

Study on the Interfacial Reaction Mechanism Between Superalloy Melt and Alkaline Earth-Rare Earth Composite Oxide System

Shigang Fan ^{1,*}, Naicheng Sheng ¹, Chenyu Lin ^{1,2}, Shijie Sun ¹, Guichen Hou ¹, Jinjiang Yu ¹, Jinguo Li ¹, Yizhou Zhou ¹, Xiaofeng Sun ¹

1. Shi-Changxu Innovation Center for Advanced Materials, Institute of Metal Research, Chinese Academy of Sciences,

Shenyang 110016, China

2. School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China *Corresponding address: e-mail: sgfan@imr.ac.cn

Abstract: Superalloys are the most important materials for aeroengine hot section. The improvement of its trace element control level has always been a hot topic in the field. The precise control of sulfur (S) and rare earth (RE) elements, which are the most harmful and beneficial trace elements affecting the properties of superalloys, has been increasingly valued by the academic and engineering fields. The Alkaline earth-Rare earth ceramic system has the application prospects of both desulfurization and increasing rare earth elements. In this paper, the phase and element distribution of interfacial reaction products between MgO-Y₂O₃, CaO-Y₂O₃, MgO-CaO-Y₂O₃ ceramics and typical high activity superalloys were systematically studied by innovative experimental methods combined with XRD and SEM-EDS characterization methods. Furthermore, the reaction mechanism equations of different refractories and superalloy melts were summarized. The CaO-Y2O3 and MgO-CaO-Y₂O₃ systems have been confirmed to have the ability of desulfurization and rare earth addition by reacting with active elements such as Al in the melt. The interface reaction mechanism is revealed.

Keywords: Alkaline earth-Rare earth composite oxide; superalloy; interface reaction; ultra-low sulfur; rare earth addition

1 Introduction

Nickel based superalloys are the most important materials for the aeroengine hot section, and their usage in advanced turbine engines has exceeded 50%^[1,2]. With the background of its temperature bearing capacity approaching the theoretical upper limit, improving the purity of the melt and accurately controlling the content of trace beneficial elements are important means to maximize the alloy performance^[3,4].

Sulfur(S) has a significant impact on the elevated temperature service performance of casting superalloys and is recognized as one of the harmful elements. Smialek^[5,6] reported that S content in superalloy is less than 1ppm, and its oxidation resistance is greatly improved. Rare earth (RE) elements (La, Ce, Y, etc.) are recognized by researchers as the most significant beneficial trace elements affecting superalloys^[7]. The addition of a small amount of REs can

significantly improve the properties of superalloys^[7-8]. Alkaline earth-Rare earth oxide refractory materials can be used as a promising refractory system for superalloys melt in desulfurization and rare earth element control.

In this study, typical Alkaline earth-Rare earth oxide systems (MgO-Y₂O₃, CaO-Y₂O₃, MgO-CaO-Y₂O₃) are taken as the research object. The interface reaction behavior between highly active K417G superalloy melt and ceramics has been systematically studied. By analyzing the morphology, phase, and elemental composition of the reaction layer before and after the reaction, the interfacial reaction mechanism is revealed.

2 Experimental procedure

The immersion method was used to observe the interface reaction between ceramics and superalloys melt. The mixed Rare earth-Alkaline earth oxide was pressed into a rod shape (8 *10*100mm). According to specific heating gradients and insulation stages, the final product was kept at 1600 °C for 1 hour and cooled in the furnace to produce a dense ceramic rod. The ceramic samples were inserted into the alloy melt and held for 5 minutes before being directly taken out and cooled to room temperature for further characterization.

3 Result and discussion

The morphology and element distribution after the reaction at 1500 °C are shown in Figure 1. There are two continuous dense reaction layers with coexisting Ca and S, as well as coexisting Ca, Al, Y, and O (Figure 1 (a)). Further microscopic elemental analysis indicates the presence of a small amount of elongated channels of CaAlYO₄ composite oxide phase in the region dominated by solid CaS in the outer reaction layer. At the same time, there is a clear trend of internal infiltration in the oxide layer dominated by CaAlYO₄, which exists between unreacted CaO and Y₂O₃ particles (Figure 1 (b)).



