Electric field treatment was performed on a Ni-Cr-W-Mo superalloy to investigate the effects of electric field treatment on its corrosion behavior. The microstructure evolution and the elements distribution at grain boundaries of both annealing twins and high angle grains were examined. The results show that the corrosion resistance can be improved by the electric field treatment and both of the corrosion weight loss and corrosion rate are decreased with the increasing treating time. When the alloy is electric field treated at 1093 K for 600 min with 4 kV-cm\(^{-1}\), the intergranular corrosion rate is 65.3 mm/y with the decreasing ratio of 57.9% compared with the untreated one, and the immersion corrosion rate is 3.9 mm/y with the decreasing ratio of 25.1% compared with the untreated one. The redistribution of elements between the original high angle grain boundaries and the annealing twins occurred by the formation and growth of the annealing twins during the electric field treatment, as well as the improvement of exhaustion of Cr and Mo elements at the grain boundaries. With the increasing treating time, a large amount of original high angle grain boundaries are replaced and the continuously distributed original grain boundaries are separated, which leads to the retardation the growth rate of the corrosion ditches. The corrosion resistance of the alloy is improved due to the changes of corrosion behavior of the grain boundary. Moreover, the promotion effect of electric field treatment on the atom diffusion rate decrease the exhaustion tendency of Cr and Mo elements on both sides of normal high angle grain boundary. Those can be considered as the reasons of improving the corrosion resistance after electric field treatment.

1. Introduction

With the rapid development of the aerospace engineering, the alloying elements ratio of superalloy is increased to meet the demands for long-term service at elevated temperatures. Besides the excellent properties including the high-temperature strength and plasticity, the oxidation existence, high-temperature corrosion resistance and irradiation resistance of the alloy are also required.\(^1\)\(^-\)\(^3\) The distribution and size of carbides at grain boundaries increase especially when the alloy was experienced long-term service. It is easy for the intergranular rupture to occur at the grain boundary under corrosive environment. Researches on nickel-base Ni-Cr-W-Mo and GH4586A superalloys after electric field treatment reveal that annealing twins occurred in alloys and the number of annealing twins increase with the increasing treated time. During the deformation, the crack propagation direction changes with the annealing twins, and this leads the increase of both the uniformity and work of plastic deformation. The plasticity can be improved greatly without strength changing.\(^4\)\(^-\)\(^7\)

The coherent twin boundary with low energy can be caused with electric field treatment on nickel-base superalloys and the fraction of low energy boundary can be increased. This agrees with the Grain Boundary Design and Control-Grain Boundary Engineering (GBE)\(^8\)\(^-\)\(^12\). It aims at preventing the intergranular rupture and intergranular corrosion by obtaining low energy and coherent boundary with high fraction in polycrystalline. As conventional GBE techniques, such as deformation heat treatments including strain recrystallization and strain heat treatment can be used to increase the fraction of coherent grain boundary in austenite steel, nickel-base alloy, copper and aluminum alloys. In other words, it can be considered that the electric field treatment will become one of the GBE techniques for obtaining high fraction of coherent grain boundary with low energy.

In the present study, the electric field was employed on a nickel-based Ni-Cr-W-Mo superalloy to investigate the effects of electric field on its corrosion resistance. The mechanisms were also discussed. The present work aims to study potential application for electric field treatment on the progress of research on superalloys.

2. Material and Experimental Procedures

The material used for the present study is a nickel-based Ni-Cr-W-Mo superalloy, the chemical composition (mass%) of the alloy is: C 0.0038, W 9.99, Mo 5.12, Al 2.18, Ti 1.29, Cr 19.97 and Ni 61.24. The alloy was double-vacuum induction melted into \(\Phi\)250 mm ingot, forged into 70 mm \(\times\) 180 mm plate and rolled into thickness of 1 mm plate. The alloy was machined into the corrosion test specimens with dimension of 30 mm \(\times\) 20 mm \(\times\) 1 mm and solution treated at 1423 K for 20 min with water quenching.

The electric field treatments were carried out in a quartz tube with heat equipment and \(N_2\) gas, where the specimen and a stainless steel sheet were set up to the anode and the cathode of the electrical source, respectively, and a 95% \(Al_2O_3\) ceramic board was used as the insulation between the anode and cathode. The specimen and stainless steel sheet were put parallel. The specimens were electric field treated at 1093 K with intensity of 4 kV-cm\(^{-1}\) for 0 min, 120 min, 300 min and 600 min (after sensitization at 1073 K for 6000 min AC), respectively, with water quenching. For comparing, aging treatment was also carried out for the specimens without electric field.

