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Effects of Nb/Ti/V/Ta on phase precipitation and oxidation resistance at 1073 K in alumina-forming austenitic stainless steels

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ABSTRACT

The present work investigated the effects of strong carbide-forming elements M (M = Nb, Ti, V, Ta) on the phase precipitation and oxidation resistance at 1073 K in alumina-forming austenitic (AFA) stainless steels (Fe-20Ni-(18–23)Cr-2.5Al-2.3Mo-0.08C-Nb/Ti/V/Ta wt%). The designed alloy rods were solid-solutioned at 1523 K for 1.5 h, and then aged at 1073 K for 24 h or oxidized at 1073 K for 500 h, respectively. Besides primary MC carbides, B2-NiAl, Fe_2M, and σ-FeCr phases would be precipitated from the γ-austenitic matrix in these aged AFA alloys. Furthermore, the precipitation of σ-FeCr could be accelerated by the B2-NiAl formation, which is related to the γ stability. The formation of MC and Fe_2M can be controlled via adjusting the ratio of M/C. The oxidation resistance of these AFA alloys can be improved effectively by V and Ta addition due to the formation of compact Al_2O_3 protective scales. This work will provide a new approach to obtain a good combination of creep strength and oxidation resistance through co-alloying with Nb/Ta/V and controlling the M/C ratio within 1.0–2.0 (in molar ratio) simultaneously.

1. Introduction

Austenitic stainless steels (ASSs) have been widely applied into the energy conversion systems such as boiler/steam turbine power plants for several decades with a temperature range of 673–923 K [1–3]. In order to further increase the energy efficiency, it is expected to operate the power plants at a much higher temperature of 1023 K [4], in which the high-temperature (HT) creep strength and oxidation resistance of ASSs in water vapor environments are specially focused on [5–7]. There exist several kinds of alloys for HT applications, such as Ni-based superalloys, oxide-dispersion-strengthened (ODS) ferritic stainless steels, etc. However, they have not been prevalently used as heat-resistant components in energy-conversion systems due to the expensive cost for Ni-based superalloys and the poor machinability for ODS steels [1, 2].

Recently, alumina-forming austenitic (AFA) stainless steels have been developed and received attentions due to not only their excellent HT performances but also low cost and better machinability [8–19]. For the AFA stainless steels, the oxidation resistance is primarily attributed to the formation of protective Al_2O_3 scales on the surface at HTs, showing a much better thermal stability than Cr_2O_3 films for conventional heat-resistant ASSs, especially in water vapor circumstances [5–7]. It was reported that a small amount addition of 2.4 wt% Al is sufficient to achieve compact alumina scales in ASSs containing a high content of Ni and Cr at 923–1073 K [9, 10, 20]. Although the oxidation resistance of ASSs could be ameliorated by increasing Al, it was always accompanied by the precipitation of some harmful phases, such as α-Fe and σ-FeCr (*tP*-CrFe type), due to the strong BCC-stabilization capability of Al [9, 10]. For the alumina-forming Fe- and Ni-based alloys, their oxidation resistance is also affected by the reactive elements, including Zr, Hf, Y, Ce, etc. Pint et al. studied the effects of Zr, Hf, Y and Ce on the oxidation behavior of FeCrAl alloys systematically, and revealed that most of doped FeCrAl alloys with single reactive element exhibit a parabolic weight-gain rate, being 2–3 times lower than undoped alloys. Moreover, the superior oxidation resistance could be further obtained by co-addition of reactive elements Hf and Y in FeCrAl alloys, due to the reduced growth rate of the alumina scale and the improved adherence of the scale during oxidation trials and thermal cycling [21–24]. Similarly, Brady et al. also claimed that the

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appropriate addition of Hf and Y can improve the quality of alumina scale and the resistance to cracking and spallation in AFA steels significantly [12, 13]. However, the addition of Zr, Ti, and S could accelerate the oxidation rate of Fe-24Ni-10Cr-5Al (wt%) alloy [25].