Figure 1 SEM-EDS results of interface between CaO-Y2O3 ceramic and superalloys after 1500 ℃ reaction



Figure 2 Interfacial reaction mechanism between CaO-Y_2O_3 and superalloy melt

The interfacial reaction can be divided into four stages. The first stage is the contact between the high temperature alloy melt (containing Al and S elements) and the uniformly distributed dense CaO-Y₂O₃ ceramics. The second stage is the initial stage of the reaction. The reaction occurs in the area where the melt contacts with CaO and Y₂O₃ particles, and the reaction products are solid CaS and CaO-Al₂O₃- Y_2O_3 ternary oxides. The third stage is the development stage of the reaction. Subsequently, the two products generated in the second stage form a continuous reaction layer. With the progress of the reaction, the solid CaS accumulates and occupies most of the physical space in the external desulfurization reaction layer containing S. At the same time, in order to ensure the continuous reaction, the CaAlYO₄ composite oxide medium layer presents a network channel to ensure the transmission of Al and S in the melt and CaO and Y₂O₃ phases in the ceramics (Fig.2).

4 Conclusion

In this study, the interfacial reaction behavior between highly active K417G superalloy melt and CaO- Y_2O_3 ceramics was studied.

(1) By in situ reaction with superalloy melt, MgO-Y₂O₃ system has the ability of rare earth addition, CaO-Y₂O₃ and CaO-MgO-Y₂O₃ systems have the ability of both desulfurization and rare earth addition.

(2) The interface reaction occurs between CaO-Y₂O₃ ceramics and Al, S elements in the superalloy melt. The reaction equation is CaO-Al₂O₃+[Al]+[S] \rightarrow CaS+ xCaO·yAl₂O₃·zY₂O₃ + [Y];

(3) CaO·Al₂O₃·Y₂O₃ multi-oxides play a decisive role as the interface reaction of the medium layer. The internal CaO, Y₂O₃ and Al, S in the melt maintain the continuity of the interfacial reaction through its transport channel.

5 Acknowledgments (Bold, 10 pt., Arial)

This work was financially supported by the National Key R&D Program of China (No. 2022YFB3708100) and the National Natural Science Foundation of China (Nos. 52104352 and U2341267), and the National Natural Science Foundation of Liaoning province (No 2023-MS-015).

References

- Tang Y T, Panwisawas C and Ghoussoub J N. Alloys-bydesign: Application to new superalloys for additive manufacturing. Acta Mater, 2021, 202: 417-436.
- [2] Xu H, Zhang Y and Fu H. Effects of boron or carbon on solidification behavior of Co-Ni-Al-W-based superalloys, J. Alloy. Compd, 2022,891: 161965.
- [3] Petrushin N V, Elyutin E S and Visik E M. Development of a Single- Crystal Fifth-Generation Nickel Superalloy, Russian Metall. Metally, 2017,2017: 936 -947.
- [4] Reed R C. The Superalloys: Fundamentals and Applications, New York, 2006 :1-5.
- [5] Smialek JL, Jayne DT and Schaeffer JC. Effects of hydrogen annealing, sulfur segregation and diffusion on the cyclic oxidation resistance of superalloys: a review. Thin Solid Films, 1994, 253(1): 285-92.
- [6] Smialek J. Origins of a low-sulfur superalloy Al2O3 scale adhesion map. Crystals. Crystals, 2021, 11(1):60.
- [7] Zhou P J, Yu J J and Sun X F. Influence of Y on stress rupture property of a Ni-based superalloy. Mater. Sci. Eng., 2012, A551: 236.
- [8] Wang R M, Song Y G and Han Y F. Effect of rare earth on the microstructures and properties of a low expansion superalloy. J. Alloys Compd., 2000, 311: 60.