Effects of B on High-Temperature Mechanical Properties and Thermal Fatigue Performance of Hot Work Die Steel for Copper Alloy Die Casting Postprint

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Abstract

The high-temperature mechanical properties of copper alloy die-casting mold steel at 850 °C were investigated using a thermomechanical simulator. The thermal fatigue properties of the mold steel from room temperature to 800 °C were studied using the Uddeholm self-restraint method. The surface thermal fatigue cracks and the depth propagation state of cross-sectional cracks in the thermal fatigue specimens of the mold steel were examined using an optical stereomicroscope and SEM. The influence of B on the mechanical properties at room and elevated temperatures, as well as the thermal fatigue properties of the material, was analyzed. The results demonstrate that after B addition, B is distributed in the austenite matrix of the experimental steel in the form of M2B-type borides (where M represents Fe, Cr, or Mn), which effectively enhances the high-temperature mechanical properties of the material. Specifically, the material hardness increases from 200 HV to 302 HV, the tensile yield strength at 850 °C increases from 144.3 MPa to 190.3 MPa, and the compressive yield strength increases from 139.7 MPa to 167.9 MPa. The results of 300-cycle cyclic thermal fatigue tests from room temperature to 800 °C indicate that the thermal fatigue rating of the B-containing mold steel is grade 2–3, which is substantially superior to grade 7–8 of the comparative ESR-H13 steel subjected to electroslag remelting. The primary mechanism is that the borides can terminate thermal fatigue crack propagation or alter the crack propagation direction, thereby preventing thermal cracks from undergoing scattered diffusion.

Full Text

Preamble

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Effects of Boron on High-Temperature Mechanical Properties and Thermal Fatigue Behavior of Copper Alloy Die-Casting Die Steel

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Abstract

The high-temperature mechanical properties of copper alloy die-casting die steel at 850 °C were investigated using a thermomechanical simulator, while thermal fatigue behavior from room temperature to 800 °C was evaluated via the Uddeholm self-restraint method. Surface thermal fatigue cracks and their depth propagation profiles were examined using optical stereomicroscopy and scanning electron microscopy (SEM). The influence of boron on room-temperature and high-temperature mechanical properties, as well as thermal fatigue performance, was systematically analyzed. Results demonstrate that after boron addition, M_2B-type borides (where M represents Fe, Cr, or Mn) precipitate within the austenitic matrix, effectively enhancing high-temperature mechanical properties. Material hardness increased from 200 HV to 302 HV, tensile yield strength at 850 °C rose from 144.3 MPa to 190.3 MPa, and compressive yield strength improved from 139.7 MPa to 167.9 MPa. Following 300 thermal cycles between room temperature and 800 °C, the boron-containing die steel exhibited a thermal fatigue rating of 2–3, substantially superior to the 7–8 rating of the reference electroslag remelting (ESR) H13 steel. This improvement primarily stems from the ability of borides to arrest thermal fatigue crack propagation or deflect crack paths, thereby preventing the formation of scattered crack networks.

Keywords: B, die-casting die steel, thermal fatigue property, copper alloy, die-casting

Introduction

Die casting is widely employed for producing non-ferrous alloy components (Al, Zn, Mg, and Cu) due to its high efficiency, cost-effectiveness, and minimal machining requirements [1,2]. The die represents the most critical component in this process, experiencing instantaneous filling by high-temperature, high-pressure molten metal, followed by spray cooling and lubrication after component ejection. This repeated thermal cycling induces alternating compressive and tensile strains in the die surface layer, making it susceptible to thermal fatigue cracking and eventual failure [3–7].

In brass alloy die casting, molten copper temperatures can reach 970 °C with filling velocities up to 15 m/s, raising the die cavity surface temperature to 826 °C [8]. In contrast, aluminum alloy die casting typically employs pouring temperatures around 700 °C, keeping cavity surface temperatures below 580 °C [9]. Consequently, copper alloy die-casting dies operate under significantly more severe conditions, resulting in extremely short service lives [10–12]. Commonly used hot-work die steels for copper alloy die casting include 3Cr2W8V, H13, and QRO90, with H13 being the most prevalent [2,13–15]. However, these steels feature a martensitic matrix strengthened by precipitation of carbide-forming elements (Cr, Mo, V) through aging treatments. While such martensitic die steels perform adequately around 600 °C, they undergo martensite decomposition above 650 °C. The repeated heating and cooling cycles cause the dispersed carbide strengthening phases to coarsen progressively, accelerating die failure. Consequently, H13 and similar hot-work die steels exhibit substantially shorter lifetimes in copper alloy die casting compared to aluminum alloy applications [16,17].

