti, Si, Al, Ni, Cu, Mo, or Nb), Fe – remainder. The specimens have been prepared by melting the constituent elements of high purity in a resistance furnace and solidified by cooling in air. X-ray diffraction with CuK_α radiation and high resolution scanning electron microscopy (SEM) using a field emission gun Jeol-2010 F equipped with an energy dispersive X-ray link system, operating at 200 kV, have been employed to characterize the phases. Microhardness (H_μ) and critical stress intensity factor (K_{IC}) of Fe(B,C)-based solid solutions have been estimated by means of PMT-3 device from the following relationships

$$H_\mu = \frac{1854P}{d^2}, \quad (1)$$

$$K_{IC} = \frac{0,15k(2c/d)^{-3/2}}{F} H\sqrt{d/2}, F = 3, k = 3.2 \quad (2)$$

where d – diagonal length of hardness indentation, m; P – load, N; c – brittle fracture zone radius, m; H – Vickers hardness, MPa.

The structure and the properties of Fe(B,C)-based solid solutions have been investigated in the range of cooling rates from 10 to 10^3 K/s. The solid solution Fe(B,C) arises on the base of FeB iron boride and grows in the form of three-dimensional dendrites (Fig. 1,a). Under the quenching from the temperatures of 1653–1443 K in the Fe(B,C) dendrites the dark and the light twin bands are revealed after etching. Deformation by the twinning is a primary mechanism of plastic flow of metal with a close-packed lattice. Therefore it may be assumed that at the elevated temperatures the crystals of Fe(B,C) possess not the rhombic (α -modification) but more close-packed lattice (β -modification). The results of thermal analysis also show the possibility of polymorphic transformation $\beta\text{-Fe(B,C)} \rightarrow \alpha\text{-Fe(B,C)}$. The weak thermal effect registered may be related with heat production in consequence of polymorphic transformation.

The following changes have been observed after alloying the Fe(B,C) crystals with the elements specified above. X-ray microanalysis shows that within the investigated range of cooling rates Mn, V, or Cr dissolve in the phase in noticeable quantities, while the solubility of Ti, Si, Al, Mo, Nb, Ni or Cu is insignificant or practically absent (Fig. 1).

Manganese dissolves in the iron monoboride to the full (Fig. 1, b), critical stress intensity factor K_{IC} of the phase increasing (Table). This element slightly decreases dendrite parameters of alloyed Fe(B,C) crystals. Vanadium dissolved to the amount of 2–5 wt. pct. gives rise to the non-homogeneous structure of the Fe(B,C)-based solid solutions (Fig. 1, c).

