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Precipitation and hot deformation behavior of austenitic heat-resistant steels: A review

Yinghui Zhou[a,b], Yongchang Liu[a,c,*], Xiaosheng Zhou[a,*], Chenxi Liu[a], Jianxin Yu[a,c], Yuan Huang[a], Huijun Li[a], Wenya Li[b]

[a] State Key Lab of Hydraulic Engineering Simulation and Safety, School of Materials Science & Engineering, Tianjin University, Tianjin 300354, China
[b] School of Materials Science & Engineering, Northwestern Polytechnical University, Xi'an 710072, China
[c] Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

The austenitic heat resistant-steels have been considered as important candidate materials for advanced supercritical boilers, nuclear reactors, super heaters and chemical reactors, due to their favorable combination of high strength, corrosion resistance, perfect mechanical properties, workability and low cost. Since the precipitation behavior of the steels during long-term service at elevated temperature would lead to the deterioration of mechanical properties, it is essential to clarify the evolution of secondary phases in the microstructure of the steels. Here, a summary of recent progress in the precipitation behavior and the coarsening mechanism of various precipitates during aging in austenitic steels is made. Various secondary phases are formed under service conditions, like *MX* carbonitrides, $M_{23}C_6$ carbides, Z phase, sigma phase and Laves phase. It is found that the coarsening rate of $M_{23}C_6$ carbides is much higher than that of *MX* carbonitrides. In order to understand the thermal deformation mechanism, a constitutive equation can be established, and thus obtained processing maps are beneficial to optimizing thermal processing parameters, leading to improved thermal processing properties of steels.

1. Introduction

The austenitic heat-resistant steels were developed since the early 1890s, and for a long time have been widely used as structural materials for elevated temperature applications such as boilers, nuclear reactors, super-heater tubes and re-heater tubes in Ultra-Supercritical power plants [1–4]. Presently, the requirements of environment protection and clean energy have promoted the application of ultra-super critical (USC) plants [5]. Owing to the increase in steam pressures and temperatures in the USC equipment, the materials with good high-temperature properties need be developed [6]. Due to the superior long-term high temperature strength, improved creep resistance, good fabric ability, excellent resistance to oxidation and corrosion as well as the low cost, austenitic heat-resistant steels are paid more and more extensive attention worldwidely [7–11].

Actually, stainless steels are the basis of austenitic heat-resistant steels. The iron is the main component of steels and chromium must be added to protect materials from rusting and corroding in service environments. Cr addition is used to achieve high corrosion and oxidation resistance and better hardenability. In addition to Cr, stainless steels also contain a large amount of other alloying elements whose existence increases particular properties. It is no doubt that the presence of Ni can enhance the stability of austenite. When the Ni and Cr are added in substantial amounts, the produced steel is called as austenitic heat-resistant steel [12–14]. The most obvious difference between austenitic heat-resistant and stainless steels is that the former is generally used over 600 °C.

Most austenitic heat-resistant steels can be divided into two categories: 18Cr-8Ni type and 25Cr-20Ni type. Many modern austenitic heat-resistant steels have been studied through composition optimization. By adding Ti, V and Nb to simple Fe–Cr–Ni steels, type 347 and 321 steels were developed. Mo is added to improve resistance against pitting. The alloying componants of Cu and V are believed to contribute to the strengthening of austenitic steels independently [15]. By adding B, V, Mo, W and Cu, the strength of austenitic steels such as Super304H and HR3C has been increased dramatically [16]. The new austenitic heat-resistant

* Corresponding authors at: State Key Lab of Hydraulic Engineering Simulation and Safety, School of Materials Science & Engineering, Tianjin University, Tianjin, 300354, China.
E-mail addresses: ycliu@tju.edu.cn (Y. Liu), tjuzhouxs@163.com (X. Zhou).

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Table 1
Typical chemical composition of austenitic heat resistant steels (in wt%).

Steels	Fe	C	Cr	Ni	Mn	Si	Mo	W	Nb	Ti	V	Cu	N
NF709	Bal.	0.15	20.0	25.0	1.0	0.5	1.5	–	0.2	0.1	–	–	0.167
Super304H	Bal.	0.1	18.0	9.0	0.8	0.2	–	–	0.4	–	–	3.0	0.1
Sanicro25	Bal.	0.08	22.0	25.0	1.0	0.1	–	3.5	0.5	–	–	3.0	0.5
TP347H	Bal.	0.08	18.0	10.0	1.6	0.6	–	–	0.8	–	–	–	0.013
HR3C	Bal.	0.06	22.0	25.0	1.0	0.5	1.5	–	0.45	–	–	–	0.2

steels such as NF709 and SAVE25 are developed by replacing part of Ni with N [17].

The microstructures of austenitic heat-resistant steels are generally characterized as the austenite decorated with precipitates such as *MX* carbonitrides and $M_{23}C_6$ carbides. At elevated temperatures, the coarsening rate of $M_{23}C_6$ carbides will be accelerated, deteriorating the creep strength [18]. It is clear that the precipitation and coarsening behavior of precipitates during long-term service at elevated temperatures would lead to the changes in mechanical properties. Therefore, it is necessary to clarify the evolution and coarsening behaviors of secondary phases.

