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Materials Characterization

Hardness and modulus of Fe_2B, $Fe_3(C,B)$, and $Fe_{23}(C,B)_6$ borides and carboborides in 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 work provides a comparative and comprehensive study of the indentation hardness and indentation modulus of iron-rich borides and carboborides of types Fe_2B, $Fe_3(C,B)$, and $Fe_{23}(C,B)_6$. In addition, the hardness and elastic modulus of Cr-rich M_7C are investigated for comparative purposes. We investigated the impact of increasing B content and indentation size effect (ISE). The phases of interest were stabilized in cast Fe-C-B alloys that varied with respect to the $B / (B + C)$ ratio and heat treatment. The resulting microstructures were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and wavelength X-ray spectroscopy (WDS). Dynamic in-situ nanoindentation experiments based on the method of continuous stiffness measurement (CSM) were coupled to SEM and EBSD investigations to determine the mechanical properties of the individual borides and carboborides as a function of the indentation depth. The results were compared to values obtained for the Cr-rich M_7C_3 carbide. It was found that the hardness of the B-rich $Fe_3(C,B)$ phase is considerably higher than pure Fe_3C and increases with increasing B content. The ISE was present in all investigated phases, and the hardness decreased as a function of indentation depth. The hardness at infinite indentation depth H_0 was estimated according to the model of Nix and Gao. The Fe_2B phase was found to be the hardest phase ($H_0 = 19.04$ GPa), followed by M_7C_3 ($H_0 = 16.43$ GPa), $Fe_3(C,B)$ ($H_0 = 11.18$ to 12.24 GPa), and $Fe_{23}(C,B)_6$ ($H_0 = 10.39$ GPa).

1. Introduction

Tools for processing of minerals or metals must simultaneously withstand combinations of high loads and high wear attack. They thus require high structural strength and toughness together with a high wear resistance. Cost-effective materials that are used in this kind of application include cold-work tool steels. From a macroscopic point of view, tool steels can be considered as isotropic materials; however, they possess a multiphased microstructure composed of an iron matrix phase and reinforcing hard phases. The iron matrix phase commonly consists of annealed martensite and provides the necessary structural strength and toughness of the material. The wear resistance is provided by hard phases, which are embedded in the iron matrix phase. Carbides such as the Cr-rich M_7C_3 carbide (1600–1790 HV) are commonly used as hard phases in tool steels [1].

The performance of these alloys in wear-protection applications depends on microstructural characteristics such as volume content, morphology, and distribution of the hard phases in the microstructure. Depending on the alloying system and composition, the hard phases crystallize either from the melt during the solidification and/or during subsequent heat treatment in the solid state. Alloying concepts and the associated solidification behavior as well as the manufacturing route and subsequent heat treatment techniques can thus be used to adapt microstructures to the respectively prevailing tribosystems. However, independent of these microstructural characteristics, superior mechanical properties (high hardness, Young's modulus, and toughness) of the hard phases themselves are a precondition for good performance in wear-protection application. These mechanical properties are determined by phase type, chemical composition, and orientation of the hard phases [2–4].

A novel alloying approach utilizes borides as hard phases in tool steels. Compared to carbides, borides feature several beneficial properties, i.e. higher thermal stability, hardness, and elastic moduli [5,6]. These borides form directly from reactions between the elements iron (Fe) and boron (B). Owing to the low solubility of B in the iron lattice (around 500 ppm), only small amounts are necessary to form high volume contents of hard phases. In addition, B increases the hardenability of the iron matrix [7]. Alloying contents of further, more expensive hard-phase forming elements, such as Mo, V, or W, can thus be reduced, which lowers the overall material costs. Carbon (C) is then decoupled