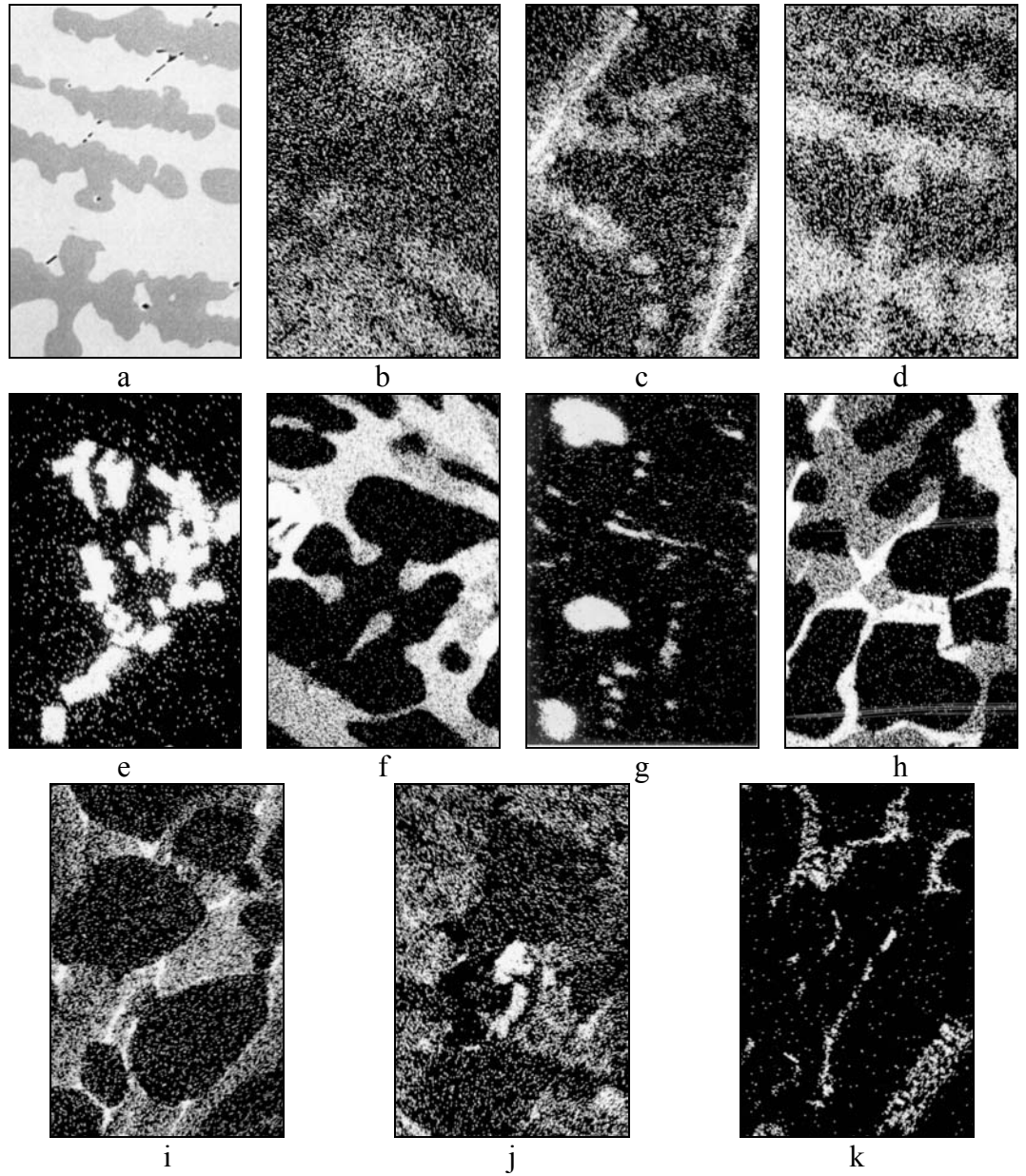


Fig.1. SEM images (x400) of Fe(B,C)-based solid solutions taken in: a – secondary electrons; b – MnK_{α} ; c – VK_{α} ; d – CrK_{α} ; e – TiK_{α} ; f – SiK_{α} ; g – AlK_{α} ; h – NiK_{α} ; i – CuK_{α} ; j – MoL_{α} ; k – NbL_{α}

A light needle-like phase is clearly seen in the dendrite interior. X-ray microanalysis data indicate this phase to be FeB_2 boride. It can be assumed that the first solid phase forming from the liquid has the composition FeB_2 . Then the peritectic reaction $L + \text{FeB}_2 \rightarrow \text{Fe(B,C)}$ takes place. Cooling through the peritectic temperature causes a type of nonequilibrium structure called surrounding. This nonequilibrium structure appears because there is not enough time for peritectic reaction to go to completion, and not all the liquid is consumed by reacting with FeB_2 to produce Fe(B,C) crystals. Instead, part of the liquid solidifies to produce a structure consisting of the phase of FeB_2 surrounded by a shell of Fe(B,C) .

Alloying with vanadium does not practically change dendrite parameters of Fe(B,C) phase but significantly enhances the critical stress intensity factor K_{IC} (Table). The dissolution of chromium in Fe(B,C) crystals is complete, as illustrated in Fig. 1, d. This element causes the largest increase in the plasticity of the phase slightly decreasing its dendrite parameters.

Titanium added to the iron monoboride dissolves in the dendrites insignificantly. Only traces of the element are revealed by X-ray microanalysis as small but noticeable background (Fig. 1, e). Consequently, at the boundaries of iron monoboride the numerous light crystals of TiC are seen in the SEM micrographs. For all that, the increase in microhardness H_{μ} and the decrease in critical stress intensity factor K_{IC} tend to be more marked while the dendrite parameters remain practically unchanged (Table).

The additions of silicon, aluminum, or nickel dissolve in the dendrites of Fe(B,C) in negligible quantities (Fig. 1, f–h). In the SEM micrographs Fe(B,C) crystals look dark. The studies indicate the presence of SiC , AlB_{12}C , or Ni_2B crystals, respectively, at the Fe(B,C) boundaries. Therefore, alloying with these elements does not essentially influence dendrite parameters (Table). Similarly, copper produces globular inclusions at the dendrite boundaries, as seen in Fig. 1, i.

Table

The influence of alloying elements on the dendrite parameters and the properties of Fe(B,C) -based solid solutions

Alloying element	Dendrite parameters, μm^*				H_{μ} , GPa**		K_{IC} , $\text{MPa}\cdot\text{m}^{1/2}$ ***	
	cooling rate, K/s				cooling rate, K/s		cooling rate, K/s	
	10	10^3	10	10^3	10	10^3	10	10^3
	d_0	l_0	d_0	l_0				
w/o	29.9	33.1	4.9	5.2	17.1	19.0	2.3	4.5
Mn	29.0	31.3	4.6	4.8	17.2	19.3	3.5	–
V	29.8	33.1	4.4	4.8	17.0	19.1	3.6	–
Cr	28.4	31.9	4.1	4.3	16.5	18.6	3.8	–
Ti	29.6	32.9	4.7	5.0	18.2	20.5	1.8	4.7
Si	29.1	31.1	4.6	4.9	17.9	20.0	2.2	5.1
Al	28.7	32.4	4.5	4.8	17.9	19.9	2.0	5.3
Ni	28.6	32.0	4.2	4.5	17.4	19.8	2.4	5.2
Cu	28.9	32.2	4.3	4.6	17.7	20.1	2.3	5.0
Mo	23.6	27.2	3.1	3.6	17.7	20.0	2.1	–
Nb	22.4	34.3	2.4	2.8	17.8	20.2	2.1	5.9