Currently, hot rolling, forging and extrusion are the thermal-mechanical processes applied to fabricate austenitic steels [19]. Most metallic materials are manufactured by hot forging operations. Thus, hot deformation behavior will also be an important issue in the process of manufacture. Since Prasad et al. proposed the processing map, it has become a powerful tool to analyze the workability and optimize the processing parameters in hot working. Therefore, lots of investigations are focused on hot deformation behavior of the austenitic steels through processing map technology [20–25].

As discussed above, the development of austenitic heat-resistant steels is always promoted by composition optimization. At present, more and more attention is paid on the microstructure evolution in austenitic steels. This paper presents an overview of the precipitation and the coarsening behavior of precipitates in austenitic heat-resistant steels. The hot deformation mechanisms of austenitic heat-resistant steels which play a significant role in optimizing the workability and controlling the microstructures of the steels, will also be discussed.

2. Precipitation behaviors of second phases during aging

Typical chemical compositions of the austenitic heat-resistant steels are presented in Table 1. Austenitic heat-resistant steels can be strengthened through precipitation hardening, solution hardening and dispersion hardening. Fine precipitates with nano-size in matrix would result in high creep strength of the materials [13,26,27]. Isothermal aging at temperatures around 700 °C can promote the precipitation of secondary phases that usually initiate changes in mechanical properties. Therefore, the evolution of secondary phases has to be recognized and understood. The microstructure is generally characterized by refined *MX*(*M* = Nb, *X* = C or N) carbonitrides dispersed in the austenitic matrix, and high density of twins are always randomly presented during aging. In some cases, certain amount of $M_{23}C_6$ (*M* = Cr)phase may be present, especially for those steels with high content of chromium. In long-term aging, Z-phase, sigma phase and Laves phase can be formed within austenitic heat-resistant steels. In addition to experimental approaches, many researchers have also made some attempts to simulate precipitation kinetics in austenitic heat-resistant steels [28–36]. By the thermo-kinetic software package MatCalc, Shim et al. simulated the phase fraction of precipitates and average precipitate sizes during aging in NF709, and the results are shown in Fig. 1 [28]. Ha and Jung calculated the fractions of equilibrium phase in 15Cr-15Ni austenitic steel by MatCalc thermal-kinetic software, and the results are shown in Fig. 2 [26]. The predominant precipitate phases in austenitic steels include *MX* carbonitrides, $M_{23}C_6$ carbides, Z phase, Cr_2N and Cu precipitates (*M* in *MX* denotes Nb, Cr, Mo or Fe; *M* in $M_{23}C_6$ stands for Cr) [37–41]. M_7C_3 carbides are also found in Fe-Cr-C alloy [42–44].

2.1. Secondary phases in austenitic steel

2.1.1. MX carbonitrides

Fig. 3(a, b) exhibits the initial morphologies of *MX* (*M* = Nb, *X* = C or N) carbonitrides. Generally, block-shaped *MX* carbonitrides with nano-size are nucleated densely along dislocations, whose size is increased with the isothermal holding time [45,46]. The formation of *MX* carbonitrides has been investigated by short-term annealing at temperatures around 700 °C, and *MX* carbonitrides are identified as intragranular carbonitrides with an fcc crystal structure. The precipitation of these carbonitrides would lead to the retardation of dislocation movements and then improve the creep strength at high temperatures [47]. Stabilizing alloying componants like Ti, Nb, V have a higher affinity to carbon than chromium, which is beneficial to the formation of *MX* carbonitride. Thus, strong carbide-forming alloying elements are usuallyintroduced to retard the formation of $M_{23}C_6$ carbides [12,48–51]. Besides, the higher nitrogen content can also contribute to the formation of *MX* carbonitride [52–55]. Above all, *MX* carbonitrides are the predominant precipitates for the strengthening of austenitic heat-resistant steels.

2.1.2. $M_{23}C_6$ phase

Another type of predominant precipitate in austenitic steels is $M_{23}C_6$ carbide with an fcc crystal structure. The relationship between $M_{23}C_6$ and grain boundary serration has been reported in several recent works. The carbides formed on grain boundaries are coherent with one of the grains following $(11\bar{1})_{M23C6}//(11\bar{1})_{\gamma}$. Orientation relationships between $M_{23}C_6$ carbides and the matrix along grain boundaries follow $(200)_{M23C6}//(200)_{\gamma}$,$(\bar{1}3\bar{1})_{M23C6}//(\bar{1}3\bar{1})_{\gamma}$and $(\bar{2}20)_{M23C6}//(\bar{2}20)_{\gamma}$ [56]. Typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of $M_{23}C_6$ carbides in TP347H austenitic heat-resistant steel are presented in Fig. 3 (c, d) [45]. The rod-like $M_{23}C_6$ carbides have been commonly observed at the grain boundaries after long-term exposures at temperatures around 700 °C, and the precipitation of $M_{23}C_6$ can cause susceptibility to intergranular corrosion [57–60]. $M_{23}C_6$ carbides generally nucleate and grow along grain boundaries. In the areas with high density of dislocation, $M_{23}C_6$ phases can also be observed. Fig. 4 illustrates the distribution of rod-shaped $M_{23}C_6$ along dislocation lines in S31042 austenitic heat-resistant steel [56]. However, the discontinuous $M_{23}C_6$ particles with small size at grain boundaries may contribute to the resistance against grain boundary sliding, leading to improvement of creep strength.

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