Communication

Precipitation of Nanosized MX at Coherent Cu-Rich Phases in Super304H Austenitic Steel

PING OU, HUI XING, and JIAN SUN

The present investigation of transmission electron microscopy reports the precipitation of nanosized and cubical-shaped incoherent Nb-rich MX at the coherent Cu-rich phases in the austenitic matrix of the Super304H steel. In addition, the nanosized Nb-rich MX phases were often observed to precipitate on dislocations during creep. It is concluded that the dense incoherent Nb-rich MX and coherent Cu-rich precipitates with a nanosized diameter contribute excellent creep resistance in the steel.

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Super304H austenitic steel is based on 18/8 Cr-Ni stainless steel alloyed mainly with about 3 pct Cu and a small amount of Nb, which is widely used in ultra-super critical (USC) power plants due to its excellent high-temperature performance, especially the outstanding high-temperature creep resistance.[1,2] The outstanding creep strength at high temperature of Super304H steel arises from the precipitation of nanosized Cu-rich and MX (Nb(C, N)) phases in the austenitic matrix during service at high temperatures.[1] Among these two kinds of precipitates, the nanosized Cu-rich phase is regarded to be of the most significant precipitation strengthening effect in Super304H steel, and many studies have concentrated on the precipitation behaviors and strengthening effect of the nanosized Cu-rich phase in Super304H austenitic steel.[3–5] In contrast, the precipitation of nanosized MX phase in Super304H austenitic steels receives little attention until now.

The precipitation of MX phase occurs when strong carbide/nitride former elements like Ti, Nb, V, and etc. are added in steels. One of the main aims of adding these elements is to stabilize the steels against intergranular corrosion during service at elevated temperature since most of carbon is tied up by MC. Additionally, MC carbides form in preference to $M_{23}C_6$, lessening sensitisation and improving mechanical properties.[6–9] The growth rate of MX is usually thought to be lower than other carbides, and the precipitation of fine MX carbides in the steels provides good creep resistance at elevated temperature.[10] The MX precipitates have a NaCl face-centered cubic structure. They have a typical shape of thin platelet and a Baker–Nutting (B–N) orientation relationship with the matrix of ferritic steels.[11] Meanwhile, the MX precipitates usually have a characteristic cuboidal shape and a cube-on-cube orientation relationship with the matrix of austenitic steels. In this work, the nanosized MX precipitates in Super304H austenitic steel after creep test under 250 MPa at 923 K (650 °C) for 447 hours were investigated by transmission electron microscope (TEM). The precipitation of the nanosized MX at Cu-rich phases and formation of the nanosized MX on dislocations have been observed in the Super304H steel. Based on these TEM results, the precipitation mechanism of the nanosized MX phase in Super304H steel was discussed additionally.

The solution-treated Super304H austenitic steel supplied by a steel plant was used for creep test under 250 MPa at 923 K (650 °C) for 447 hours in this study. The samples of the Super304H austenitic steel after creep test were investigated. The chemical composition of the Super304H steel is 0.08C, 0.787Mn, 0.022P, 0.001S, 0.29Si, 8.88Ni, 17.98Cr, 3.066Cu, 0.58Nb, 0.07N, 0.012Al, and 0.0026B (in wt pct) with the balance of Fe. The initial microstructure of the solution-treated Super304H specimens was examined by using JSM-7600F field emission scanning electron microscope (SEM). The TEM samples of the Super304H steel after creep test were prepared by twin-jet electrolytically polishing in a 5 vol pct perchloric acid and 95 vol pct ethanol solution at about 243 K (−30 °C) and at 60 V. TEM observations were conducted on JEM 2100F machine operating at 200 kV with energy dispersive X-ray spectrometer (EDS).