Our research group has extensively investigated high-boron iron-based alloys [18–23], revealing that substituting Fe-C eutectic with Fe-B eutectic and replacing carbides with borides as strengthening phases can reduce carbon content while achieving a tough, ductile matrix. Boron exhibits extremely low solubility in Fe, while carbon is virtually insoluble in borides. Moreover, borides demonstrate exceptional thermal stability and resistance to coarsening during high-temperature tempering [24–28]. This study explores a novel copper alloy die-casting die steel design based on an austenitic matrix, where boron is added to form hard boride reinforcement phases rather than employing conventional carbide-forming elements like Mo and V. The effects of boron on the mechanical properties at both room and elevated temperatures, as well as thermal fatigue performance, are investigated.

1. Experimental Methods

To evaluate the influence of boron on high-temperature mechanical and thermal fatigue properties, two experimental steels were prepared: an austenitic base steel (3Cr10Mn7Ni6SiCu) and a boron-containing variant (3Cr10Mn7Ni6SiCuB0.7). Raw materials included electrolytic manganese, ferroboron, ferrosilicon, low-carbon ferrochrome, nickel plates, copper rods, carbon particles, and pure iron. The steels were melted in an induction furnace and poured into resin-bonded sand molds to produce Y-block castings (220 mm × 25 mm). All test specimens were sectioned from the Y-block at the 75 mm position using wire electrical discharge machining to eliminate size and cooling rate effects on microstructure and properties.

Given that the novel die steel relies on borides rather than precipitated carbides for strengthening, the heat treatment process is relatively simple. The sectioned blocks underwent diffusion annealing at 930 °C for 3 hours, followed by forging between 1150 °C and 950 °C with a forging ratio of 3, resulting in final dimensions of 270 mm × 72 mm × 22 mm. Test specimens were prepared directly from the as-forged material.

Chemical compositions were determined using a PDA-7000 direct-reading spectrometer, with boron content analyzed via inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are presented in Table 1 . The base steel 3Cr10Mn7Ni6SiCu utilizes economical Mn as an austenite stabilizer, providing a direct comparison with the boron-containing variant.

To ensure an austenitic solidification structure in 3Cr10Mn7Ni6SiCu, phase composition was simulated using JMatPro thermodynamic software. The simulation results, shown in Figure 1 [Figure 1: see original paper], confirm that the as-cast microstructure consists of austenite with minor carbides.

Room-temperature impact toughness was measured using a ZBC2302-2 impact tester at 18 °C with standard Charpy V-notch specimens (10 mm × 10 mm × 50 mm). High-temperature tensile and compressive properties were evaluated using a Gleeble-1500D thermomechanical simulator. Tensile specimens measured 6 mm in diameter and 120 mm in length, while compressive specimens were 8 mm in diameter and 12 mm in length. Tests were conducted at 850 °C after 1-minute holding at a loading rate of 0.1 mm/s.

Thermal fatigue testing employed the Uddeholm self-restraint method using specimens with dimensions shown in Figure 2 [Figure 2: see original paper]. Commercial ESR-H13 hot-work die steel (composition in Table 1) was tested concurrently for comparison. In industrial practice, copper alloy die-casting die life is primarily evaluated based on surface cracking severity and its impact on product quality. Therefore, thermal fatigue performance was assessed according to the Uddeholm rating system in GB/T 15824-2008. Testing involved 300 cycles between room temperature and 800 °C, with surface crack morphology examined using stereomicroscopy after acid etching. To investigate crack initiation and propagation mechanisms, specimens were sectioned using an SYJ-200 precision cutter.

Microstructural characterization included X-ray diffraction (XRD) analysis using a D/max-IIIA diffractometer (Cu $K\alpha_1$ radiation, 40 kV, 100 mA, 10°–100° continuous scan at 4°/min with 0.02° step size), optical microscopy (Neophot32 OM), and scanning electron microscopy (JSM-6460 SEM).

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2. Results and Discussion

2.1 Microstructure and Mechanical Properties

Figure 3 [Figure 3: see original paper] presents SEM micrographs and EDS spectra of the forged die steels. The 3Cr10Mn7Ni6SiCu steel exhibits a single-phase austenitic microstructure (Figure 3a) with relatively low hardness (200 HV) but exceptionally high room-temperature impact toughness (252 J). Boron addition to 3Cr10Mn7Ni6SiCuB0.7 introduces numerous borides distributed uniformly throughout the matrix (Figure 3b). These borides appear relatively rounded with a network-like distribution that is not fully continuous. The matrix remains dense, with borides primarily located along grain boundaries and fine dispersed precipitate particles visible in their vicinity. Alloy hardness increased substantially to 302 HV, while impact toughness decreased to 16 J. Thus, boron addition reduces room-temperature impact toughness but significantly improves the hardness of the austenitic steel. EDS analysis (Figures 3c and 3d) identifies the compound at point 1 as a boride and that at point 2 as a carbide.

