Materials Science and Engineering A 532 (2012) 511–521

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Supersolidus liquid-phase sintering of ultrahigh-boron high-carbon steels for wear-protection applications

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ARTICLE INFO

Article history:
Received 15 September 2011
Received in revised form 27 October 2011
Accepted 29 October 2011
Available online 11 November 2011

Keywords:
Boron
Steels
Wear resistance
SLPS
HIP

ABSTRACT

Powder metallurgy (PM) represents an alternative to conventional casting processes for the production of wear-resistant materials. PM hard alloys for wear-protection applications feature both higher strength and fracture toughness compared to cast hard alloys due to their more finely grained microstructure. However, densification by hot-isostatic pressing (HIP), the conventional PM-compaction method, is relatively expensive and thus partially counteracts low-cost processing. To increase the economic efficiency of the processing route, supersolidus liquid-phase sintering (SLPS) was investigated. In addition, expensive Ni- and Co-base hard alloys were substituted by boron-rich Fe-base hard-facing alloys.

In this study, three ultrahigh-boron hard-facing alloy powders were densified by SLPS and HIP. The sintering temperatures were optimized by means of sintering experiments that were supported by thermodynamic calculations. Both densification states were investigated and compared with respect to the microstructure and the tribological and mechanical properties of the compacted hard-facing alloys. It was shown that the mechanical and tribological properties are strongly influenced by the microstructure. Although the microstructure is affected by the chemical composition, it can also be adapted by the densification process. SLPS-densified hard-facing alloys have a coarse microstructure that imparts not only a high wear resistance but also a detrimental effect on the mechanical properties.

1. Introduction

White cast irons are widely used for wear protection applications in the mining, mineral processing, and cement industries owing to their high hardness, high wear resistance, low price, and easy production [1–3]. These characteristics arise from a microstructure consisting of primary and/or eutectic hard phases that are finely distributed in an austenitic, pearlitic, or martensitic matrix [4,5]. White cast iron with added boron has recently been receiving more attention owing to the higher hardness of borides compared to carbides and the lowering effect of boron on the solidus temperature of steels. This means that steels containing sufficient boron can be processed at lower temperatures. One main attribute of boron-containing steels is the low solubility of boron in γ-Fe and α-Fe and the formation of hard Fe-rich borides of the type M_2B, $M_3(C,B)$, and $M_{23}(C,B)_6$ [5–7]. As a result, it is not necessary to add hard-phase forming elements such as Mo, V, and Nb to obtain an Fe-base alloy with a large amount of hard phases.

Only a few authors have dealt with boron additions higher than 1 mass%. This is due to the fact that an increasing boron content decreases the fracture toughness [8–11]. The microstructure of ultrahigh-boron, high-carbon alloys is characterized by primary solidified metal cells (hypoeutectic) or hard phases (hypereutectic) that are surrounded by a low-melting and almost brittle eutectic. This fine eutectic, in particular, promotes crack propagation because its fracture toughness is lower than that of the metal matrix, which results in insufficient mechanical properties. Godfrey et al. investigated Ti-base MMCs with added boron that were processed by hot-isostatic pressing. Their results indicated spheroidization of the hard phases during HIP treatment, which promotes an increase in mechanical strength [5,12,13]. Furthermore, boron addition inhibits strong coarsening of the microstructure due to precipitation of borides at the grain boundaries [12]. If a high wear resistance and good mechanical properties are required, the HIP process seems to be a promising processing route for boron-containing PM alloys.

The addition of a small amount of boron to PM steels has been reported to have a major effect on the densification behavior during supersolidus liquid-phase sintering (SLPS) [14–16]. Sercombe investigated the effect of a small boron addition on the sintering behavior of a freeformed maraging PM steel. He showed that

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doi:10.1016/j.msea.2011.10.118

the optimized sintering temperature (OST) could be decreased by increasing the boron content from 0 mass% to 0.4 mass% [17]. Boron forms a low-melting eutectic with Fe and therefore promotes the formation of a liquid phase at lower temperatures. However, boron forms stable phases with Mo, Ti, and Cr. This alters the phase composition of the steel matrix, which may have an effect on the mechanical and tribological properties after heat treatment. Based on the results of Sercombe and Lal et al., boron-containing PM steels are suitable materials for SLPS densification to achieve wear-resistant materials with a low porosity [17–20].

The aim of the present paper is to study the densification behavior of three ultrahigh-boron, high-carbon gas-atomized Fe-base powders by means of supersolidus liquid-phase sintering and hot-isostatic pressing. The SLPS process was used to achieve fast densification due to the presence of low-melting, boron-rich eutectics. In addition, Weber et al. mentioned the possibility of influencing the size and shape of the hard phases in a ledeburitic cold-work tool steel by means of SLPS processing with the aim of adjusting the diameter of the hard phase to the wear system [21,22]. In contrast, spheroidization of hard phases due to a decrease in the surface energy during HIP is well known. It increases the mean free path of the metal matrix between two adjacent hard phases, which thus improves the mechanical properties. Therefore, this work investigated the influence of the densification process on the microstructure and on the mechanical and tribological properties.

