Kinetics of cellular precipitation in a 24Cr-15Ni-4Mn-0.03C-0.35N steel

M. E. RODRIGUEZ-CASTILLO, V. M. LOPEZ-HIRATA, M. L. SAUCEDO-MUÑOZ, H. J. DORANTES-ROSALES *Instituto Politecnico Nacional (ESIQIE), Apartado Postal 118-018, Admon. GAM, Mexico, D.F. 07051*

The precipitation process for austenitic stainless steel is extremely complex. For example, more than eigthteen different precipitates were reported for an isothermallyaged type 316 steel [1]. Thermal processing can promote intergranular and transgranular precipitation of carbides, nitrides, and other phases. Furthermore, the exposure of austenitic stainless steels to relatively high temperatures has been reported [1, 2] to cause the deterioration of mechanical properties, including ductility and toughness. In addition to the transgranular and intergranular precipitation, discontinuous or cellular precipitation has been observed to occur in different aged austenitic stainless steels. The following cellular precipitations $\gamma \to \gamma + Cr_2N$ and $\gamma \to \gamma + M_{23}C_6$ were reported to take place in N-containing and C-containing austenitic stainless steels, respectively [3, 4]. Additionally, the cellular precipitation of Cr_2N was reported [2] to cause a decrease in toughness for an aged 19Cr-5Mn-5Ni-0.2N-0.7 N steel.

The purpose of this work was to study the kinetics of cellular precipitation for an isothermally aged 24Cr-15Ni-4Mn-0.03C-0.35N austenitic stainless steel.

The material used in this work was a forged-steel plate and its chemical composition was 0.03 wt% C, 0.35 wt% N, 4 wt% Mn, 25 wt% Cr, 15 wt% Ni, 0.01 wt% Al, 0.002 wt% S and 0.025 wt% P. The solution treatment of this steel was carried out at 1273 K for 3600 s under an argon atmosphere, and it was then waterquenched. The aging temperatures and times were 973, 1073, 1123 and 1173 K from 600 to 540000 s, respectively. All samples were encapsulated in a quartz tube with an argon atmosphere prior to the different heat treatments. Samples were prepared metallographically and etched with Villela's reagent and observed with a scanning electron microscope (SEM) at 20 kV. The SEM/EDX microanalysis of the precipitates was also carried out using the extraction replica technique [1]. The precipitates in the aged samples were extracted electrolitically by dissolution of the austenitic matrix in a solution of 10 vol%HCl-CH₃OH at 4 volts. The X-ray diffraction patterns of extracted precipitates were measured with a diffractometer using K_{α} Cu radiation.

The SEM observation of the solution treated sample showed no precipitation, and a mean austenite grain size of about 162 μ m. Fig. 1 shows the SEM micrographs of samples aged at 973, 1073, and 1123 K for different times. The intergranular precipitates were formed during the early stages of all aging treatments. The volume fraction and size of intergranular precipitates increased with aging time. The cellular precipitation took place after the intergranular precipitates covered

