



Formation of core (M_7C_3)-shell ($M_{23}C_6$) structured carbides in white cast irons: A thermo-kinetic analysis

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ABSTRACT

Core-shell structured carbides in white cast irons help reduce interfacial stress and failure, leading to higher resistance to wear. The present study is conducted to understand the mechanism for the formation of core-shell structured carbides in white cast irons through computational thermodynamics. In particular, efforts are made to determine the compositional ranges in which the core-shell structured carbides can form. Arrays of phase diagrams in stable and metastable equilibria were calculated to determine the stable regions of $M_{23}C_6$, M_7C_3 and Matrix, which are the basic phase assemblage for the core-shell morphology in high-Cr cast irons (HCCIs). Scheil-Gulliver and Lever-Rule solidifications were simulated for nine alloys with compositions selected from the stable/metastable regions to investigate the phase precipitation sequence, as-cast microstructures and compositions. The contour diagrams for the nucleation driving force were mapped and used to analyze the precipitating ability of each type and the configuration of carbide in its appropriate domains in casting during heat treatment. Thorough discussion is given to the effects of parent microstructure, temperature, and overall composition on the nucleation driving force for the $M_{23}C_6$ shell growth in order to guide fabrication of HCCIs with desired core-shell structured carbides.

1. Introduction

High-Chromium Cast Irons (HCCIs) have received great attention due to their high resistance to wear under different conditions encountered in various industrial sectors, e.g., cement manufacturing, mineral processing and slurry pumping [1–3]. Traditionally, chromium-base cast irons are classified into three groups in terms of the chromium content and applications in different technical areas: (1) the low-Cr irons with their Cr concentrations below 12 wt%, which are used for less severe wear situations, e.g., small grinding facilities; (2) the medium-Cr irons with their Cr concentration within 18–22 wt%, which are widely used as cost-effective materials to resist wear in many industrial applications; (3) HCCIs with their Cr concentration above 25 wt %, which are developed to provide resistance to wear and corrosive wear under very harsh working conditions such as wet grinding and

high-velocity slurry transport. The HCCIs widely used in the oil sands and mining industries are usually in the hypereutectic state with their carbon content in the range of 2.7 wt% C or higher. The excellent performance of HCCIs is attributed to the combination of hard carbides (e.g., M_7C_3 and $M_{23}C_6$) and relatively ductile ferrous matrix (martensite and/or austenite). The matrix benefits the absorption of impact energy and enhances the fracture toughness of the material, while the hard carbides play a crucial role in withstanding the wearing stress [4,5]. Although the individual phases may possess superior mechanical properties, the carbide/matrix interface strongly influences the overall performance of HCCIs. For instance, primary M_7C_3 carbides largely contribute to the high hardness of HCCIs but the lattice mismatch stress at the interface between the hard carbide and soft matrix may raise the probability of interfacial failure and thus lower the alloys' fracture toughness. It was recently noticed that core (M_7C_3)-shell ($M_{23}C_6$)

Abbreviations: CALPHAD, Computer Coupling of Phase Diagrams and Thermochemistry; HCCIs, High-Chromium Cast Irons; E, eutectic reaction; P, peritectic reaction; U, übergangsebene reaction; SEM, scanning electron microscopy; Microstructure, the solidification morphology of castings such as austenite dendrites (FCC) and eutectic austenite (partially transformed to martensite or ferrite) with interdendritic eutectic M_7C_3 carbide; Matrix, austenite (FCC)/ferrite (BCC)/martensite (BCT) that encompasses M_7C_3 in castings; The eutectic colony, the eutectic microstructure composed of Matrix and M_7C_3 ; MLE, Metastable Local Equilibrium characterizing the interface state of the eutectic colony; The dichotomy composition, roughly standing for the compositional gradient from the inner matrix to the matrix interface which simplifies the driving-force computations; Matrices, austenite/ferrite/martensite in various eutectic colonies (varying in composition) precipitated from the Scheil-Gulliver cooling

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structured carbides formed in HCCIs exhibited advantageous influence on their wear resistance. This influence is mainly contributed to the decrease in hardness from the hardest core (M_7C_3), through medium hard shell ($M_{23}C_6$), to the relatively softer ferrous matrix [6–12], which reduces the stress concentration at the carbide/matrix interface and consequently minimizes the risk of interfacial failure as demonstrated by an illustrative finite element analysis [7,8,13]. The effectiveness of the shell in reducing interfacial failure is affected by the shell thickness [13]. If the shell is sufficiently thick, the wear resistance would be decreased due to the decrease in hardness of the carbide as a reinforcement. It has been experimentally observed that the core-shell carbide morphology is not only limited to the combination of M_7C_3 (core) and $M_{23}C_6$ (shell) but also reflected by the assemblages of M_3C (shell)/ M_7C_3 (core) and $M_{23}C_6$ (shell)/ M_6C (core) [14,15]. Thus, it is of importance to identify the fabrication conditions to achieve suitable core-shell structures and determine their impact on the overall mechanical and tribological properties of HCCIs.

The above-mentioned studies reported in the literature show the benefits of core-shell carbides to the mechanical behavior and wear resistance of the alloys and material processing conditions, such as temperature and alloy composition, where the core-shell carbides form in the alloys [7–10,13–16]. However, to the authors' knowledge, there are no studies reported in the literature regarding the formation mechanism, which is of importance to identification and control of key process parameters for production the core-shell structured carbides during alloy processing. The main objectives of this study based on thermo-kinetic analysis are (1) to clarify the mechanism for the formation of core-shell combinations, and (2) to identify the composition range and conditions, with which the M_7C_3 (core)- $M_{23}C_6$ (shell) structured carbides could be produced. In this study, we also analyze the driving force, which is related to the formability of the core-shell structured carbides in a quantitative manner.