* d_0 – diameter of dendrite branches of II order; l_0 – spacing between the dendrite branches of II order, both accurate ± 2 pct.;

** – accurate up to 1–3 pct.;

*** – accurate up to 3–4 pct.; “–” indicates the impossibility to determine K_{IC} in case of no cracking

The dendrites of Fe(B,C) alloyed with molybdenum and niobium do not yield any significant changes in the structure. Only negligible content of these elements is revealed by X-ray microanalysis (Fig. 1,j,k). Correspondingly, the light crystals of Mo_2B , $\text{Mo}_2(\text{B,C})$, or NbB_2 are seen at the Fe(B,C) boundaries. Molybdenum and niobium cause substantial reduction in dendrite parameters, as shown in Table. In this case the microhardness and the critical stress intensity factor are not influenced.

The increase in a cooling rate up to 10^3 K/s brings about a significant increase in the microhardness and the critical stress intensity factor of Fe(B,C)-based solid solutions (Table). The results of alloying elements influence on dendrite parameters and micromechanical characteristics prove to be similar to those obtained for alloyed Fe(B,C) crystals cooled at the rate of 10 K/s. And what is more, not only manganese, chromium, or vanadium, but aluminum, molybdenum, or niobium as well reduce brittleness of Fe(B,C) phase, most likely because its crystals become smaller. Thus, the brittleness of Fe(B,C)-based solid solutions is dependent on alloying, with higher cooling rate giving rise to a higher K_{IC} .

The results obtained can be explained by the peculiarities in the structure formation of Fe(B,C)-based solid solutions. The stability of Fe(B,C) crystals depends on B–B and Fe–B bonds energy. The strength of these bonds is determined by the distraction of collectivized valence electrons of iron [7]. The ions of such elements as Mn, V, Cr, Mo, or Nb have p^6 -shells and form with boron the same valence bonds like the atoms of iron. As a result of substitution of iron atoms by the atoms of Mn, V, or Cr the fewer electrons take part in the electron exchange. The B–B and the Fe–B interactions weaken and therefore the microhardness and the brittleness of the solid solutions are found to decrease. The reverse is true for titanium. When alloying with this element, quantity of non-located electrons tends to increase. It causes strengthening above all the B–B bonds and, accordingly, gives rise to higher microhardness and brittleness of (Fe,Ti)(B,C) crystals.

Aluminum and silicon are sp -elements, whereas nickel or copper atomic configurations tend to the stable d^5 -states. It makes difficult the delivery of electrons and imposes restrictions on the electron exchange. Therefore the atoms of Al, Si, Ni, or Cu do not practically substitute for the iron atoms in the Fe(B,C) lattice. When dissolving, these elements are most likely able to form the metal–metal (M–M) bonds. In the electron exchange, some electrons of iron localized in the d^{10} -states pass over to the d^5 -states with the energy gain. It causes strengthening M–M bonds and weakening Fe–B bonds in the lattice of the crystals. Taking into account the negligible dissolution of these elements and small contribution of the above bonds in the bond energy balance their insignificant influence on micromechanical properties stands to reason.

The probability that molybdenum and niobium valence electrons are localized in the stable d^5 -configurations is high. That is why these elements are electron acceptors. Any redistribution of electrons in such system will result in the energetically non-advantageous destruction of the stable configurations. Therefore the solubility of molybdenum and niobium in Fe(B,C) crystals is negligible and they do not affect the micromechanical properties.

Conclusions

Alloying of Fe(B,C)-based solid solution with manganese, chromium, or vanadium can be recommended to lower the brittleness of the phase. As the results of X-ray microanalysis show, the effect can be achieved due to a high solubility of the above elements in Fe(B,C) crystals. Their atoms mainly substitute for the iron atoms in the Fe(B,C) lattice, this leads to weakening “metal–metal” and “boron–boron” bonds of the solid solutions.

The negligible dissolution of titanium, aluminum, silicon, nickel, copper, molybdenum, or niobium in Fe(B,C) crystals is responsible for the appearance of new phases based on these elements at the Fe(B,C) boundaries. The results can be explained by electron structure of the alloying elements that do not supply necessary electrons for the electron exchange and do not influence the properties of Fe(B,C)-based solid solutions.

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