Effect of Carbon on Interfacial Reaction and Wettability between a Nickel-Based Superalloy and Ceramic Shell [Postprint]

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Abstract

The effects of carbon on the interfacial reactions and wettability between a superalloy and ceramic shell were investigated using the sessile drop method. The interfacial microstructure and morphology as well as elemental distribution in the reaction zone between the alloy and ceramic shell were studied by SEM and EPMA. The activities of carbon, chromium, and aluminum in the alloy melt were calculated using Thermo-Calc software, and the influence of carbon content on the activities of carbon, chromium, and aluminum in the alloy melt was analyzed. The relationship between the alloy/ceramic interfacial reaction and wettability was discussed. The results show that when the carbon content in the alloy exceeds 0.1%, the activity of carbon increases significantly, interfacial reaction occurs between the alloy melt and ceramic shell, the alloy melt/ceramic system transitions from non-reactive wetting to reactive wetting, a sand adhesion layer forms on the alloy surface, and chromium and aluminum from the alloy diffuse to the ceramic surface.

Full Text

Effect of Carbon on the Interfacial Reaction and Wettability Between a Nickel-Based Superalloy and Ceramic Mould

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Abstract

Superalloy components are always produced by investment casting. During investment casting, interfacial reactions may take place and bring about metal contamination and defect formation on the surface of the components. The influence of carbon content on the interfacial reaction and wettability between a Ni-based superalloy and ceramic mould was investigated using a sessile drop method. The interfacial morphology and element distribution were studied by SEM and EPMA. Activities of C, Cr and Al were calculated using Thermo-Calc software. The relationship between interfacial reaction and wettability was discussed. It was found that when carbon content was higher than 0.1%, the activity of carbon increased greatly and interfacial reaction took place. The wettability varied from non-reactive wetting to reactive wetting. In the reactive wetting systems, sand adhesions appeared and Al and Cr diffused to the ceramic surface.

Key words: superalloy, ceramic mould, interfacial reaction, wettability, activity, carbon

1. Introduction

With the continuous increase of turbine inlet temperature in aero-engines, the temperature-bearing capacity of turbine blades must be improved accordingly. Generally, there are three approaches to enhance blade performance: First, employing directional solidification to produce directionally solidified or single-crystal blades, which significantly improves alloy properties by eliminating transverse grain boundaries perpendicular to the stress axis [1–3]. Second, modifying alloy composition, such as increasing refractory element content (Ta, W, Mo, Re, etc.) to develop higher-performance alloys, as exemplified by second- and third-generation single-crystal superalloys characterized primarily by Re addition [4–7]. Third, improving blade cooling structure to enhance cooling efficiency [8–10]. Regardless of the technique employed, superalloy blade manufacturing relies on investment casting technology, which has become the primary method for producing superalloy blades.

During investment casting, the mould serves as a “container” filled with molten metal. Interfacial interactions between molten metal and mould involve thermo-mechanical penetration and thermo-physical-chemical effects, influencing both internal and external casting quality. For instance, molten alloy can erode the mould surface, destroying the bond between face-coat particles and back-coat particles, causing face-coat particles to enter the molten alloy and resulting in surface inclusion defects [11]. Additionally, significant stresses develop on the casting surface during solidification, and low-strength mould face-coats may detach and adhere to the casting surface, causing sand adhesion defects that range from surface roughness to formation of metal-sand mixtures firmly bonded to the casting surface, substantially increasing cleaning workload [12,13].

Typically, ceramic mould surfaces are not fully dense and contain numerous pores. The penetration of molten alloy into the ceramic mould is closely related to the wettability of the alloy/mould system, which is primarily determined by the chemical composition of both the molten alloy and ceramic mould. The wettability is expressed as follows (where $\gamma\{sv\}$, γ{sl}, and γ_{lv} represent solid-vapor, solid-liquid, and liquid-vapor interfacial energies, respectively; denotes the solid-liquid contact angle). A smaller indicates better wettability. Furthermore, mould surface roughness, pouring temperature, enrichment of active elements at the interface, and interfacial chemical reactions all affect wettability [14,15].

