

Effect of Graphite Addition on Oxidation Behavior of Ni-Cr-Based Superalloy at 900 °C

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Abstract: Nickel-based alloys with different contents of graphite were prepared by powder metallurgy method. High temperature oxidation resistance of these alloys was studied by high temperature test at 900 °C for 100 h in static air. Morphology of oxides was studied by SEM and their composition was analyzed by XRD. The result shows that the kinetic curves of oxidation for nickel-based alloys with lower content of graphite obey the parabolic law. The oxide films consist of Cr_2O_3 and NiCr_2O_4 when the alloy contains no graphite. The oxide film consists of Cr_2O_3 when the alloy contains 3% graphite. If graphite content increases to 6%, the oxidative decomposition of graphite leads to severe initial oxidation, and mass gain takes place significantly; the cavity after decomposition of graphite accelerates the process of oxidation reaction. The oxidation mechanism of the alloy has also been suggested by the phase composition analyses of oxide film.

Key words: Ni-based superalloy; graphite; oxidation kinetics; oxidation mechanism

Superalloy is a key material for turbine engine blades, advanced jet engines etc, and further improving of its anti-oxidation ability has been a very important subject in recent decades. Ni-Cr-based alloy has not only excellent mechanical properties, but also the advantages of anti-oxidation and resistance to hot corrosion at ambient temperature and at elevated temperature, which makes them widely used in gas turbine, high temperatures engine, high temperatures boiler etc^[1-7]. Graphite is an effective lubricant additive for its self-lubricating properties deriving from its lamellar structure; therefore the usage scope of Ni-Cr-based alloy at elevated temperature could be widened by the addition of graphite^[8,9]. Oxidation is the most common corrosion mode, when parts and components serve in the high temperature environment. In recent years, the high temperature oxidation behavior of Ni-Cr-based alloy have been extensively studied^[10-14].

To access the performance of Ni-Cr based alloy, the present work is to investigate the oxidation behavior of Ni-Cr based alloys with strengthening phase tungsten and different contents of lubricant phase graphite. Strengthening phase W and lubricant phase graphite reinforced Ni-Cr based alloys were developed by a powder metallurgy

method, which are recommended to be used for high temperature applications.

1 Experimental

The chemical compositions of Ni-Cr based alloys are shown in Tab.1.

Alloyed Ni-20Cr powder, tungsten powder and graphite [0%, 3% and 6% (mass fraction)] were fully mixed to get the mixtures with different contents of graphite, and then the mixtures were cold pressed into green discs with Φ 45 mm×10 mm. Afterward the greens were hot pressed into the blanks in FVPHP-R-10 vacuum hot pressing furnace. The hot pressing conditions were as follows: pressure 16 MPa, temperature 1240 °C, heating rate 20 °C /min, holding time 20 min and argon protection after degassing to 10^{-5} Pa.

Table 1 Chemical compositions of Ni-20Cr/graphite composites (mass fraction, %)

Ni-20Cr	W	Graphite
76-85	15	0-9

Received date: June 25, 2008

Foundation item: Project Supported by Qing Lan Project of Jiangsu Province

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The alloy blanks were fabricated into the samples with 10 mm×4 mm×4 mm, which were ground with emery papers washed in water, alcohol and finally dried. The oxidation dynamic experiments of the alloys were performed in a chamber furnace at 900 °C for 100 h in air. After being oxidized for certain time (1, 3, 5, 10, 25, 50, 75 and 100 h) the samples were taken out and weighed by DT2100 analytical balance with an accuracy of 0.1 mg. The phase constitutions were analyzed by XRD, and the morphologies of the sample cross sections were observed by SEM.

2 Results and Discussion

2.1 Morphology and structure of alloys

Fig.1 shows the morphologies and XRD pattern of the alloys after hot pressing. There are a few gray blocks and black dot impurity phases dispersed in the matrix of the alloy with no graphite addition, as shown in Fig.1a. The gray blocks and black dots increase with the increase of graphite content. XRD result indicates that besides some Ni-based solution and graphite, there are a few tungsten carbides, which were formed by tungsten and graphite reaction.