High-temperature mechanical properties at 850 °C are summarized in Table 2 . The boron-containing 3Cr10Mn7Ni6SiCuB0.7 steel shows marked improvements in tensile strength (R), tensile yield strength ($R_{0\cdot 2}$), compressive strength (R c), and compressive yield strength ($R\ c_{0\cdot 2}$) compared to the boron-free base steel, with particularly significant enhancements in compressive properties. The yield strength increase is especially notable, raising the yield ratio of the austenitic experimental steel. Although elongation (A) and reduction of area (Z) decreased slightly, the more pronounced yield strength improvement minimizes any adverse effects on thermal fatigue performance. When Cr content exceeds 8%, borides transition from Fe_2B to $(Fe, Cr)_2B$ type, and increased Cr content in M_2B borides enhances both hardness and fracture toughness [31]. Consequently, 3Cr10Mn7Ni6SiCuB0.7 exhibits superior high-temperature mechanical properties compared to the boron-free austenitic steel.

2.2 Thermal Fatigue Performance

Surface crack morphologies after 300 thermal cycles between room temperature and 800 °C are shown in Figure 4 [Figure 4: see original paper]. The 3Cr10Mn7Ni6SiCu steel developed relatively uniform, interconnected network cracks (Figures 4a and 4b), corresponding to a thermal fatigue rating of 5–6 on the Uddeholm scale. In contrast, the boron-containing 3Cr10Mn7Ni6SiCuB0.7 steel exhibited fewer and finer surface cracks (Figures 4c and 4d), achieving a superior rating of 2–3. The ESR-H13 reference steel displayed wide surface cracks with dominant primary cracks showing interconnection tendencies (Figures 4e and 4f), resulting in a poor rating of 7–8. Clearly, the thermal fatigue resistance of ESR-H13 steel is inferior to both 3Cr10Mn7Ni6SiCu and 3Cr10Mn7Ni6SiCuB0.7 steels under these conditions.

Figure 5 [Figure 5: see original paper] illustrates crack depth propagation in 3Cr10Mn7Ni6SiCu steel. The arrows in Figures 5a–d indicate the direction of primary crack propagation perpendicular to the specimen surface toward the core. Figure 5a shows transverse branch cracks developing between two primary cracks, suggesting incipient structural damage in the branch crack region. Figure 5b depicts primary cracks with transverse branch crack initiation and growth. Figure 5c reveals branch crack formation at primary crack tips, with subsequent propagation toward the core. Figure 5d demonstrates multiple branch cracks radiating from a primary crack. Crack initiation occurs preferentially at grain boundaries, with propagation primarily perpendicular to the surface. The formation of new branch cracks during propagation indicates both intergranular and transgranular characteristics. In the boron-free 3Cr10Mn7Ni6SiCu steel, cracks initiate at the surface and propagate inward, generating branching cracks that radiate outward, thereby causing severe structural damage.

Figure 6 [Figure 6: see original paper] shows crack propagation behavior in 3Cr10Mn7Ni6SiCuB0.7 steel. After boron addition, thermal cracks still initiate at strain-concentrated grain boundaries and boride agglomerations, but their propagation is altered upon encountering borides. As indicated by arrows in Figure 6a, cracks are arrested when meeting borides. Figure 6b shows cracks deflecting around borides before continuing propagation. Figure 6c illustrates crack redirection and subsequent arrest after limited extension. Figure 6d depicts the widest primary crack at the specimen center, where the crack width indicates maximum thermal stress and damage severity. Borides distributed along this crack boundary effectively reinforce the matrix against through-cracking, functioning analogously to a “dam” for structural stabilization.

Figure 7 [Figure 7: see original paper] presents an optical micrograph of 3Cr10Mn7Ni6SiCuB0.7 steel after 300 thermal cycles. Ferrite appears as irregular blocks surrounding the borides, with thicknesses in the hundreds of nanometers. Previous studies [27] have observed ferrite precipitation around borides in boron-containing steels after prolonged high-temperature exposure or slow cooling, a phenomenon also reported in Guo's doctoral thesis [32].

