Research Progress of the Effects of Trace S Element on the Microstructure of Cast Nickel-base Superalloys

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Abstract. In the process of alloy melting and vacuum pouring, the impurity S element will inevitably be introduced into the nickel-base superalloys, which will cause adverse effects on the microstructure and properties of the cast nickel-base superalloys. In this paper, the research progress of S element in cast nickel-base superalloys is summarized. The effects of S element on the microstructure are described in detail from experimental researches and first-principles. The reasons for the grain boundary embrittlement caused by S atom are discussed, and the authors wish to provide some references for the better development of cast nickel-base superalloys.

1 Introduction

The development of new generation of aero-engines with high thrust-weight ratio requires hot components with higher properties. Nickel-base superalloys are widely used in hot components such as aero-engine blade due to their excellent high temperature mechanical properties. As we know, it is inevitable to introduce impurity elements into superalloy during melting and vacuum pouring. Although the content of these impurity elements is low, they can still have an adverse effect on the high temperature performance, thereby deteriorating the service performance of the hot components. Therefore, purity is one of the important indicators to measure the manufacturing level of superalloys. With the increasing requirements for the service performance of superalloy components, the content of impurity elements, especially S element, is strictly controlled at home and abroad. For example, the content of S in the second generation single crystal alloy CMSX-4 produced by Cannon-Muskegon is controlled within 2 ppm, the S content of the third generation single crystal alloy CMSX-4 Plus is controlled within 0.5 ppm [1]. After the S content is strictly controlled, the oxidation resistance and thermal corrosion resistance of the alloys can be improved obviously [1].

In this paper, the research progress of S element on the microstructure of cast nickel-base

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superalloy in recent years is summarized from experimental researches and first-principles calculation, and the reason of grain boundary embrittlement caused by S element is discussed. The authors wish to reveal the key mechanism of S element, optimize the control methods of S content, and provide reference for realizing the comprehensive balance of cost and performance in key components.

2 Effect of s element on microstructure of nickel-base superalloys

S element is one of the most common harmful impurity elements in superalloys, and its content is always controlled strictly. This is because S element is generally considered to segregate at grain boundaries or phase boundaries, thus weakening the strength of grain boundaries and phase boundaries and making them easier to become channels for crack initiation and propagation. As early as the 1970s, some researchers studied the segregation behavior of S element in superalloys. For example, Walsh et al. [2] studied the element distribution characteristics of a series of traditional cast and directionally solidified superalloys. Auger electron spectroscopy (AES) showed that S element mainly segregated at the grain boundary. Xie et al. [3] also studied the segregation behavior of S element in IN718 alloy by AES, and found that S element is easy to segregate at the interface between carbide and matrix. In recent years, with the continuous progress of computational materials science and material analysis methods, first-principles, synchrotron radiation, three-dimensional atomic probe and other methods have been used to analyze and calculate the occupation and segregation behavior of S element more accurately.

The emergence of first-principles calculation based on density functional theory has greatly facilitated the researchers to explore the rules of S atom occupying different positions in nickel-base superalloys. Dmytro et al. [4] found that S atoms in Ni matrix are more prone to substitution doping than interstitial doping, because when S atom replaces Ni atom, there is a strong interaction between S atoms and the nearest vacancies, which increases the stability of the structure. Dong et al. [5] investigated the S-doping at octahedral site in detail, and they found that the binding energy of the system in this case was greater than 0, which proved that the system was highly unstable, and the binding energy gradually increased with the increase of S atoms in the Ni matrix. That is, the stability of Ni matrix will become worse with the increase of S content.