Intergranular corrosion test was carried out based on national standard of GB/T 15260-94. The corrosive agent is 25% HCl and 75% \(H_2O\) boiling solution. Immersion
corrosion test was carried out according to GB 10124-88 national standard and corrosive agent is CuCl\textsubscript{2} (25 g), HCl (500 ml) and C\textsubscript{2}H\textsubscript{5}OH (500 ml) at room temperature (298 K). Intergranular and immersion corrosion duration are 600 min and 1440 min, respectively.

The microstructure evolution, morphology of the annealing twins and the appearance of corrosive surface and cross-section were examined by the optical microscope (OLYMPUS GX71), scanning electron microscope (Shimadzu, SSX505) and transmission electron microscope (TECNAI G\textsuperscript{2}). The element distribution at grain boundaries was examined using electron probe micro analyzer (Shimadzu 1610).

3. Experimental Results

3.1 Effects of electric field on corrosion resistance of the alloy

The changes of corrosion behavior of the tested alloy with the electric field treated time are shown in Fig. 1. It can be seen that the weight loss of both intergranular and immersion corrosion are decreased. After electric field treatment for 600 min, the intergranular corrosion rate decreased from 87.1 to 65.3 mm\textsuperscript{-1}y\textsuperscript{-1} with the decreasing ratio of 25.1% and the immersion corrosion rate decreased from 9.3 to 3.9 mm\textsuperscript{-1}y\textsuperscript{-1} with the decreasing ratio of 57.9%.

The decrease of weight loss of the alloy is fastest when it is electric field treated for 120 min. With the increasing treatment time, the weight loss sequentially decreases, but change rate decreases. The weight loss for intergranular corrosion of the alloy is almost stable when the electric field treated time is longer than 300 min, while the immersion corrosion rate is sequentially decreasing.

As the aging time increases, the change of corrosion rate of the aging specimens without electric field treatment is not so much as that with the electric field treated specimens at 1093 K for the same time. It indicates that the improvement of corrosion resistance with electric field treatment is not influenced by aging treatment.

3.2 Microstructure evolution of the alloy after electric field treatment

Figure 2 shows microstructure evolution of the alloy before and after the electric field treatment. After electric treatment, the annealing twins occurred, and the number of annealing twins increased with the increasing of treated time. While, when the treated time was longer than 300 min, the number of the twins has no obvious change. The change of the grain size and morphology of precipitation before and after electric field treatment was not observed.

3.3 Effects of electric field treatment on corrosion behavior of the alloy

Figure 3 shows the change of intergranular corrosion surface morphology of the alloy with electric field treated time. The corrosion surface of the alloy is typical intergranular corrosion morphology. There are carbides networks at the grain boundary on the corrosion surface of the alloy. Corrosion ditches appear on both sides of the carbides on the grain boundary. At the same time, corrosion also occurred at the $\gamma/\gamma'$ interface and the interface between carbides and matrix. They are not simple intergranular corrosion. With electric field treatment, both the corrosion surface roughness and the width of the corrosion ditch of the alloys are decreased.

Figure 4 shows the change of corrosion surface morphology of the alloy after immersion corrosion test with the electric field treated time. The obvious changing of surface roughness can not be examined after immersion corrosion, however, the corrosion at the grain boundary has been improved and the shallow corrosion ditches in the alloy almost disappeared after electric field treatment.