Figure 1(a) shows the initial microstructure of the solution-treated Super304H steel, where equiaxed austenitic grains with an average diameter of about 15 μm and some primary carbide particles can be observed. The EDS result plotted in Figure 1(b) indicates that the primary carbide particles are Nb-rich MX phases. A general feature of deformation microstructure of the Super304H austenitic steel after creep test is shown in Figure 2. High density of wavy dislocations and a large amount of precipitates with nanosized diameter were observed in the austenitic matrix of the steel. Figure 3(a) is a high-resolution TEM micrograph taken along the [011] direction, showing a characteristic Moiré fringes of a cubical-shaped precipitate with a nanosized diameter in the austenitic matrix. The Moiré fringes are parallel to the (1-11) and (11-1) planes of the austenitic matrix, respectively. The measured spacing between the Moiré fringes is consistent with the values given as $1/\Delta \mathbf{g}_1$ and $1/\Delta \mathbf{g}_2$, where $\Delta \mathbf{g}_1 = \mathbf{g}_{(1\text{-}11)\text{MX}} - \mathbf{g}_{(1\text{-}11)\gamma}$ and $\Delta \mathbf{g}_2 = \mathbf{g}_{(11\text{-}1)\text{MX}} - \mathbf{g}_{(11\text{-}1)\gamma}$. These indicate that the Moiré fringes result from a interference between the {111} reflections of the Nb-rich MX phase and austenite. The extra satellite spots around the reflections of the Nb-rich MX phase and the austenitic matrix in the corresponding fast

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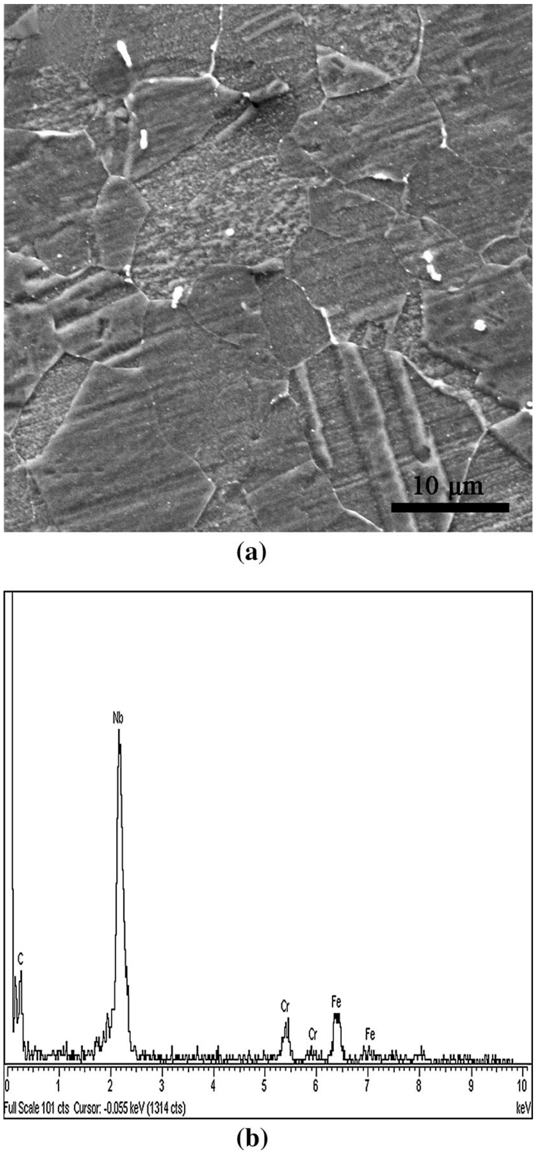


Fig. 1—SEM microstructure of the solution-treated Super304H steel (*a*) and EDS result of the primary MX particle (*b*).

