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Microstructural evolution of a titanium- and cobalt-modified nickel-based repair alloy during exposure to high temperatures

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ABSTRACT

Spray forming (SF) is a near net shape manufacturing process in a wide variety of alloys. A titanium- and cobalt-modified repair alloy has been prepared by the SF process and was presented excellent properties of friction and wear in previous published article. In this paper, the microstructural evolution of the alloy exposed at 750 °C for different isothermal aging time was analyzed. Microstructure observations reveal that equiaxed grains formed in the ingots whether after aging process or not. The size and the volume fraction of γ' precipitates increase with the ongoing of aging process, which could result in the change of the lattice misfit of γ'/γ and the precipitation of new σ, η phases. Intergranular fracture and transgranular fracture are main fracture mechanisms in aged state. Its tensile properties were attributed to the size and the volume fraction of γ' precipitates, γ'/γ misfit, grain boundary carbides and the number of harmful phases (σ and η phases) during aging process.

1. Introduction

Spray forming (SF) is an advanced rapid solidification technology that stems from metal atomization and powder metallurgy, together with the advantages of near-net-shape manufacturing and retaining a powder metallurgy (PM) type microstructure. Problems associated with the PM method, such as complicated processing and surface oxidation of powders, can be avoided in the SF process [1]. SF has attracted considerable attention in recent years [2–10]. Gas turbine components are subjected to high temperatures and stresses during engine service [11]. Under such conditions, SF has been proposed to spray the melt to repair the damaged components. In our previous study, three kinds of spray forming nickel-based repair alloy billets have been prepared by changing the content of Ti and Co, and these alloys were presented excellent properties of friction and wear [12]. And this paper mainly aims to evaluate the microstructural stability and phase transformation at high temperature.

As a typical nickel-based repair alloy, it possesses high strength at temperatures of 700–760 °C, but insufficient creep resistance at higher temperatures [13]. The superior strength and high temperature resistance of this kind of nickel-based repair alloy are attributed to its high-volume fraction of regularly aligned cubical γ' precipitates coherent with γ matrix [14]. The size of γ' precipitates could influence the formation of topologically close-packed phases (TCP) which are harmful to high temperature properties [14]. Therefore, the main characteristic of repair alloy is the microstructural stability during exposure to high temperatures for a long time [15]. Since mechanical properties are affected by various microstructural features, it is important to study the microstructural evolution associated with long-term exposure at high temperatures. The effects of microstructure on mechanical properties were investigated for nickel-based alloys [13–19]. Various types of carbides and precipitates like γ', γ'' and σ were formed during high temperature exposure depending on exposure temperatures and chemical compositions. The presence of those precipitates reduced the ductility of the alloy by hindering dislocation movement.

To gain a deep insight into the problems above, efforts will be devoted to studying the relationship between microstructures and mechanical properties of the repair alloy exposed to 750 °C high temperature for different time.

2. Materials and experimental setup

The chemical composition of the spray formed nickel-based

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repair alloy in this study is listed in Table 1. The test material was provided for standard heat treatment: first, solution heat treated at 1140 °C for 2 h followed by oil quenching; and then, heat treated at 815 °C for 2 h followed by air cooling to room temperature. For the aging process, blocks of the spray formed nickel-based repair alloy were exposed at 750 °C for 200, 500, 800 and 1200 h in a box furnace, respectively. After aging, the blocks were removed from the furnace and air cooled to room temperature. The samples for microstructural observation and tensile test were taken from these blocks.

The microstructure features including the γ' precipitates, carbides and other phases were observed using a scanning electron microscope (SEM, LEO1450) with secondary electrons mode. The samples were prepared by electropolishing with 20% H_2SO_4-CH_3OH, followed by electrolytic etching in a CrO_3-H_3PO_4-H_2SO_4 solution with etching time of 20s. The size and the volume fraction of primary and secondary γ' precipitates of the samples before and after the aging were measured using an image analyzer (TOMORO analysis TS).

In addition, a transmission electron microscope (TEM, H-800), equipped with energy dispersive spectroscopy (EDS) and selective area diffraction (SAD), was used to identify the phases before and after the aging. Thin foils for the TEM investigations were prepared by the twin-jet polishing at −20 °C, using 5% perchloric acid and 95% ethanol as electrolyte.

For the tensile tests, the specimens with 70 mm in length and 5 mm in diameter were machined. The tests were conducted at a temperature of 704 °C under stretching velocity control (2.5×10^{-2} mm/s). The tensile strength of the samples with different aging time was recorded and the tensile fractures were observed using a scanning electron microscope (SEM, LEO1450).