4. Discussions

The testing alloy is a wrought nickel-base superalloy with the matrix of FCC-structured austenite. The twinning easy occurs in the alloy due to the low stacking fault energy of austenite. During the electric field treatment, the alloy is in the electric potential field with high energy, so that the defects of vacancies and dislocations are in high energy situation. It leads the defects to be unstable and easy for the defects to remove to grain boundary and crystal surface or react to form stack fault. Moreover, the electric field increases the atoms (especially for the alloying elements, such as Cr and Mo etc.) energy level and accelerates the diffusion rate of atoms. The stack fault formed due to the movement of vacancies and atoms. On the other hand, the
Stack fault exists stably to become the crystal nuclei of twins, because interfacial energy of coherent grain boundary of twins is less than that of high angle grain boundary. With the increasing electric field treated time under certain temperature and intensity of the electric field, a large number of annealing twin formed.
Based on the above results, it seems that the reducing corrosion rate of the alloy with electric field treatment and the improvement of the corrosion resistance relations to the appearance of the annealing twins. Figure 5 shows the cross-sectional morphology of the alloy after intergranular corrosion test with electric field treated for 300 min. It is clear that the corrosion ditches extended to inside the grains along the grain boundary, while it has been stopped on across of the annealing twin. Figure 6 shows the elements distribution at grain boundary between annealing twins and high angle grain boundary with electric field treatment for 300 min. From Fig. 6, it can be clearly found that the morphology of the grain boundary between original high angle boundary and annealing twin (marked with arrow) has no obvious change compared with that of the original high angle boundary. The distributions of carbides are chain-like. It is also noticeable from the results of elements distribution of the alloy that the exhaustion of Cr and Mo at both sides of grain boundary has been obviously improved compared with that at original high angle grain boundary.

Because of the formation of annealing twins, grain boundary energy decreased and the fraction of coherent boundaries increased. Since the exhaustion of alloying elements at high angle grain boundary can be decreased with the formation of low energy boundaries (such as grain boundary of twins), the corrosion resistance of the alloy can be improved. During the formation and growth of the annealing twins in the alloy, the redistribution of elements at the crossing of the original high angle grain boundaries and annealing twin occurred. The exhaustion of alloying elements can be locally improved and the number of such kind of interface increases with the electric field treated time. The original high angle grain boundaries will be replaced and the some of continuously distributed original grain boundaries will be partitioned. When the original high angle grain boundary falls across the grain boundary which exhaustion degree is obviously lower, the sides of corrosion ditches are retarded. It can be considered as the reasons of improving of corrosion resistance after electric field treatment.

When the alloy is in the electric field with high energy, the energy can provide the power for moving of defects and accelerating the diffusion rate of atoms in the alloy. Figure 7 shows the elements distribution at high angle grain boundary in the alloy without electric field treatment. It is remarkable that exhaustion of Cr and Mo elements on both sides of high angle grain boundary has been improved with electric field treatment (see Fig. 6(d)). This fact is consistent with the reducing corrosion phenomena at high grain boundaries of the alloy after corrosion test in solution of CuCl₂, HCl and C₂H₅OH with electric field treatment. Based on the above experimental results, it can be understood that the atom diffusion in the alloy can be accelerated electric field treatment, at the same time the exhaustion of alloying element on high grain boundaries can be also improved, which are attributed to the improving corrosion resistance of the testing alloy after electric field treatment.

Fig. 4 Surface morphology of the alloy after immersion corrosion: (a) aged at 1093 K for 300 min, (b) electric field treated at 1093 K for 300 min with intensity of 4 kV·cm⁻¹.

Fig. 5 Cross-sectional morphology of the alloy after intergranular corrosion with electric field treatment.
5. Summary

The resistance of both intergranular corrosion and immersion corrosion of the testing superalloy can be improved by the electric field treatment and the corrosion rate is decreased. The formation and growth of the annealing twins during the electric field treatment cause the alloy elements redistribution between the original high angle grain boundaries and the annealing twins, as well as the improvement of exhaustion of Cr and Mo elements at the grain boundaries. With the increasing electric field treated time, a large amount of original high angle grain boundaries are replaced and the continuously distributed original grain boundaries are partitioned. This leads to the retardation of the corrosion ditches to extend. The corrosion resistance of the alloy is improved due to the improving intergranular corrosion behavior on the grain boundary.

Moreover, the promotion effects of electric field treatment on the atom diffusion rate decrease the exhaustion tendency of Cr and Mo elements on both sides of normal high angle grain boundary, which is considered to be one of the reasons for improving of corrosion resistance after electric field treatment.

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Fig. 6 Elements distribution at grain boundaries of annealing twin and high angle grain boundary: (a) morphology of twins of the alloy with electric field treated at 1093 K for 300 min with intensity of 4 kV cm⁻¹, (b) elements distribution at location I, (c) elements distribution at location II, (d) elements distribution at location III.

Fig. 7 Elements distribution at high angle grain boundary in the alloy without electric field treatment (aged at 1093 K for 300 min).