2. Experimental procedure

2.1. Materials

Three ultrahigh-boron, high-carbon steels were used as gas-atomized powders. Two of these were commercially available hypereutectic high-boron steels, X200CrNiBMo10-4-3-3 and X360NiBCrCu4-2, and the third was a self-developed hypoeutectic high-boron steel X60CrB2-2. The chemical composition of the bulk samples after HIP was measured by optical emission spark spectroscopy (QSG750 spectrometer OBLF) (Table 1). Prior to SLPS and HIP densification, the gas-atomized steel powders were analyzed with respect to their microstructure, particle size, and particle distribution by means of laser diffraction.

2.2. Thermodynamic calculations

Determination of the optimized sintering and HIP temperatures was supported by thermodynamic equilibrium calculations using the Calphad method. Software package Thermo-Calc version R (Thermo-Calc AB, Stockholm, Sweden) and database TCFE6.2 were used to calculate the solidification path, phase diagrams, and the chemical composition of each phase in the equilibrium state. The calculations were performed with a phase set reduced to LIQUID, BCC_A2, FCC_A1, CEMENTITE, M7C3, M2B_tetr, Cr2B_orth, M23C6, and M6C.

2.3. Thermal analysis, sintering, and HIP

Thermal analysis was performed to confirm the Thermo-Calc results concerning the sintering window. Differential thermal analysis (DTA) was performed by heating small amounts of gas-atomized steel powder (~100 mg) in alumina crucibles at a heating rate of 10 K min^{-1} in an argon gas atmosphere.

The optimized sintering temperatures were investigated experimentally by sintering at different temperatures above the solidus temperature (T_{SOL}). The metal powder was filled into alumina preforms and precompacted to tap density. Sintering was performed in a batch furnace (⌀ = 50 mm, L = 120 mm) under a vacuum (0.5 Pa) with a temperature accuracy of ±5 K. The specimens were first heated to 300 °C to degas the metal powder and to drive out residual vapor. They were then heated to the sintering temperature at a rate of 20 K min^{-1}. The isothermal holding time at the sintering temperature was 10 min for all specimens. SLPS was followed by a slow furnace cooling at a rate of approx. 15 K min^{-1}. After sintering at the different temperatures, the specimens were characterized by means of metallographic analysis, hardness measurements, and determination of the density by the Archimedes method.

Besides SLPS-densification, the gas-atomized powders were compacted by hot-isostatic pressing (HIP) for 2 h in an argon atmosphere at a temperature of 1000 °C and a pressure of 100 MPa. Ferritic steel capsules were filled with gas-atomized steel powder, which was then precompressed to tap density by vibration. The capsules were evacuated for 30 min and finally sealed by TIG welding.

2.4. Heat treatment

To achieve a martensitic microstructure, the HIP- and SLPS-densified specimens were austenitized at 850–1050 °C, quenched in water, and double-tempered in a temperature range from 100 to 600 °C for 2 h.

2.5. Metallography and microscopy

Microstructural examinations were carried out using optical and scanning electron microscopy (SEM). Specimens were sectioned, ground on abrasive paper, and polished with a 1 μm diamond suspension. If necessary, the specimens were etched with 3% Nital. X-ray diffraction was used for phase analysis. Measurements were performed with a Siemens-D500 X-ray diffractometer using chromium K_α radiation and a step size of 0.02° 2θ in a range of 40–165° 2θ. The diffractograms were evaluated by the program ADM and the JCPDS database.

2.6. Hardness measurements and abrasive wear tests

Macro- and microhardness measurements were carried out on the cross-section of the respective specimen using a Vickers indenter and a load of 294.3 N or 49.15 N. The wear resistance of the heat-treated specimens was investigated by a pin-on-paper test against the abrasives flint (SiO_2) and corundum (Al_2O_3). This type of test involves rotating a cylindrical specimen with a diameter of ⌀ = 6 mm against an abrasive paper with an average particle size of 80 mesh (~200 μm) or 220 mesh (~66 μm). The dimensionless value of the wear resistance was calculated on the basis of the weight loss Δm of the specimen during testing, the specimen's contact surface A, the coating density ρ_{COAT}, and the distance travelled L (Eq. (1)).

$$W_{ab}^{-1} = \frac{A \cdot L \cdot \rho_{COAT}}{\Delta m} \quad (1)$$

2.7. Four-point bending tests

The mechanical properties were analyzed by four-point bending tests using specimens with a length of 70 mm and a cross-section of 5 mm × 5 mm. The testing method was based on DIN EN 53452 with a cross-head speed of 0.5 mm min^{-1}. The deflection of the specimens was measured by cross-head displacement and an extensometer.