from processes of hard phase formation and primary alloyed to adjust properties of the iron matrix such as toughness, strength, and austenite stability [8]. This alloying approach is based on the hypoeutectic region of the ternary Fe-C-B system. However, the literature provides short and partly contradictory information about this system [9]. Solidification behavior as well as solid-state transformations were the focus of previous studies [10,11]. It was shown that, during primary solidification of Fe dendrites, the remaining melt strongly enriches with B and C. Subsequently, the hard phases Fe_2B and/or $Fe_3(C,B)$ precipitate from a eutectic reaction that depends on the B / (C + B) ratio in the residual melt. Thus, the microstructures are characterized by primary Fe dendrites, which are surrounded by the eutectic hard-phase structure. At temperatures below 800 °C, the $Fe_3(C,B)$ phase undergoes a solid-state transformation into the $Fe_{23}(C,B)_6$ phase. With increasing agglomeration and a higher local B / (C + B) ratio of the parental $Fe_3(C,B)$ phase, this transformation process is incomplete and parts of the $Fe_3(C,B)$ phase remain within the eutectic structure and/or the Fe_2B phase forms in addition to the $Fe_{23}(C,B)_6$ phase. These phase transformation processes are governed by local equilibria. Thus, depending on the local B / (C + B) ratio and (heat treatment) temperature, the Fe_2B, $Fe_3(C,B)$, and $Fe_{23}(C,B)_6$ hard phases can be present next to each other.

The M₂B-type phase is the hardest phase present in the hypoeutectic region of the Fe-C-B system. Investigated microstructures include M₂B layers on borided steel substrates, precipitates in cast steel as well as cast or sintered bulk samples [8,12–26]. In this manner, indentation methods are applied to determine the hardness, modulus, and toughness of the M₂B phase. It was shown that the chemical composition (especially the Cr content) as well as the orientation are key factors that influence its mechanical properties. In addition, the indentation size effect (ISE) was found to be present, and the measured hardness of the Fe_2B phase decreases with increasing indentation depths [19,20,23]. In the case of borided M₂B layers, the properties are also a function of layer thickness and surface distance as traced back to interactions with the FeB phase, porosity, residual stresses, crystal anisotropy, and differences in chemical composition [20,23]. Affected by these parameters, a huge range of ~1500–1900 HV for the hardness and modulus of the M₂B phase can be found in literature. As an example, values for the hardness are 1520 HV 0.025 (cast material with 0.5 mass% Mn-addition) [8], 1560 HV1 (Fe-C-B cast material) [25], 20 GPa HV2 (borided surface on low alloy steel with Cr) [26], 1650–1920 HV0.5–HV3 (borided surface on ductile cast iron) [15], 1854 HV3 (borided surface on cold work steel) [16] and 1760–1880 HV0.05 (pure, oriented Fe_2B crystals) [13].

However, less experimental work is available for the micromechanical properties of the carboborides $Fe_3(C,B)$ and $Fe_{23}(C,B)_6$. Umemoto et al. reported that the hardness of cementite (Fe_3C) of 10 GPa (~920 HV) is increased with Cr or Mn addition to 13.5 GPa (20 atom% Cr) or 15 GPa (30 atom% Mn) [27]. Berns et al. experimentally showed that the hardness of boron-cementite ($Fe_3(C,B)$) is further increasing with B-additions and is in a range of 1248–1360 HV 0.025 [28]. This increase of hardness is utilized in a new group of low-cost, Fe-C-B alloys, which take advantage of the $Fe_3(C,B)$ phase as reinforcing hard phase [29]. Thereby, the $Fe_3(C,B)$ phase is the major hard phase present in ternary Fe-C-B alloys at austenizing temperatures between 950 and 1100 °C. At heat treatment temperatures lower than 950 °C the $Fe_3(C,B)$ can transform into $Fe_{23}(C,B)_6$, which is then additionally present in the microstructure [10]. The hardness of the Cr-rich M₂₃C₆-carbide is known to increase from 1080 HV in $(Fe,Cr)_{23}C_6$ to 1450 HV with Tungsten (W)- or Molybdenum (Mo)-addition [30,31]. Recently, ab-initio calculation showed that the covalent bonding character of the M₃(C,B) and M₂₃(C,B)₆ phases depends on the chemical composition of the metal elements as well as the ratio of the metalloid elements B / (C + B) present in these compounds. It is shown that the stability, elastic moduli and hardness of theses phases can be increased by additions of Cr, Mn, W and Mo and also by high B / (C + B) ratios [18,28,32–41].