As for the HT creep resistant properties of AFA stainless steels, it is prone to be affected by the precipitation behaviors during isothermal aging [8–10, 13]. The creep resistance could be improved effectively by precipitation hardening of nano-sized MC-type carbides (with a cF-NaCl structure and M = Nb, Ti, and V, being strong carbide-forming elements). Yamamoto et al. investigated the influences of alloying elements on creep resistant properties of AFA steels, i.e., high-temperature ultrafine precipitation strengthened (HTUPS) ASSs, which possess a composition range of Fe-20Ni-(12–15)Cr-(2.5–4.0)Al-2.5Mo-(0.2–3.0) Nb-0.08C-Ti/V (wt%) [9]. Among them, the HTUPS-4 alloy containing 0.9 wt% Nb exhibited a prominent creep resistant property at 1073 K due to a much more amount of NbC nanoprecipitates. Moreover, the creep resistance of AFA alloys could be further enhanced by a combined addition of Nb, Ti, and V [8–10]. However, the oxidation resistance of AFA steels will be deteriorated by Ti/V co-alloying because Ti and V might increase the oxygen permeability or inhibit Al diffusivity. Thus, the oxidation will change from external oxidation for protection to internal oxidation, leading to a continuous permeation of oxygen [9, 12]. Actually, this detrimental effect is not obvious when adding Ti or V separately [11, 26]. In addition, the optimization of the ratios of (Nb + Ti + V) to C is also of importance since the amount of strong carbide-forming elements M indeed affect the precipitation behaviors of ASSs at HTs [18, 27]. Besides the MC carbides, the excessive M also induce the formation of coarse Fe_2M-Laves phase, otherwise, the less M leads to the formation of $Cr_{23}C_6$ [18, 27]. Similar to the Nb, Ti, and V, the Ta element is also a strong carbide-forming element, but its effect on creep strength and oxidation resistance of AFA steels has never been reported.

As a typical example of ASSs, the 310S (Fe-23Cr-20Ni-0.08C, wt%) ASS exhibits prominent performances at HT due to the high Ni/Cr contents, and the HT strength can be further enhanced by adding a minor amount of strong carbide-forming element M [28, 29]. In our previous work, the influences of the addition of Mo and M elements (M = Nb, Ti, Ta, and Zr) into 310S on the microstructural stability and second-phase precipitation at 973 K were investigated systematically. Among them, the co-addition of Mo/Zr and Mo/Ta can render the alloys with a higher microstructural stability, in which the precipitation of harmful phases of σ-FeCr and $Cr_{23}C_6$ is inhibited effectively even after a long-term aging for 408 h, as a final result of the improvement of mechanical properties [30, 31]. However, the high-temperature strength would be deteriorated by Zr addition in AFA alloys due to the reduction of precipitation strengthening by MC particles coarsening [32]. By far, the effects of co-additions of Al and M into 310S on phase precipitation behaviors have not been elucidated systematically. Therefore, in the present work, based on 310S ASS, the effects of both Al and strong carbide-forming elements M (M = Nb, Ti, V, and Ta) on the phase precipitation behaviors of alloys at 1073 K will be investigated. The oxidation resistance at 1073 K of this series of alloys will be then evaluated. The Vickers microhardness tests will be conducted to study the aging hardening behaviors of alloys. Finally, the formation mechanism of σ-FeCr and its effect on oxidation resistance will be also discussed.

2. Experimental Procedures

The designed alloy compositions are listed in Table 1, in which the 310S-Nb represents the Nb-alloyed 310S alloy with a composition of Fe-20Ni-23Cr-2.2Nb-0.08C (wt%), and the co-additions of Al, Mo, and Nb/Ti/Ta/V into alloys are designated as AFA-M. For example, the AFA-Nb denotes the 0.89 wt% Nb alloying of Fe-20Ni-18Cr-2.5Al-2.3Mo alloy. Based on AFA-Nb, the other AFA-NbM (M = Ti, V, Ta) alloys were designed by a half amount of Ti, V, and Ta substituting for Nb in equal-molar atomic fraction, respectively. In order to form single austenitic matrix, the Cr content is reduced to 18 wt% in these AFA-M alloys due to the addition of Al and Mo. In addition, Si and Mn were intended to be added into these alloys for the consideration of the impurity contents in such kinds of industrial ASSs.