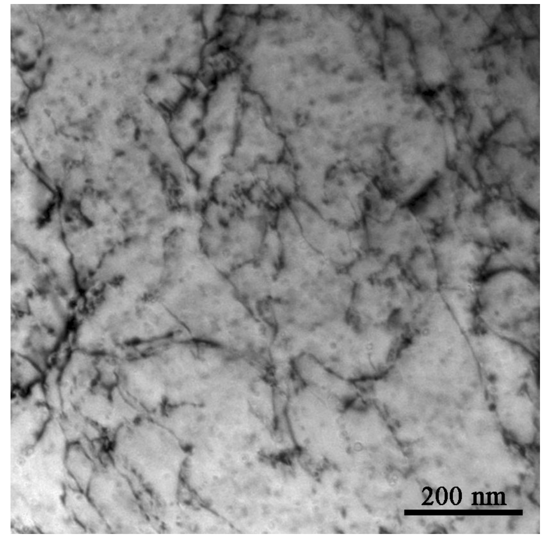
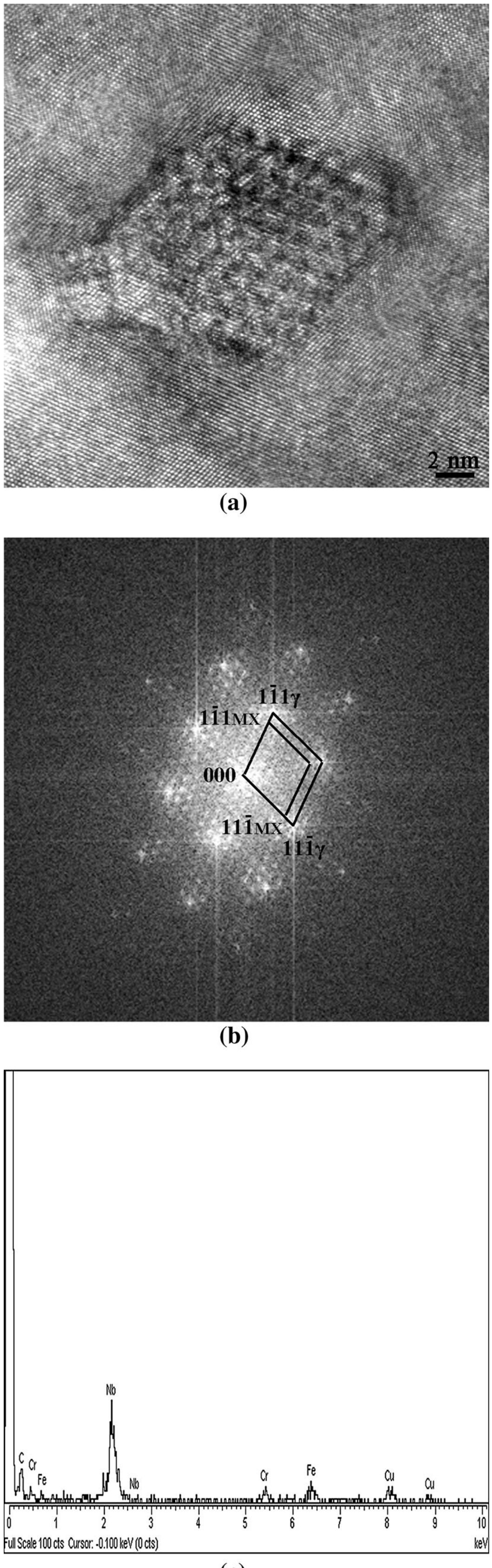


Fig. 2—TEM micrograph of deformation microstructure of Super304H steel crept under 250 MPa at 923 K (650 °C) for 447 hours, showing wavy dislocations and dense-nanosized precipitates in the austenitic matrix.

Fourier transformation (FFT) diffractogram arise from the Moiré fringes, as shown in Figure 3(b). Therefore, the precipitate is identified as Nb-rich MX phase with an fcc structure and has a cubic-on-cubic crystallographic relationship with the austenitic matrix. The EDS result in Figure 3(c) acquired from the precipitate further confirms that the cubical-shaped precipitate is Nb-rich MX phase. The observed habit plane of the nanosized Nb-rich MX precipitate is $\{111\}_\gamma$ in the austenitic matrix. The lattice constant misfit $\Delta a/a$ between the precipitate and austenitic matrix is estimated to be about 24 pct by using the lattice constant of 0.447 nm of the Nb-rich MX phase and of 0.360 nm of the austenitic matrix. This relatively large misfit implies that the interface between the Nb-rich MX precipitate and austenitic matrix is incoherent.