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almost all the grain boundary. Small transgranular precipitates were observed to form almost simutaneously to the cellular precipitation. The above sequence of precipitation is in agreement with that observed in high nitrogen austenitic stainless steels; however, no transgranular precipitation was detected for this type of steel [4]. The XRD patterns indicated the presence of two phases M_2N and $M_{23}C_6$ in the aged samples. The SEM microanalysis of precipitates revealed that the intergranular precipitates were carbides and nitrides, mainly composed of chromium. The lamella of cellular precipitates and transgranular precipitates were chromium nitrides. Thus, the isothermal aging of this steel promoted the cellular precipitation of $Cr₂N$. The celullar precipitation of Cr_2N has been reported [4, 5] to occur in N-containing Cr-Ni and Cr-Mn steels with N contents from 0.4 to 0.97%. The cellular precipitation started from grain boundaries and its morphology was close to a hemispherical shape. The precipitate lamellae were not regularly aligned, and rod-shaped precipitates were observed in some parts. The volume fraction of $Cr₂N$ within the cells decreased with aging time. These characteristics were also observed in the cellular precipitation of N-containing Cr-Ni steels [4]. Fig. 2 shows the change in volume fraction of a cellular precipitate as a function of time for aging treatments at 973, 1073, 1123 and 1173 K. The volume fraction of cellular precipitates increased with aging time and was a maximum, 0.092, for aging at 1073 K. Kikuchi *et al.* [4] reported volume fractions of about 0.13 and 0.6 for steels with a nitrogen content of 0.42 and 0.59%, respectively. This confirms that the volume fraction of cellular precipitation never reached the value of 1 (100%) in this steel composition, 0.35% N. The analysis of the plot of the volume fraction vs. aging time, Fig. 2, was carried out using the Johnson-Mehl-Avrami equation. A time exponent *n* was determined to be about 0.87. This value is close to 1, which was found in the cellular precipitation for N-containing Cr-Ni steels [4]. An exponent *n* of 3 was determined for the cellular precipitation in binary alloys [5]. In contrast, an exponent *n* of about one was determined in a multicomponent alloy system, in which the diffusion rate is expected to be slower than that in a binary alloy. The shortest incubation time of cellular precipitation was about 600 s for aging at 1073 K. This aging temperature also promoted the fastest overall precipitation kinetics for this steel. Kiuchi *et al.* [4] pointed out that the higher the N content, the shorter the incubation time for the cellular precipitation in Cr-Ni-Mn steels with a Cr content similar to that of this work. This behavior

Figure 1 SEM micrographs of samples aged for (a) 1800, (b) 3600, and (c) 21600 s, at 1123 K, for (a) 1800, (b) 3600, and (c) 21600 s at 1073 K, and for (a) 1800, (b) 3600, and (c) 21600 s at 973 K.

is attributed to the faster nitrogen diffusion in steels containing higher initial nitrogen concentration [6]. They found that the incubation time is shorter than 3600 s for nitrogen contents higher than 0.50%. That is, the incubation time was expected to be longer than 3600 s for the cellular precipitation of the aged 24Cr-15Ni-4Mn-0.03C-0.35N steel . This discrepancy in incubation time might be attributed to the increase in Cr diffusion during the aging of this steel. That is, the addition of chromium to the iron lattice increases the interatomic bond strength in the austenitic lattice, which decreases the rate of difusión [7]. The aging of 24Cr-15Ni-4Mn-0.03C-0.35N steel caused the formation of intergranular Cr_2N and $Cr_{23}C_6$ precipitates. Thus, the austenite matrix had a Cr depletion near the grain boundaries. This fact increased its diffusion rate in this area, promoting faster kinetics of cellular precipitation. The change in interlamellar spacing as a function of aging time for aging treatments at 973, 1073, 1123, and 1173 K is shown in Fig. 3. The interlamellar spacing increased with aging temperature and time. This behavior is different from that observed for the typical cellular precipitation with a constant interlamellar spacing in binary alloy systems [9]. Fig. 4 shows the change in mean migration rate of the moving cell boundary with time for aging at 973, 1073, 1123, and 1173 K. The order of magnitude for migration rate for this work is in agreement with those reported in the cellular precipitation for N-containing Cr-Ni steels [4]. The migration rate shows a decreasing tendency with time. Its change is more clearly marked during the early stages of aging. This behavior is also contrary to the constant migration rate detected in the cellular precipitation of binary alloy systems [9]. The increase in lamellar spacing and decrease in migration rate with time have also been observed in austenitic steel

Figure 2 Volume fraction of cellular precipitate vs. aging time at 973, 1073, 1123, and 1173 K.

Figure 3 Interlamellar spacing of cellular precipitation vs. aging time at 973, 1073, 1123, and 1173 K.

Figure 4 Mean migration rate of moving cell for cellular precipitation vs. aging time at 973, 1073, 1123, and 1173 K.

containing from 0.42 to 0.97% N [4, 5]. In the theories of steady cooperative growth [9, 10], the migration rate is inversely proportional to the lamellar spacing. Thus, if the interlamellar spacing decreases, the migration rate increases. However, there is no theory for unsteady cooperative growth to explain the above behavior [8].

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