Carbon, as a trace element in superalloys, strengthens grain boundaries through segregation [16,17]. In single-crystal superalloys, carbon strengthens low-angle grain boundaries and reduces recrystallization tendency. Consequently, most single-crystal superalloys contain a certain amount of carbon. However, in high-temperature melts, carbon is a highly reactive element that cannot coexist with many ceramic oxides (such as Al_2O_3 and SiO_2) at elevated temperatures [18]. Previous research [19] has shown that carbon can react with ceramic moulds to generate CO gas bubbles, which become entrapped in the molten alloy and form pores 30–50 m in size near the casting surface after solidification. These pore defects promote fatigue crack propagation and reduce fatigue strength. Interfacial chemical reactions release heat, altering alloy melt/ceramic mould interfacial tension and affecting wettability. Moreover, formation of reaction products replaces the original interface with an alloy melt/reaction product interface, further changing interfacial tension and influencing wettability, thereby affecting sand adhesion defects. However, limited research has been reported on the effect of carbon content on interfacial reactions and wettability in superalloy melt/ceramic mould systems. Therefore, this study not only helps reveal the intrinsic relationship between interfacial reactions and wettability but also enables reduction of interfacial reactions and improvement of casting surface quality through reasonable control of trace carbon content, decreasing post-processing requirements.

This work employs the sessile drop method to investigate the effects of carbon content on interfacial reactions, wettability, and sand adhesion between a single-crystal superalloy melt and ceramic mould. By measuring contact angles, the influence of carbon content on wettability was examined. Through characterization and analysis of interfacial reaction products, the correlation between interfacial reactions and wettability in the superalloy melt/ceramic mould system was established.

2. Experimental

The base alloy was a Ni-based single-crystal superalloy containing 2% Re, with composition (mass fraction, %) of: Cr 4.37, Co 8.95, W 7.5, Mo 2.02, Al 5.72, Nb 1.05, Ta 6.7, Re 2.02, Ti 0.022, C 0.008, Hf 0.09, Ni balance. Different amounts of carbon were added to the base alloy (designated A1) to prepare five alloys with increased carbon content via medium-frequency induction remelting: A2 (0.01% C), A3 (0.05% C), A4 (0.1% C), A5 (0.2% C), and A6 (0.3% C). Alloy blocks 5 mm in length were cut by wire electrical discharge machining, surface traces were removed with sandpaper, and samples were ultrasonically cleaned in acetone. Ceramic substrates 20 mm × 20 mm × 6 mm were prepared using the investment casting mould fabrication process. The ceramic slurry for the face coat consisted of ceramic powder and silica sol, with ceramic powder composition of 95% Al_2O_3 + 5% SiO_2 (volume fraction) and SiO_2 content of 30% (mass fraction) in the silica sol. Ceramic substrates were ultrasonically cleaned in acetone before experiments.

The sessile drop method was used to study interfacial reactions and wettability of alloy melts on ceramic substrates. The experimental apparatus was a high-temperature wettability testing furnace, with schematic structure shown in [Figure 1: see original paper]. The ultrasonically cleaned ceramic substrate was placed on a high-purity Al_2O_3 sample support and leveled. The alloy to be melted was placed in a feed tube outside the vacuum chamber. After evacuating the system to 5×10^{-4} Pa, the furnace was heated to 1000 °C at 20 °C/min, then high-purity Ar (99.999%) was introduced at 5–10 L/min until the furnace pressure reached 1.2×10^5 Pa. Heating continued at 20 °C/min to 1550 °C. When temperature and pressure stabilized, the outlet and inlet valves were closed to maintain furnace pressure at 1.1×10^5–1.2×10^5 Pa. The alloy was dropped from the feed tube onto the ceramic substrate through an Al_2O_3 tube, while images were captured at up to 2 frames/s using a CCD digital camera with 1504 pixel × 1000 pixel resolution. The moment when the alloy completely melted into a sphere was defined as time zero ($t = 0$). Captured images were processed using axisymmetric drop shape analysis software (ADSA, SESDROPD, and FTA32) to determine contact angles. Some specimens were cold-mounted and sectioned longitudinally through their centers.

A JSM-6301F field emission scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) was used to examine ceramic surface and alloy/ceramic interfacial morphologies. Elemental distributions in the reaction zone were characterized using an EPMA-1610 electron probe microanalyzer (EPMA). Thermo-Calc software was employed to calculate activities of carbon, aluminum, and chromium in the alloys.