In summary, several systematic characteristics, such as structural and morphological effects, contamination, doping of the phases with further elements (mainly Cr and Mn) as well as the ISE and phase orientation significantly influence the measured values of hardness, modulus, and fracture toughness of the hard phases. It is thus important to further characterize the properties of the Fe_2B, $Fe_3(C,B)$, and $Fe_{23}(C,B)_6$ hard phases and to obtain a comprehensive and comparative analysis in which systematic conditions are kept constant as far as possible. It is the objective of this paper to investigate these mechanical properties with respect to the ISE as well as the effect of the B / (C + B) ratio of the $Fe_3(C,B)$ phase. On this account, cast specimens from the pure Fe-C-B system are investigated using nanoindentation techniques so that the influence of further alloying elements, such as Cr or Mn can be neglected, and the microstructures are comparable to the desired application state of a tool steel. Furthermore, the properties of the Cr-rich M₇C₃ carbide are measured to allow for subsequent comparison and benchmarking of the values.

2. Experimental Procedure & Methods

2.1. Materials

Three laboratory melts (melt size 200 g) from the hypoeutectic region of the Fe-C-B system were cast in an induction furnace. In order to investigate the effect of the B / (C + B) ratio on the mechanical properties of the $Fe_3(C,B)$ phase, the B content of the laboratory melts was increased from 0.2 to 0.6 to 1.8 mass% B. The C content was kept constant at 0.6 mass% C to maintain martensitic hardenability of the iron matrix. The pre-alloys, electrolytic iron, raw iron, and ferroboron (Fe-18.8 atom% B) were mixed in an alumina crucible and melted in an argon atmosphere. Furthermore, a hypereutectic alloy with high B content of 5 mass% was cast to obtain coarse, primary precipitates of the Fe_2B phase (alloy 5B). In addition, the commercial cold-work steel X210Cr12 (1.2080) was used to obtain values of the hardness and modulus of the Cr-rich M₇C₃ carbide.

Cubic specimens with an edge length of 10 mm were prepared from the cast laboratory alloys. Specimens of alloys 0.2B, 0.6B, and 1.8B were tempered in a vacuum furnace for 288 h at a temperature of 1000 °C and subsequently quenched in water. The heat treatment, which took account of the phase diagrams and microstructural investigations presented in our previous studies [10,11], stabilized and homogenized the $Fe_3(C,B)$ phases in the microstructure. Furthermore, a specimen of alloy 0.2B was tempered at 700 °C to produce the $Fe_{23}(C,B)_6$ phase in the microstructure. In the following, the samples are designated according to their alloying composition and tempering temperature (e.g. 0.2B-1000, 0.2B-700, 0.6B-1000, and so on). Sample designation, hard phase present, and nominal chemical composition of the sample are listed in Table 1. The chemical composition of alloys 0.2B, 0.6B, 1.8B, 5B and X210Cr12 was validated using optical emission spectroscopy (Table 2).

The metallographic procedure for microstructural investigations of the included stepwise grinding using SiC abrasive paper (320 to 1000 mesh) and subsequent polishing using diamond suspensions (18 to 1 μm grain size). Furthermore, the samples were vibro-polished for

Table 1
Sample designation, nominal chemical composition in mass%, and properties obtained from the respective samples.

Sample	Phase	C	B	Cr	Fe
0.2B-1000	$Fe_3(C,B)$	0.6	0.2	–	Bal.
0.6B-1000	$Fe_3(C,B)$	0.6	0.6	–	Bal.
1.8B-1000	$Fe_3(C,B)$	0.6	1.8	–	Bal.
0.2B-700	$Fe_{23}(C,B)_6$	0.6	0.2	–	Bal.
5B	Fe_2B	–	5	–	Bal.
X210Cr12	M_7C_3	2.1	–	12.0	Bal.