Beyond boride formation, trace amounts of boron remain in solid solution within the matrix. Research [33–35] indicates two types of boron segregation at austenite grain boundaries: equilibrium and non-equilibrium segregation, which operate through different mechanisms and vary with external conditions. Equilibrium segregation depends primarily on heating temperature, whereas non-equilibrium segregation is highly sensitive to cooling rate. In 3Cr10Mn7Ni6SiCuB0.7 steel, the ferrite layers around borides result from equilibrium segregation. During high-temperature heating, the vacancy concentration in specimens becomes elevated. Rapid quenching during thermal fatigue testing creates supersaturated vacancies that migrate to and annihilate at grain boundaries. Strong interactions between boron atoms and vacancies cause some vacancies to complex with boron and migrate to grain boundaries, producing non-equilibrium segregation that intensifies with greater quenching temperature differentials [36]. With continued thermal cycling, solid-solution boron segregates non-equilibrium from grain interiors to boundaries, expelling carbon inward and forming narrow carbon-depleted ferrite layers around borides.

While thermal fatigue cracks typically initiate at boride-matrix interfaces due to mismatched thermal expansion coefficients, the presence of ductile, carbon-depleted ferrite layers surrounding borides during thermal fatigue testing absorbs thermal stresses and suppresses crack initiation and propagation at these interfaces [32]. The crack arrest and deflection observed upon encountering borides demonstrate their effectiveness in strengthening the matrix and resisting thermal fatigue crack growth. Borides possess significantly higher hardness and favorable fracture toughness compared to the austenitic matrix [31], which helps strengthen the microstructure and resist fatigue crack propagation. In contrast, ESR-H13 steel experiences continuous hardness degradation with increasing thermal cycles [37], leading to diminished thermal fatigue resistance and substantially poorer performance compared to 3Cr10Mn7Ni6SiCuB0.7 steel.

To verify microstructural stability before and after thermal fatigue testing, XRD analysis was performed on 3Cr10Mn7Ni6SiCuB0.7 steel (Figure 8 [Figure 8: see original paper]). The results confirm an austenitic matrix with M_2B borides (primarily $Fe_{1\cdot1}Cr_{0\cdot9}B_{0\cdot9}$) as the main strengthening phase. Due to the thin ferrite layers, only a weak ferrite peak at 44.43° was detected, which is not labeled in the figure due to its proximity to the boride peak. The microstructure remained essentially stable after thermal fatigue testing, with XRD patterns showing minimal changes. A slight variation at 44.09° after testing corresponds to minor carbide formation ($Cr_{22\cdot23}Fe_{0\cdot77}C_6$) during thermal cycling, as evidenced by the fine bright particles in the rectangular regions of Figures 6c and 6d. However, the carbide content is too low for distinct XRD detection. Thus, the microstructure exhibits remarkable stability during thermal fatigue testing, and boron addition helps maintain high thermal fatigue resistance and stable crack propagation resistance.

Boron exists primarily as stable M_2B borides in the steel, forming a network along grain boundaries in the as-cast condition [26,30]. After forging, the microstructure becomes dense with the boride network disrupted, while the austenitic matrix remains stable. Consequently, 3Cr10Mn7Ni6SiCuB0.7 steel achieves an excellent combination of toughness and strength. Comparative testing against ESR-H13 steel demonstrates superior high-temperature performance. The Cr content in 3Cr10Mn7Ni6SiCuB0.7 steel (9.86%) exceeds that of ESR-H13 steel (5%), improving oxidation resistance and hardenability [17]. Dispersed borides provide pinning and strengthening effects, and their superior thermal stability compared to carbides prevents coarsening during thermal fatigue, ensuring sustained and stable strengthening. The intimately bonded endogenous borides effectively block thermal fatigue crack propagation, making the boron-containing experimental steel significantly superior to ESR-H13 steel in high-temperature mechanical properties and thermal fatigue resistance, thus showing promise as a novel copper alloy die-casting die steel.

Conclusions

(1) Boron addition to 3Cr10Mn7Ni6SiCu austenitic base steel forms M_2B borides distributed within the austenitic matrix, increasing hardness from 200 HV to 302 HV, tensile yield strength at 850 °C from 144.3 MPa to 190.3 MPa, and compressive yield strength from 139.7 MPa to 167.9 MPa, thereby effectively improving high-temperature mechanical properties.

(2) The austenitic matrix and boride strengthening phase in 3Cr10Mn7Ni6SiCuB0.7 steel exhibit excellent stability, conferring superior thermal fatigue performance. After 300 thermal cycles between room temperature and 800 °C, the steel achieved a thermal fatigue rating of 2–3, substantially outperforming the reference ESR-H13 steel (rating 7–8).

(3) Borides effectively strengthen the austenitic matrix by arresting thermal fatigue crack propagation or deflecting crack paths, thereby preventing the formation of scattered crack networks.

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Note: Figure translations are in progress. See original paper for figures.