In nickel-base superalloys, S atoms in the Ni matrix tend to gather at the interface, such as grain boundary, phase boundary and surface. Peng et al. [6] studied the occupation of S atom at the Ni/Ni3Al interface in detail through first-principles. As shown in figure 1, the S atom at the Ni/Ni3Al interface will give the highest priority to replace Ni-2, followed by the Ni-1 site. Han et al. [7] found that the content of the S atom at the grain boundary increased with the aging temperature increasing and finally reached the peak value. However, Masatake et al. [8] used McLean's equation to calculate the concentration of S atoms in the Ni $\sum 5$ (012) [100] grain boundary model (figure 2(a)) under different temperatures and different S concentration, and the calculated results (figure 2(c)) were consistent with the experimental results. In addition, Masatake et al. calculated the segregation energy of S atoms from grain boundaries to different positions on the surface respectively, and the results were shown in figure 2(b). As can be seen from figure 2(b), in terms of grain boundary, S atom occupies the O-interstitial position or replaces Ni-2 atom in the first place. However, as a whole, S atom has more negative segregation energy near the surface, which indicates that S atom has the greatest tendency to occupy the surface to achieve the optimal microstructure stability.

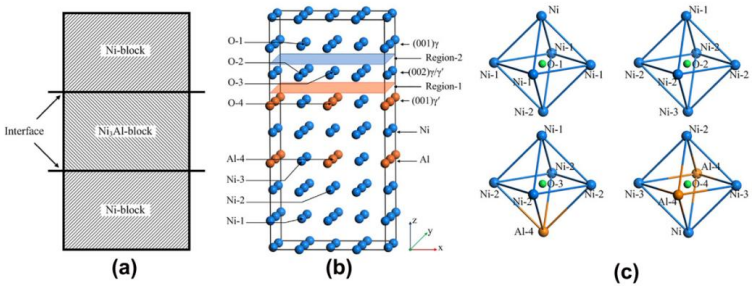

Fig.1. Ni/Ni3Al phase interface model and occupation site of S atom [6]

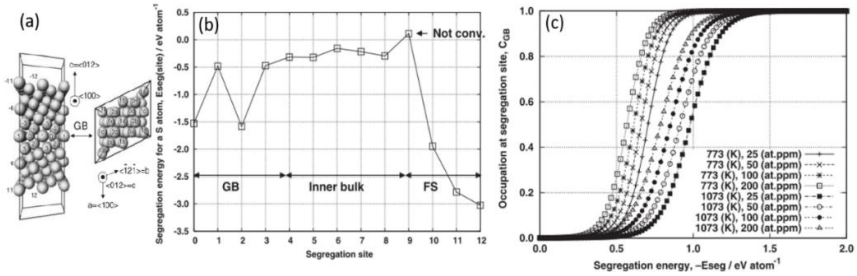

Fig. 2. The segregation of S atoms at Ni inner grain, grain boundary (Ni ∑5 (012) [100]) and surface [8] (a) grain boundary model of Ni ∑5 (012) [100], (b) segregation energy corresponding to S atoms at different positions in grain boundary of Ni ∑5 (012) [100], (c) plots of McLean' s equation for some segregation conditions (ageing temperature and bulk impurity concentration).

The S element can be combined with other elements in the alloy after segregation. For example, S element can combine with Ni to form Ni-Ni3S2 eutectic structure, or combine with Ti to form sulfide M2SC, i.e. Y phase. Y phase is a kind of harmful phase in nickel-base superalloys. Cracks tend to initiate and propagate along the edge of Y phase, thus reducing the toughness of the alloy. At the same time, the micro solution of S element at the grain boundary can cause the micro-hardening near the grain boundary, which is more harmful to the grain boundary [9]. However, some elements can reduce the bad effect of S element by combining with it. Chen et al. [10] found that when S atom and Re atom coexist at the Ni/Ni3Al interface, a strong covalent bond is formed between them, thus enhancing the bonding strength of the interface. Yong et al. [11] also found that Hf atoms tend to approach S atoms in nickel-base grains, and strong covalent bonds can be formed between them, as shown in figure 3. Therefore, Hf doping can reduce the tendency of S atoms to segregate towards the interface.