3. Results and discussion

3.1. Microstructure evolution

Fig. 1 (a) and (b) show the microstructure of the as-sprayed nickel-based repair alloy. The microstructure of the alloy consists of homogenous fine equiaxed grains and the overall density is up to 98%. The precipitates on the grain boundary are mainly γ', MC, $M_{23}C_6$, M(C, N) and M_3B_2. In the late stage of solidification, the segregation of Ti and Al elements leads to the eutectic transition $L \rightarrow (\gamma + \gamma')$ in the crystal front. A large number of eutectic $(\gamma+\gamma')$ precipitates in alloy will reduce the mechanical properties, owing to its low melting point. But $(\gamma+\gamma')$ in the spray-formed repair alloy can hardly be found, which mainly attributes to the airflow turbulence in the spray forming process and the intensified semi solid metal solute diffusion caused by particle impact, reducing the segregation of Al and Ti. The γ' phase size of the alloy is relatively small, which is the typical microstructure characteristics of rapid solidification.

After standard heat treatment, no significant microstructure changes are observed as compared to the as-sprayed condition as shown in Fig. 1 (c)-(f). The average grain size of ASTM standard is in a degree of about 6.4 (Fig. 1 (c)). There are many coarse primary γ' particles distributed on the grain boundaries and in the grains (Fig. 1 (e)). In addition, grain boundaries are covered with fine dispersed carbides which are known as the secondary Cr-rich $M_{23}C_6$ and W-rich M_6C and formed during the cooling process from solution treatment (Fig. 1 (e)). Meanwhile, fine spherical secondary γ' phases are precipitated from the matrix which are uniformly distributed around the large size γ'. Then after heat treatment at 815 °C, secondary γ' phases and carbides grow up, and many third γ' phases also precipitate from γ matrix. Compared with the microstructures of as-sprayed alloy, the standard heat treated alloy has smaller sized carbides and γ' phases, and both of their volume fractions increase.

With the increase of the aging time from 200 h to 1200 h, OM shows the grain size of the alloy did not change obviously, but the grain and the grain boundary have been covered with the precipitates in the specimen aged at 1200 h (long-rod shape precipitates in Fig. 2 (d)).

The SEM images of the repair alloy after 200/500/800/1200 h aging are shown in Fig. 2. Unlike those after standard heat treatment, the carbides on the grain boundary begin to connect as a chain after 200 h aging, which is mainly the MC carbide (M is mainly Ti, Nb, Ta or Zr). Meanwhile, a relative large and stable bulk carbonitride can be found (Fig. 2 (a)). In addition, a few of fine carbides were dispersed in grains. With the increasing of aging time (Fig. 2 (b)-(d)), the carbides on the grain boundary (mainly $M_{23}C_6$) continue to nucleate and grow, and become chain-like, leading to a gradual coarsening of the grain boundary; intragranular carbides like $M_{23}C_6$, granular MC and acicular M_6C gradually increase. That is to say, in the aging process, the third γ' phases and secondary MC carbides precipitated from the oversaturated γ matrix in the same time, and then the secondary MC carbides was decomposed into $M_{23}C_6$. While under the action of high temperature, the diffusion of atoms at grain boundary was accelerated, which promoted the dissolution of bulk MC carbides, and the carbon elements provided by dissolved MC carbides combined with Cr, Mo from γ matrix formed the $M_{23}C_6$ carbides. The behavior of carbides was reported by Ref. [20].

From Fig. 2 (b), a few short needle-like precipitates appear in the alloy when the specimen is aged for 500 h. With the increase of aging time up to 800 h, the growth of those precipitates is not obvious (see Fig. 2 (c)). However, after 1200 h aging, the precipitates grow sharply, indicating a long-rod shape, and surround the entire grain (see Fig. 2 (d)). These precipitates were mostly in 60° or 120° orderly distributed.

3.2. γ' phase evolution

The change of the γ' phase morphology ascribed to the competition between the interfacial energy and the diffusion effect during the long-term aging process. When the diffusion effect plays a major role, the morphological instability of γ' phase results in the morphology degradation; otherwise, γ' will coarsen, and the morphology will not change too much. The competition between the elastic strain energy and the interfacial energy caused by the lattice mismatch is the main cause of the instability of γ' phase. The diffusion of solid solution elements and the change of phase thermal expansion coefficient will result in a change of the coherent characteristics along with the phase decomposition and transformation: When the two-phase cohesive strain increases and the elastic strain energy is high, γ' will split to release the strain energy, the total surface energy will be increased, but the total energy is reduced; when the surface energy plays a major role, the decrease of the surface energy is responsible for the growth of γ', the cubic γ' particles are passivated at the edge and gradually change into the spherical shape.

Fig. 3 (a)-(d) shows the morphology evolution of γ' phase around the grain boundary during the aging process. In the first 500 h of aging, the lattice misfit of γ'/γ is relatively small, and the

Table 1
Chemical composition of spray formed nickel-based repair alloy (wt.%).

Co	Cr	W	Al	Ti	Mo	Ta	Nb	Ni
21.75	12.77	4.12	3.6	3.54	2.95	1.52	1.51	Bal