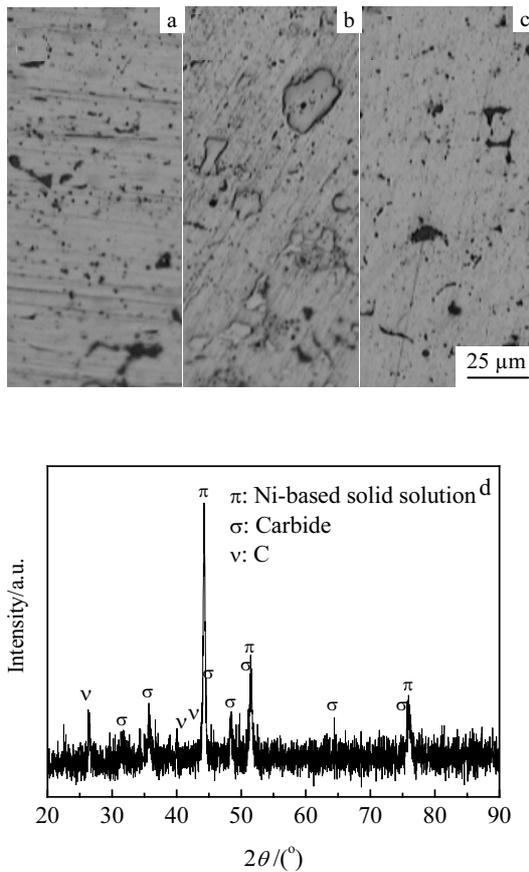


Fig.1 Optical photographs of the alloys with different contents of graphite (mass fraction): (a) 0%; (b) 3%; (c) 6%; and (d) XRD pattern of P/M products of Ni-Cr-W-C alloy

2.2 Oxidation dynamic curve

The oxidation dynamic curves of the alloys with different contents of graphite (A=0%, B=3%, C=6%)(mass fraction) at 900 °C for 100 h are presented in Fig.2. In initial period of 10 h, oxidation speeds up. This is the formation period of oxide film. Then, the oxidation speeds down, and enters the oxide film growth period, which lasts for 20 h. During the oxidation process, a surface reaction changes into diffusion gradually. At the same temperature, the mass gain of the alloy with addition of 3% (mass fraction) graphite is higher than that of Ni-Cr-W alloy; however, the mass gain of the alloy with addition of 6% (mass fraction) graphite is the lowest. According to the dynamics curve, the equation can be written as $\Delta m=at^b$, where Δm is the mass gain and t is the oxidization time. From the equation, the formula of Ni-Cr-W alloy at 900 °C is $\Delta m=0.27 t^{0.30}$. It can be concluded that the oxide dynamic curve approximately follows cube rule, which shows that the oxides formed at high temperature have a restraining effect on oxidation process. The formula is changed into $v=0.08 t^{-0.70}$, through a derivative transformation, where v is the oxidation velocity. The formula of sample B and C at 900 °C is $\Delta m=0.36 t^{0.30}$ and $\Delta m=0.16 t^{0.26}$ respectively. The formula is changed into $v=0.11 t^{-0.70}$ and $v=0.04 t^{-0.74}$ respectively, through a derivative transformation. It can be concluded that oxidation speeds down with prolonging of the time.

2.3 Constitution of oxidation film

Fig.3 shows the SEM images of the samples with different contents of graphite(A=0%, B=3%, C=6%)(mass fraction) at 900 °C after 100 h oxidation. Fig.4 shows X-ray diffraction results for the surface of the samples after oxidation. It can be seen that there are dense oxidation films on the surface without graphite. The oxides on the surface consist of Cr_2O_3 and $NiCr_2O_4$ spinelle. With 3% (mass fraction) content of graphite, the oxide grains on the surface become larger and more protruded, the main component of the oxidation film is Cr_2O_3 , and oxidation mass gain is higher than that of sample A,

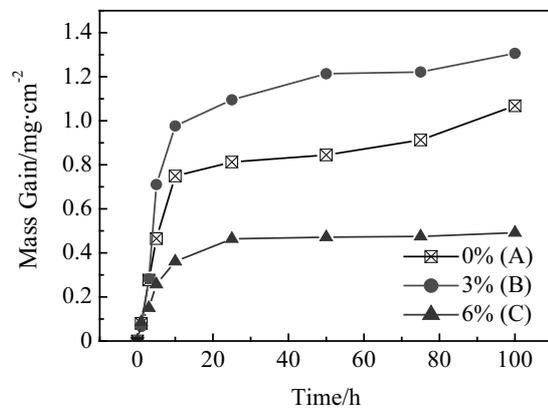


Fig.2 Oxidation kinetics curves of Ni-based alloys in air at 900 °C for 100 h

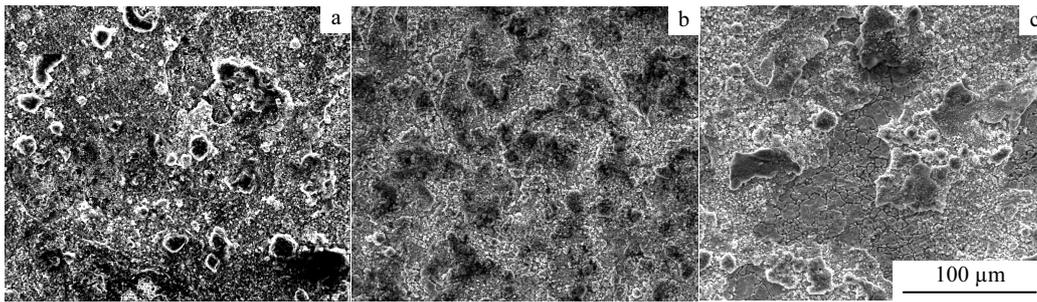


Fig.3 SEM images of samples oxidized for 100 h at 900 °C: (a) Ni-Cr-W-0%C; (b) Ni-Cr-W-3%C; and (c) Ni-Cr-W-6%C