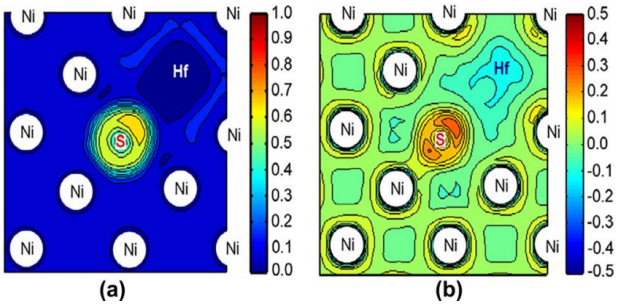

Fig. 3. Interactions between S and Hf in Ni matrix characterized by various charge analysis [11] (a) the contour plot of electron localization function of the interaction between S and Hf in Ni matrix; (b) the differential charge densities of the interaction between S and Hf in Ni matrix.

S element can also reduce the final solidification temperature of nickel-base superalloy, resulting in the increase of the solidification temperature range of the alloy, thus promoting the segregation of element Nb in K4169 alloy, resulting in the precipitation of Nb-rich Laves phase. Laves phase not only consumes the strengthening Nb element and reduces the strength of the superalloy, but also significantly reduces the stress rupture life and ductility of the alloy [12]. S element can also change the distance of the dislocation network. Studying the effect of S on TMS-1700 alloy, Joh et al. [13] found that with the increase of S content, the raft structure gradually coarsens, As shown in figure 4, the distance of dislocation networks between the γ/γ′ interface becomes larger.

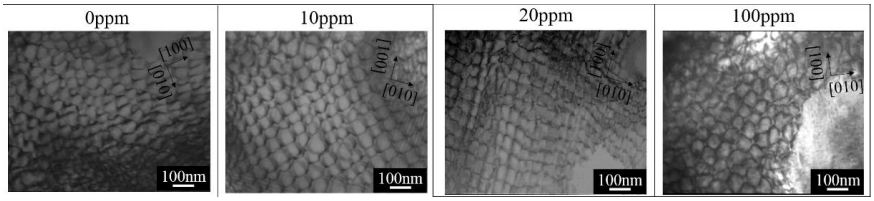

Fig.4. Dislocation network configuration of nickel-base superalloy containing 0 ppm, 10 ppm, 20 ppm and 100 ppm S element after creep test [13]

3 S-induced embrittlement mechanism of grain boundary

S-induced embrittlement mechanism of grain boundary in nickel-based superalloys is a classic problem that has puzzled the materials researchers for nearly a century, and some researchers have conducted a lot of researches on this problem. Based on first-principles, Li et al. [14] found that five impurity atoms, S, P, H, O and N, have different effects on different slip systems in Ni matrix using Rice-Wang model. These impurity atoms all increase the unstable and intrinsic stacking fault energies of <110>{111} slip system in Ni matrix, thus inhibiting the slip and plastic deformation of dislocation in <110>{111} slip system to a certain extent, while leading to the opposite result for Ni<112>{111}. Considering the effect of the two slip systems on the plastic deformation, they finally concluded that the impurity atoms S, P, H, O and N would not change the essence of the plastic deformation caused by partial dislocation slip in the Ni matrix, and the doping of S atoms in the Ni matrix would not damage the toughness of the alloy. However, Georg et al. [15] further compared the energy changes of each slip system after the addition of S atoms at different concentrations in Ni grain boundaries, and found that the energy required for intergrain debonding of ideal Ni crystals decreased by 7%-31% after the introduction of S element at grain boundaries.

Many researchers speculate the S-induced embrittlement mechanism from the perspective of electron. They believe that the reason leading to grain boundary embrittlement is that the S atom at the grain boundary changes the electron distribution state of the matrix atoms at the grain boundary. Although a strong covalent bond is formed between S atom and the nearest neighbor Ni atom, the strength of Ni-Ni bond perpendicular to the grain boundary is also greatly reduced, resulting in the weakening of the force between atomic layers perpendicular to the grain boundary, which leads to brittleness and reduces the bond strength of grain boundary by an order of magnitude [8, 16, 17]. However, when Masatake et al. [18] studied the relationship between the concentration of S atom and the tensile strength of grain boundary, they found that the above prediction could not explain the critical concentration of S atom, so Masatake et al. made a speculation: There is a short-range overlap between the adjacent S atoms, which makes the adjacent S atoms repel each other. The length of S-S bond is larger than that of Ni-Ni bond, so it will cause grain boundary expansion, as shown in figure 5, which will lead to grain boundary embrittlement and debonding, and reduce the