2. Experimental Results

[Figure 2: see original paper] shows the variation of contact angle with time for alloy melts with different carbon contents on ceramic substrates. The initial contact angle was 145° ± 3° for all carbon contents. For carbon contents of 0.008%, 0.01%, and 0.05%, the contact angle remained essentially constant at 145° ± 3° with increasing holding time, indicating non-reactive wetting. At 0.1% carbon, the contact angle rapidly decreased to 128° within the first 100 s, then slowly decreased to 115° and reached equilibrium after 700 s. For carbon contents of 0.2% and 0.3%, the contact angle decreased exponentially with holding time, reaching equilibrium values of 110° and 90°, respectively, demonstrating clear reactive wetting characteristics. Thus, the transition from non-reactive to reactive wetting occurred at 0.1% carbon content.

[Figure 3: see original paper] presents macrographs of alloy and ceramic surfaces after wetting experiments. For non-reactive wetting systems, both alloy and ceramic surfaces remained clean and uncontaminated. In reactive wetting systems, a purple ring-shaped region was visible on the ceramic surface. Microstructural analysis of the ceramic surface corresponding to the 0.2% carbon alloy (A5) revealed two distinct morphologies [Figure 4a: see original paper]. The light-colored region on the left represented the ceramic surface in contact with the alloy. Higher magnification observation of Area I in [Figure 4a: see original paper] showed that the ceramic surface in contact with the alloy was uneven, with non-uniformly distributed and partially detached ceramic face-coat particles [Figure 4b: see original paper]. The dark-colored region on the right corresponded to the purple ceramic surface area in [Figure 3: see original paper], with microstructure distinctly different from the light-colored region. High-magnification observation of Area II in [Figure 4a: see original paper] revealed numerous spherical products [Figure 4c: see original paper]. EDS analysis indicated these spheres were rich in Al and O with some Cr. EPMA elemental mapping of the ceramic surface also showed an Al- and Cr-rich ring-shaped region near the alloy/ceramic contact area [FIGURE:4d1–d4]. Since the ceramic itself is an oxide, O distribution showed no significant change. These results suggest that when alloy carbon content exceeds 0.1%, improved wettability causes ceramic face-coat detachment, and Al and Cr enrich on the ceramic surface near the alloy/ceramic contact region through some transport mechanism.

[Figure 5a: see original paper] and [Figure 5b: see original paper] show interfacial microstructures for non-reactive (0.05% C) and reactive (0.2% C) wetting systems, respectively. For the non-reactive system, the alloy/ceramic interface was flat without sand adhesion or reaction layers [Figure 5a: see original paper]. In contrast, the reactive system exhibited extensive mixing of ceramic face-coat material with alloy melt at the interface, forming a sand adhesion layer [Figure 5b: see original paper]. EPMA elemental mapping of the sand adhesion interface [FIGURE:5c1–c4] revealed that ceramic particles adhering to the alloy surface were Al_2O_3 with pores between particles. Chromium diffused into the ceramic face-coat, forming a Cr-containing diffusion zone 80 m thick. Although the ceramic face-coat contained SiO_2, EPMA analysis showed no distinct Si distribution.

3. Analysis and Discussion

Reactive wetting between alloy melt and ceramic mould requires carbon content to reach a critical concentration. Since wetting behavior changed significantly at 0.1% carbon and macroscopic appearance differed markedly from samples with lower carbon content, 0.1% is considered the critical concentration. When carbon content exceeds 0.1%, the system exhibits reactive wetting because chemical reactions must satisfy the thermodynamic condition of negative Gibbs free energy change. Gibbs free energy is a function of temperature, activity, and other parameters. Increasing carbon content may affect carbon activity, thereby altering the Gibbs free energy change. Possible reactions between carbon and ceramic mould materials Al_2O_3 and SiO_2 include [20]:

$3C + Al_2O_3 \rightarrow 2Al + 3CO(g)$
$C + SiO_2 \rightarrow SiO(g) + CO(g)$

Based on observation of alloy/ceramic interfacial microstructures and EPMA results, SiO_2 is identified as the primary ceramic component participating in the interfacial reaction. For reaction (2), the Gibbs free energy change ΔG can be expressed as:

$$\Delta G = \Delta G^\circ + RT \ln(P_{SiO} \cdot P_{CO} / (a_C \cdot P^{\circ 2}))$$