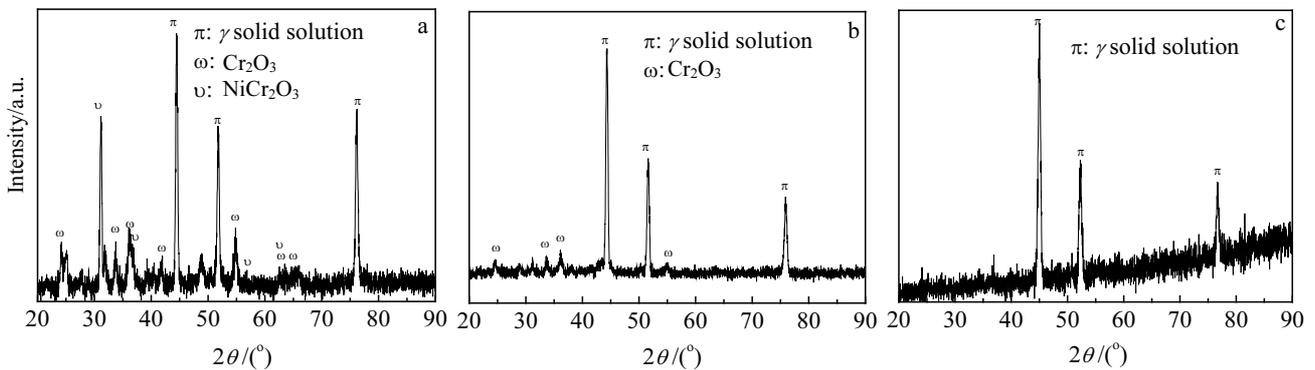


Fig.4 XRD patterns of samples after oxidation for 100 h at 900 °C: (a) Ni-Cr; (b) Ni-Cr-W-3%C; and (c) Ni-Cr-W-6%C

as shown in Fig.2. When the alloy with 6% (mass fraction) content of graphite, the oxides flake away, resulting in the matrix oxidized further; there are only a few oxides on the surface instead of continuous oxide films, which means that the alloy has no ability of oxidation resistance. In each sample there is γ phase (nickel base solid solution); this is because the oxides thickness was limited in the oxidation process, X-ray penetration depth is large, thus penetrate oxide layer, and shows the phase constitution of the substrate material.

The addition of W promotes strengthening of the solid solution, raising recrystallization temperature of the matrix and reducing the diffusion rate of atoms in the matrix. Some research indicated that a selective oxidation for nickel-based alloy will occur when the content of active lively element chromium in the nickel-based alloy exceeds a critical concentration, resulting in the formation of single Cr_2O_3 oxide layer^[1]. The oxidation of graphite in the alloy will occur at high temperature, and part of it becomes gas which escapes, resulting in the formation of the cavity in the oxide film. Metal transporting outward will take place through oxide film and cavity in next oxidation process; along with the oxidation, the curve of oxide film will exacerbate^[15], and the oxide shedding happens when the curve of oxide reaches a certain degree. Upon the lower content of graphite, the oxidations of graphite and metal matrix take place simultaneously in oxidation process; however, the oxidation mass gain significantly exceeds the gas escape.

The effect of graphite oxidation on the oxidation resistance of alloys increases with increasing of graphite content.

3 Conclusions

- 1) The graphite content of Ni-Cr-based alloy has the remarkable influence on the oxidation resistance and oxidation mechanism at 900 °C.
- 2) The isothermal oxidation kinetics of the alloy containing various contents of graphite obeys the parabolic law at 900 °C.
- 3) Without graphite, the dense oxidation film of Ni-Cr-based alloy consists of spinel structure NiCr_2O_4 and Cr_2O_3 , and the oxidation rate of the alloy is reduced. With the addition of graphite, a loose Cr_2O_3 film on composite surface will be formed, and the oxidation rate increases.

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石墨含量对镍基高温合金在900 °C氧化行为的影响

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摘要: 采用粉末冶金方法制备不同石墨含量(0%、3%、6%)的镍基高温合金, 研究合金材料在 900 °C 和 100 h 下的恒温氧化行为, 用扫描电镜和 X 射线衍射对其氧化表面形貌和成分进行观察和分析。结果表明: 石墨含量较低(0%, 3%)时, 镍基合金氧化动力学符合抛物线规律, 表面氧化膜无剥落; 石墨含量为 0%的合金氧化膜由 Cr_2O_3 和 NiCr_2O_4 组成, 石墨含量为 3%的合金氧化膜由 Cr_2O_3 组成, 当石墨含量增加到 6%时, 大量石墨的氧化分解导致合金初始氧化严重, 石墨分解后的孔洞加速氧化反应过程。根据氧化膜的组成分析了合金的氧化机制。

关键词: 镍基高温合金; 石墨; 氧化动力学; 氧化机制

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