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Mechanism of the Fe₃(B,C) and Fe₂₃(C,B)₆ solid-state transformation in the hypoeutectic region of the Fe-C-B system

Jonathan Lentz[*], Arne Röttger, Werner Theisen

Ruhr-Universität Bochum, Institut für Werkstoffe, Lehrstuhl Werkstofftechnik, Universitätsstraße 150, D-44801, Bochum, Germany

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ABSTRACT

This study investigates the microstructural mechanisms involved in the solid-state transformation of the Fe₃(B,C) → Fe₂₃(C,B)₆ phases in the hypoeutectic region of the iron-carbon-boron (Fe-C-B) system. We analyzed the influence of different initial microstructural characteristics on the Fe₃(B,C) → Fe₂₃(C,B)₆ transformation with regards to the matrix phase, matrix C content, B/(C + B) ratio, and agglomeration of the parental Fe₃(B,C) phase. We performed thermodynamic calculations using the CALPHAD method, validated by laboratory melts with varying B/(B + C) ratios. These laboratory melts were then microstructurally characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and wavelength-dispersive X-ray spectroscopy (WDS). We particularly focused on solid-state transformation of borides and carborides of type M₃(C,B) and M₂₃(C,B)₆ in the hypoeutectic region of the ternary system Fe-C-B, investigated via both *in situ* and *ex situ* XRD measurements. It was found that the solid-state transformations are influenced by enriched B inside the eutectic structure, a result of solidification. This increased B content is not reduced in solid state due to the kinetic limitations of B and C inside the hard-phase structure. Thus phase stability is subject to local equilibria depending on the local C and B concentration of the hard-phase structure. In this process the Fe₂₃(C,B)₆ phase also forms a shell-like structure surrounding the Fe₃(B,C) and Fe₂B phases.

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1. Introduction

Tool components used in mining or materials processing need to resist high abrasive wear. The most cost-effective materials for this application are tool steels and wear-resistant cast irons, featuring a high hardness and a sufficient toughness, simultaneously. One challenge of modern alloy development is optimizing application properties, such as wear resistance and toughness, while increase cost effectiveness in terms of tool manufacture, maintenance, and lifespan. From a microstructural perspective, high wear resistance is the result of a sufficient volume fraction of hard phases, formed primarily or eutectically during the solidification sequence. These hard phases are embedded in and supported by a metallic matrix, which therefore requires high strength and toughness. Wear resistance can be optimized by tailoring the properties of the hard phases to the tribological interaction. Thus the most important parameters influencing wear protection performance are parameters relating to the distribution, morphology, and micromechanical

properties of the hard phases, such as hardness, Young's modulus, and fracture toughness. In this context, a comparison of different types of hard phases (carbides, nitrides, and borides) shows that borides generally display better micromechanical properties due to their high hardness and adequate fracture toughness. For example, it was shown that boron-cementite Fe₃(B,C) (hardness 1300−1400 HV0.05) or (Fe,Cr)₂B (hardness 1600−2000 HV0.05) have hardness of the same order of magnitude or even higher than that of Cr-rich carbides of type M₇C₃ (hardness 1400−1600 HV) [1−3]. In addition, these borides are based on the ternary alloying system Fe-C-B, which allows a reduction in the amount of more expensive but commonly alloyed hard-phase forming elements such as Cr, Mo, V, or W. Hence, boron (B) seems a promising hard-phase forming element for a novel alloying approach for tool steels or white cast iron.

However, the current state of research shows controversial or limited results for phase stability and phase formation mechanisms for the hypoeutectic alloying region of the ternary system Fe-C-B. There is particular disagreement surrounding the formation mechanisms and stability region of the Fe₂₃(C,B)₆ phase (τ-phase). For instance, the stable temperature region for the Fe₂₃(C,B)₆ phase

* Corresponding author.
  E-mail address: Jonathan.Lentz@Ruhr-Uni-Bochum.de (J. Lentz).

was found to lie in a wide temperature range from 600 to 950 °C in solid state. In contrast, some authors reported primary stability and eutectic solidification at temperatures higher than 1100 °C. A brief summary can be found in the literature [4], which considers the differences in the experimental setup of the various studies, such as melt size and quenching rates. In this context, the strong segregation effects of B and rapid non-equilibrium solidification processing shift the phase field of the liquid phase to lower temperatures and thus enable crystallization of the τ-phase from the melt. In addition, it was found that alloying elements like chromium increase the stability of the τ-phase and thus shift the formation of the τ-phase to higher temperatures close to the solidus temperature [1].

From a technical perspective, B additions in the order of 50—100 ppm are used to form small precipitations of the B-bearing τ-phase (around 100 nm in size) in low-alloyed ferritic/martensitic steels to increase creep resistance [5—7]. Furthermore, B grain boundary segregation and precipitation of the τ-phase on grain boundaries is discussed in the context of reducing the interfacial energies of γ-Fe grains, thus retarding the nucleation of α-Fe and increasing hardenability, e.g., for press-hardening steels for automotive use [8—10]. For wear protection, B is alloyed in the order of magnitude of 1 mass% to promote the formation of hard borides and carboborides. In the hypoeutectic region of the ternary system Fe-C-B, the three Fe-rich hard phases of type $Fe_3(B,C)$, Fe_2B, and $Fe_{23}(C,B)_6$ are known. In this context, the τ-phase ($Fe_{23}(C,B)_6$) displays lower hardness (hardness 1100 HV0.05) than the $Fe_3(B,C)$ (hardness 1400 HV0.05) and Fe_2B (hardness > 1600 HV0.05) hard phases, which are therefore preferred. However, the formation of the $Fe_{23}(C,B)_6$ phase and its interrelation with the transformation of $Fe_3(B,C)$ and Fe_2B hard phases is a precondition for successful alloy development in the Fe-C-B system. A previous study investigated the solidification behavior of the hypoeutectic region of the Fe-C-B system in this context [11]. It was found that, subsequent to primary crystallization of γ-Fe matrix phase, the Fe_2B and $Fe_3(B,C)$ hard phases are continuously solidifying due to a eutectic transition reaction and forming a network-like structure. Furthermore, the $Fe_{23}(C,B)_6$ phase was not found to crystalize from the melt.