where ΔG° is the standard Gibbs free energy change; P_{SiO} and P_{CO} are partial pressures of SiO and CO gases; P° is standard atmospheric pressure; a_C is carbon activity in the alloy melt; R is the gas constant; and T is temperature. The standard Gibbs free energy change for reaction (2) is approximately 50.110 kJ/mol. Due to low carbon content in the alloy, SiO and CO gas pressures are low and difficult to measure, making accurate ΔG values challenging to determine. However, compared with P°, P_{SiO} and P_{CO} can be treated as small constants, making a_C the dominant factor influencing ΔG when carbon content increases. Thermo-Calc software was used to calculate carbon activities in alloys A1–A6 at 1550 °C, with results shown in . Carbon activity increased significantly with carbon content, suggesting that interfacial reaction occurs when carbon activity reaches 0.0026. The interfacial reaction reduces alloy melt/ceramic mould interfacial energy, thereby decreasing contact angle and improving wettability.

Wettability is closely related to sand adhesion defects, which can be classified as mechanical or chemical. Mechanical sand adhesion occurs when liquid metal penetrates mould surface pores, forming a mechanical mixture of metal and sand particles on the casting surface after solidification. Chemical sand adhesion involves formation of low-melting-point compounds through interaction between metal oxides and sand particles. Based on analysis of interfacial reaction products, the sand adhesion observed in this study at high carbon content is mechanical. The condition for mechanical sand adhesion is that alloy pressure P must exceed a critical pressure P__c, given by [21]:

P__c = P__g - (2γ__{lv} cos)/r

where P__g is gas pressure in ceramic face-coat pores, which hinders metal penetration; γ__{lv} is liquid metal surface tension; is the contact angle of alloy melt on the mould; and r is the pore radius of the ceramic face-coat. Generally, P__g is small and can be neglected [21]. Thus, when increased carbon content causes reactive wetting, the contact angle decreases, reducing P__c and promoting sand adhesion.

When carbon content exceeds 0.1%, distinct ring-shaped enrichment zones of Al and Cr appear on the ceramic surface near the alloy/ceramic contact region. Al and Cr may enrich on the ceramic surface through volatilization-deposition or diffusion. For volatilization, the vapor pressure P__i of element i in the alloy is determined by its activity a__i and the saturated vapor pressure P__i^0 of pure component i:

P__i = a__i P__i^0 = __i γ__i P__i^0

where __i is the mole fraction and γ__i is the activity coefficient of component i. According to thermodynamic theory, the saturated vapor pressure of pure component i at a given temperature follows:

log P__i^0 = A - B/T + C log T + D T

where A, B, C, and D are substance-specific constants available in thermodynamic data handbooks [22]. Using equation (6) and these constants, the saturated vapor pressures of pure Al and Cr at 1550 °C were calculated as 4.8 Pa and 0.14 Pa, respectively. Assuming Al and Cr enrich on the ceramic surface through volatilization-deposition, their vapor pressures should vary with carbon content. Thermo-Calc calculations of Al and Cr activities in alloys A1–A6 at 1550 °C () show that carbon content hardly affects Al and Cr activities. Therefore, vapor pressures of Al and Cr in alloys A1–A6 are essentially identical, and carbon content does not influence their volatilization behavior. Thus, Al and Cr enrichment does not occur via volatilization-deposition but more likely through diffusion. Literature [23] also indicates that certain elements in alloy melts can diffuse along solid surfaces to form ring-shaped diffusion zones. Since ceramic surfaces contain adsorbed oxygen and Al and Cr have strong affinity for oxygen, diffused Al and Cr readily form oxides on the ceramic surface. Studies [24] have reported that a purple-red substance forms on casting surfaces after superalloy pouring, identified as a solid solution of Cr_2O_3 and Al_2O_3. The purple material observed on ceramic surfaces near the alloy/ceramic contact region in this study is likely also a Cr_2O_3-Al_2O_3 solid solution.

4. Conclusions

(1) When carbon content is below 0.1%, the superalloy/ceramic mould system exhibits non-reactive wetting, with contact angle remaining essentially constant with holding time. The alloy melt does not penetrate the ceramic mould, and no sand adhesion forms on the alloy surface.

(2) When carbon content exceeds 0.1%, the superalloy/ceramic mould system exhibits reactive wetting, with contact angle decreasing over time. Mechanical sand adhesion defects form on the superalloy surface, requiring physical or chemical removal after casting.

(3) When carbon content exceeds 0.1%, Al and Cr enrich on the ceramic surface near the alloy/ceramic contact region through diffusion, forming a purple solid solution.

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