The thermo-kinetic analysis in this study was conducted within the framework of the CALPHAD method, in which thermodynamics and phase diagrams are combined to deal with multicomponent alloy systems. This research area has been very active over past 30 years and received increasing attention for applications in computational material processing, development of structure-property relationships, prediction of material properties, and material design [17]. The CALPHAD method requires not only computational skills but also extensive thermodynamic database and versatile solution models, such as the compound energy formalism [18,19]. In this work, the Pandat thermodynamic software developed by Chen [20–23] is employed, which can handle various types of phase equilibria and thermodynamic calculations involving stable/metastable phase diagrams, liquidus projections, solidification paths and contour properties. The Fe-Cr-C ternary system is constructed on the thermodynamic database with the optimized parameters reported by Khvan [24]. With the established Fe-Cr-C model system, thermo-kinetic analysis can be conducted to investigate the formation of the core-shell structured carbides in HCCIs that may contain minor impurities such as Si, Mn, Al and P etc. (less than 2 wt%). As long as the impurities have their concentration less than 2 wt%, the influence of the impurities on phase equilibria and thermodynamic properties is negligible.

This article reports results of our computational analysis on the formation of core-shell structured carbides in terms of the formation mechanism and conditions. The results would help guide determining the adequate composition ranges and processing conditions in order to obtain core-shell structured carbides in fabricated HCCIs. The article has five parts, among which the Sections 2–4 present or report equilibrium phase diagrams, solidification-path analysis and post heat treatments. The stable/metastable phase diagrams manifest possible regions with two variables, temperature and composition, for the formation of core-shell structured carbides. In the solidification-path analysis, the solidification processes were simulated under rapid cooling and Lever-Rule cooling conditions using Scheil-Gulliver and

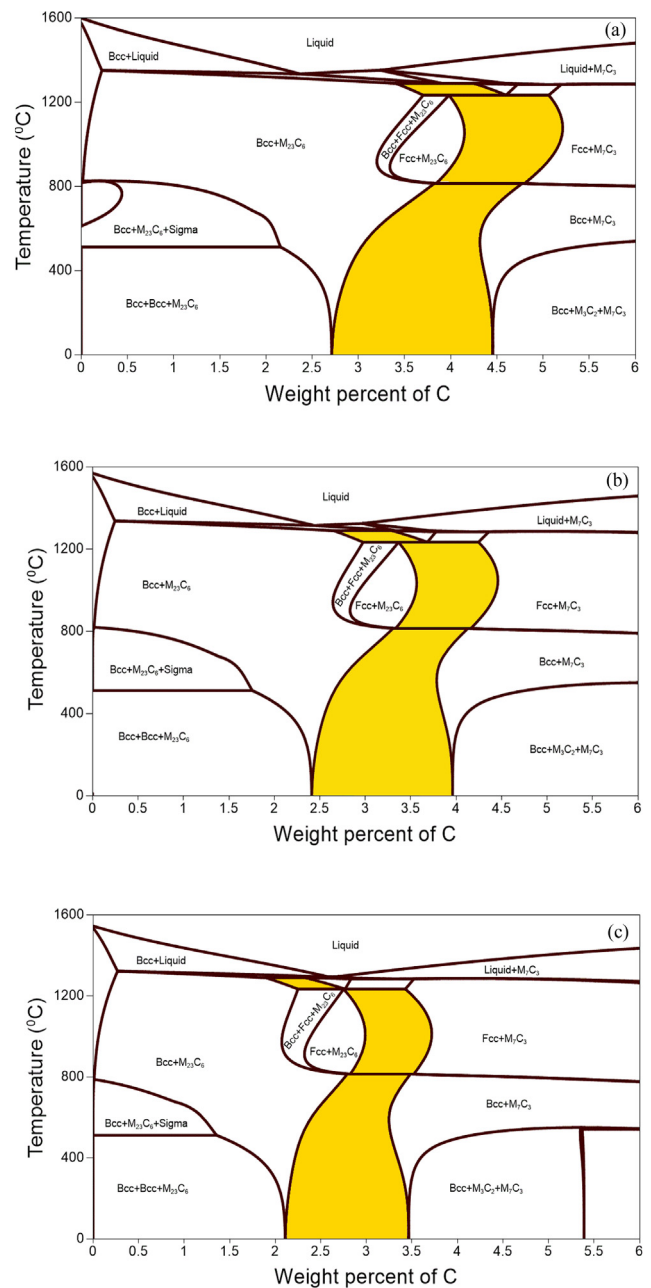


Fig. 1. The calculated stable phase diagrams for HCCIs in (a) 45%Cr; (b) 40%Cr; (c) 35%Cr; (d) 30%Cr; (e) 25%Cr; (f) 20%Cr; (g) 15%Cr; (h) 10%Cr; (i) 3D diagram; (j) enlarged 3D diagram for the ternary Matrix + M_7C_3 + $M_{23}C_6$ region. In figures (a)–(h), the regions in which M_7C_3 , $M_{23}C_6$ and Matrix co-exist are highlighted in yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Lever-Rule methods, respectively. Both of the methods may provide valuable information on the as-cast microstructures and corresponding microstructural composition distributions for the driving force calculation in post heat treatments. Post heat treatments for carbide precipitation are studied through analyzing driving forces for carbide nucleation in the inner matrix and at the eutectic M_7C_3 /Matrix interface; the former generates secondary carbides while the latter creates the core-shell structure. Background information is provided in Section 1. Conclusions are drawn and given in Section 5.

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