tensile strength of grain boundary. Kart et al. [19] further confirmed this speculation. Based on previous studies on charge density at Ni grain boundaries, the authors investigated the charge transfer of S atom doping in γ′-Ni3Al intrinsic stacking fault model by using first-principles. The isosurfaces of bonding charge density of stacking faults in Ni3Al doped S atom at the octahedral site of fault layers (S-0) and the first, second, third, and fourth nearest octahedral sites (S-1/2/3/4) are shown in figure 6. It can be seen from figure 6 that when S atom is doped in the non stacking fault region, S atom tends to form a strong covalent bond with the neighboring Al atom, while in the stacking fault region, S atom has the strongest bond with the nearest Ni atom. But on the whole, S atom makes a strong charge aggregation near its neighboring atoms.

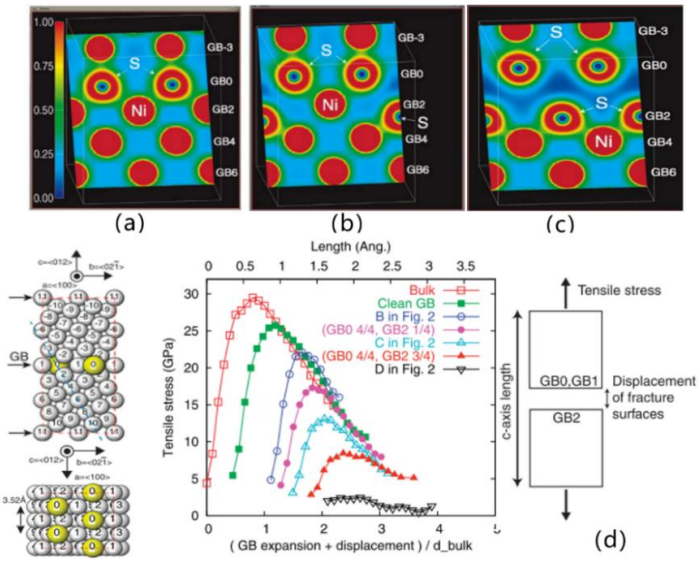

Fig. 5. The changes of electronic structure and tensile stress caused by different numbers of S atoms in the Ni ∑5 (012) grain boundary [18] (a) the differential charge density of four S atoms at GB0 sites; (b) four S atoms at GB0 sites and two S atoms at GB2 sites; (c) four S atoms at GB0 sites and GB2 sites respectively; (d) tensile tests calculated from first principles on the Ni ∑5 (012) grain boundary model with different number of S atoms

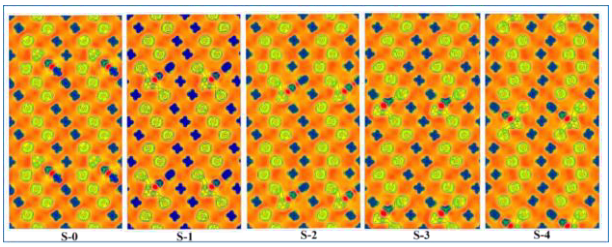

Fig. 6. The isosurfaces of bonding charge density of stacking faults in Ni3Al doped S atom at the octahedral site of fault layers (S-0) and the first, second, third, and fourth nearest octahedral sites (S-1/2/3/4)