Each of the alloy ingot with about 15 g was prepared by vacuum arc melting furnace with inconsumable tungsten electrode. The purities of the raw metals are 99.99 wt% for Fe, Ni, Ti, and C, 99.95 wt% for Mo, Nb, V, and Ta, 99.9 wt% for Cr and Mn, 99.999 wt% for Al and Si, respectively. Before melting, the vacuum of the furnace was controlled below 6×10^{-3} Pa, and the melting process was protected by the argon atmosphere with a purity of 99.999%. The button ingots were flipped and melted repeatedly five times for composition homogeneity, and then cooper-mold suction-cast to make cylindrical rods with a diameter of 6 mm. The mass loss could be controlled below 0.1 wt% in the melting process. All cylindrical rods were sealed into a vacuum quartz cube for solid-solution treatment (ST) at 1523 K for 1.5 h and plus water-quenched, and then aged at 1073 K for 24 h.

Oxidation specimens with a height of about 12 mm were cut from the solid-solutioned cylindrical rods and polished using SiC paper to a 1200-grit surface finish. Cyclic oxidation tests were conducted at 1073 K for 500 h in dry air. They were air-cooled after each 25/100 h-cycle at 1073 K, weighed and returned to the furnace, in which the process was repeated for eight times.

Structural identifications of alloys with different heat treatments and oxidized specimens were carried out by means of a BRUKER X-ray diffractometer (XRD) with a Cu K_α radiation ($\lambda = 0.15406$ nm), in which the measurements were performed by scanning 2θ from 20° to 80°/100° using a scan speed of 1°/min, and MDI Jade software was used to identify phase structures in the alloys. Microstructures were analyzed by using Zeiss Supra55 scanning electron microscopy (SEM). The elemental distributions were conducted by a SHIMADZU electron probe micro-analyzer (EPMA). The precipitated phase structures were further identified by the Philips Tecnai G^2 transmission electron microscopy (TEM), where the TEM samples were prepared by twin-jet electro-polishing in a solution of 20% HNO_3 + 80% CH_3OH (volume fraction) at about 243 K. The statistical analysis of the volume fractions of precipitated particles were measured from the SEM morphology images (at least 6 images) by using the Image-Pro Plus 6.0 software. Moreover, micro-hardness tests were performed using a HVS-1000 Micro Hardness apparatus with a load of 500 g for 20 s, in which each alloy sample was tested at least for ten times.

3. Results

3.1. Microstructural Characterization of Solid-solutioned and Aged Alloys

Fig. 1 shows XRD patterns of the designed alloys in the solid-solution state and after aging for 24 h at 1073 K. The diffraction peaks of γ austenitic and MC carbides appear in most of the solid-solutioned alloys, as shown by the XRD pattern of AFA-NbTa-ST in Fig. 1. It was also verified by the typical SEM morphologies of 310S-Nb and AFA-NbTa alloys in Fig. 2. The primary MC particles are precipitated on the γ matrix randomly, and the particle size of 0.5–2 μm in the AFA-NbTa is much smaller than that in 310S-Nb. It is noted that this kind of coarse MC carbides were generally formed during solidification and it is hard to be dissolved during the high-temperature solid-solution treatment. The total volume fraction of the primary MC is estimated to be about 2.3% and 1.3% in 310S-Nb and AFA-NbTa alloys, respectively.

After being aged at 1073 K for 24 h, only Fe_2Nb-Laves phase was checked in Nb-alloyed 310S (310S-Nb) alloy, besides primary MC particles in γ matrix. While anther two phases, B2-NiAl with a simple cubic structure and σ-FeCr with a tetragonal structure appear in AFA alloys, besides the MC carbide, as shown clearly in the enlarged XRD patterns in Fig. 1(b). It should be noted that the diffraction intensity of MC-related peaks in the AFA-NbV alloy is not obvious as that in other