A deeper understanding of the formation mechanisms of the τ-phase is motivated by the technical utilization of B as an alloying element in tool steels and to create a basis for a targeted microstructural tailoring of tool steels based on the hypoeutectic region of the Fe-C-B system. However, numerous influencing parameters are involved in the τ-phase formation mechanisms and the solid-state transformations occurring in the underlying hypoeutectic region of the ternary Fe-C-B alloying system. This high complexity of the mechanism of action complicates investigations and has led to contradictory observations being published. As a result, the following investigations focus on the ternary Fe-C-B system and ignore the influence of additional alloying elements. This study aims to characterize the phase formation mechanisms of the $Fe_{23}(C,B)_6$ phase, which is formed in a temperature close to the austenite-ferrite-transition temperature (700—1000 °C). Particular focus is placed on the formation processes taking place in the region of the eutectic hard-phase structures rather than small precipitates for example on grain boundaries, as the former are relevant for wear protection.

2. Experimental procedure

2.1. Production of laboratory melts and specimens

Laboratory melts from the hypoeutectic region of the Fe-C-B system were cast and experimentally characterized. The effect of increasing B content was reproduced through systematic variation of the laboratory melt's B content between 0.2 and 1.4mass%. To establish the basis for a prospective alloy design for tool steels, the carbon (C) content was kept constant at 0.6 mass% to maintain martensitic hardenability of the iron matrix. Accordingly, the B/$(C + B)$ ratio was varied between 0.25 and 0.7, as shown in Table 1.

For this purpose, the compounds FeB, electrolytic Fe, and raw iron were weighed in amounts of 200 g and melted in alumina crucibles using a vacuum induction furnace with argon atmosphere of 1 bar present. The chemical composition of the laboratory melts was validated using Optical Emission Spectroscopy (OES) (see Table 1).

Specimens were cut from the casting using a CBN cutting disc. The phase stability was investigated at temperatures of 700, 800, 900, and 1000 °C. To adjust phase stability of the high temperature condition, specimens were tempered in a vacuum furnace at 700, 800, 900, and 1000 °C for 366 h and subsequently quenched in water to freeze the high temperature microstructure. In the following, the particular specimens will be designated using the alloying composition and tempering temperature (e.g., 0.2B-0.6C-700 °C).

2.2. Thermodynamic calculations

Thermodynamic equilibrium calculations based on the CALPHAD method were performed to calculate phase and property diagrams using Thermo-Calc software version 4.1. Thermodynamic data were taken from the TCFe7 database, considering the liquid phase (LIQUID), ferrite (B2_BCC), austenite (FCC_A1), $Fe_{23}(C,B)_6$ (M23C6), $Fe_3(B,C)$ (CEMENTITE), Fe_2B (M2B_TETR), FeB (BM), and B_4C (B4C). The simulation was run with a pressure and quantity of p = 10^3 mbar and n = 1 mol, respectively.

2.3. Metallography & microstructural characterization

The metallographic preparation was performed by embedding the samples in Cu-based conductive polymer Technovit5000, followed by a stepwise grinding with SiC paper from 80 to 1000 mesh and polishing using 54 μm—1 μm diamond suspension. The microstructure of the specimens was contrasted by etching the samples with 3% alcoholic HNO_3 acid.

For microstructural characterization, a scanning electron microscope (SEM) (MIRA3, Tescan) with secondary-electron (SE) and back-scatter-electron (BSE) detector was used at an acceleration voltage of 20 kV and a working distance of 8 mm. Quantitative phase analysis was performed via image binarization. Five images per specimen were taken using the SE detector and subsequently analyzed using A4i (Archive4Images) analysis software. Electron backscattered diffraction (EBSD) measurements were performed for samples tilted for 70° using an Oxford Nordlysnano detector. Noise inside the EBSD maps resulting from indexing problems of the cubic (super-)lattice structures of the α-Fe and $Fe_{23}(C,B)_6$ phases was reduced through digital smoothing. Quantitative measurements of the chemical composition of the hard phases were carried out via wavelength dispersive spectrometry (WDS) using a microprobe (CAMECA, SX5-FE). Certified reference materials were used to standardize the elements B (using B_4C), C and Fe (using Fe_3C). WDS measurements were performed at an acceleration

Table 1
OES measurements of the alloy composition in mass%.

Alloy	B/(C+B)-ratio	C	B	Mn	Si	Fe
0.2B-0.6C	0.25	0.53	0.19	0.09	0.19	Bal.
0.6B-0.6C	0.5	0.56	0.55	0.01	0.15	Bal.
1.4B-0.6C	0.7	0.61	1.48	0.10	0.26	Bal.