The researchers also try to explain the grain boundary embrittlement using grain boundary embrittlement energy. The researchers believe that the total grain boundary embrittlement energy can be divided into two parts: the mechanical part and chemical part. The contribution of mechanical part to the total grain boundary embrittlement energy is always positive, which promotes the degree of grain boundary embrittlement, while the

contribution of chemical part caused by the change of electronic structure is positive or negative. For S atom (as shown in figure 7), the energy of these two parts is both positive, resulting in severe grain boundary embrittlement [20]. Vsianska [21] studied the changes of atomic magnetism at Ni∑5 (210) grain boundary and (210) free surface caused by the addition of various sp-type impurity atoms. Many impurities, including S element, could significantly reduce the magnetism of atoms at grain boundary or several layers of atoms near the surface, or even made it zero. It can be explained that there is strong hybridization between sp-impurity and Ni-d. In addition, there are other theories that the grain boundary embrittlement is caused by the amorphous Ni interface induced by S atom [22]. The researchers studied the actual grain boundaries in S-doping nickel polycrystals through experiments and found that the ordered and disordered interfaces alternately formed amorphous and double-layered facets at the grain boundaries. These two kinds of structure were arranged on the two opposite directions [23], the bipolar interface structure leaded to the intergranular brittle fracture between the S-Ni, as shown in figure 8.

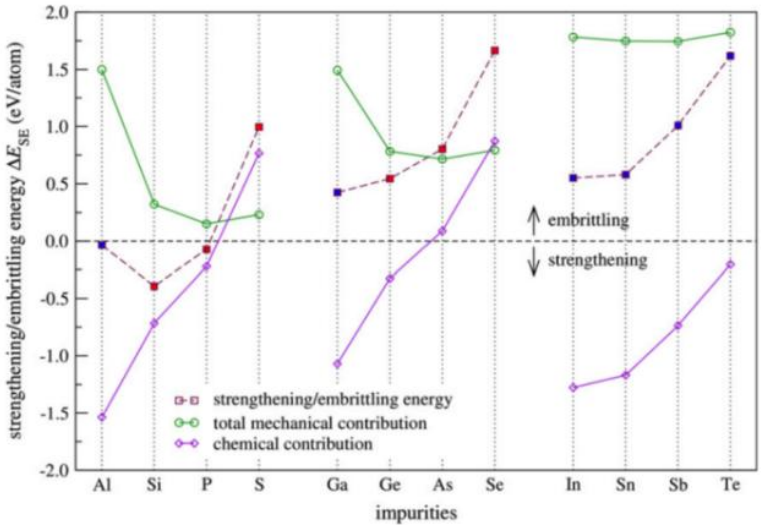

Fig.7. Variations of the mechanical and chemical energy caused by the segregations of different impurities at the grain boundary of Ni [20]

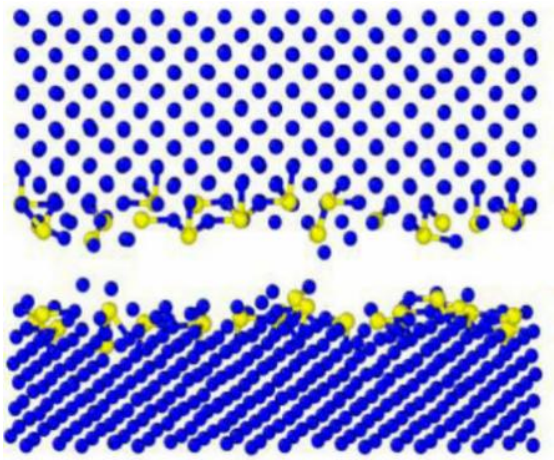

Fig. 8. Diagram of brittle intergranular fracture caused by bipolar interface structure [23]

4 Conclusion

In order to develop aeroengines with high performance, the influence of impurity elements on engine components has attracted more and more attention of researchers. For over a hundred years, vast researches of S element on microstructure of nickel-base superalloys have been carried out. At home and abroad, the content of S element in nickel-base superalloys has been strictly controlled, but the control of S at ppm level will cause the multiplication of the manufacturing cost in aeroengines. In the future, the cost of removing impurity elements will be reduced by optimizing the alloy smelting and casting process. Applying targeted experimental design, the key mechanism of S element affecting the microstructure and properties of nickel-base superalloys will be revealed, and the economical methods of controlling S element will be carried out to achieve the comprehensive balance between the cost and performance. And the mechanism will give important guiding significance for the formulation of standards with scientific significance and economic value.

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