An interesting fact is that the Nb-rich MX phases were often observed to precipitate at the nanosized Cu-rich phases in the austenitic matrix of the steel, as shown in Figure 4(a). The EDS result plotted in Figure 4(b) indicates that the nanosized circular-shaped particle with a weak contrast is a Cu-rich phase. The Nb-rich MX phases with the morphology of Moiré fringes attached the Cu-rich phase with a nanosized diameter as shown in Figure 4(a). Moreover, a high-resolution TEM micrograph taken along the [011] direction, showing the precipitate with characteristic Moiré fringes attached to the nanosized Cu-rich particle in the austenitic matrix, is shown in Figure 5(a). The characteristic Moiré fringes are the same to those shown in Figure 3(a). The corresponding FFT diffractogram acquired from the Moiré fringes shown in Figure 5(b) is consistent with that shown in Figure 3(b). These indicate that the nanosized precipitate with characteristic Moiré fringes is Nb-rich MX phase, which precipitates at the Cu-rich particle with a nanosized diameter. Figure 5(c) is an FFT diffractogram acquired from the interface area between the Cu-rich particle and austenitic matrix, confirming a cubic-on-cubic crystallographic relationship and coherency interface between the nanosized Cu-rich particle and austenitic matrix of the steel. Chi et al. proposed a mechanism of precipitation process of Cu-rich phases in the Super304H austenitic steel based on the results achieved by atom-probe tomography (APT) technique.[3] Copper atoms quickly concentrate as a cluster at very early aging stage. With increasing aging time, the copper atoms continuously concentrate to form a Cu-rich phase without crystallographic structure transformation due to the same fcc structure and close lattice parameter of the Cu-rich phase and austenitic matrix. Meanwhile, both Ni and Cr and minor elements such as Nb and interstitial C and N atoms simultaneously diffuse away from the cluster or Cu-rich phase into the austenitic matrix. Therefore, the nanosized Nb-rich MX phases easily nucleate on the



◀Fig. 3—HRTEM micrograph of nanosized and cubical-shaped Nb-rich MX phase with morphology of characteristic Moiré fringes along the [011] direction (*a*), the corresponding FFT diffractogram (*b*), and EDS result (*c*) of Nb-rich MX phase in the austenitic matrix.

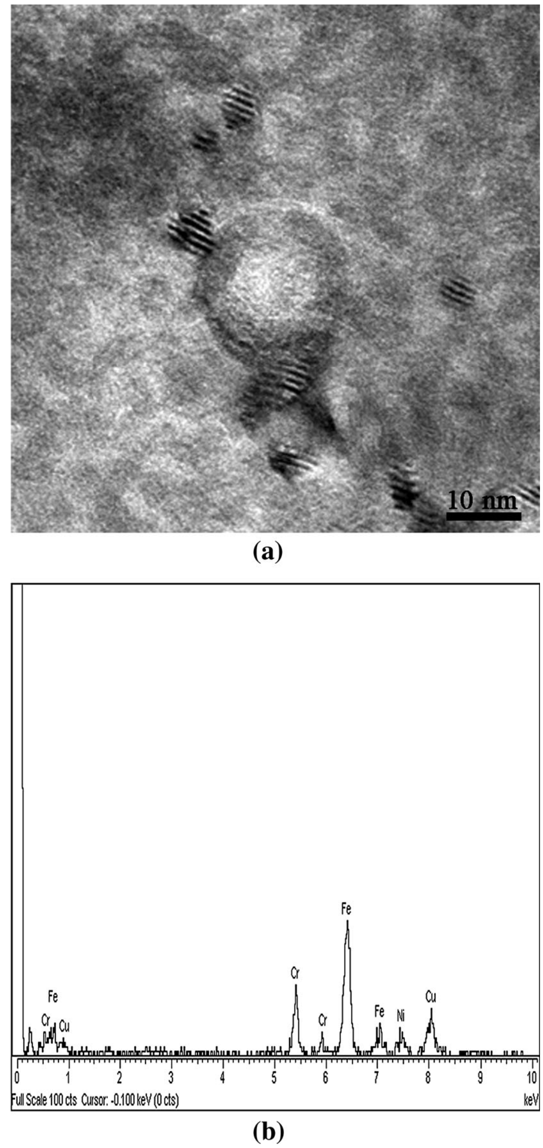
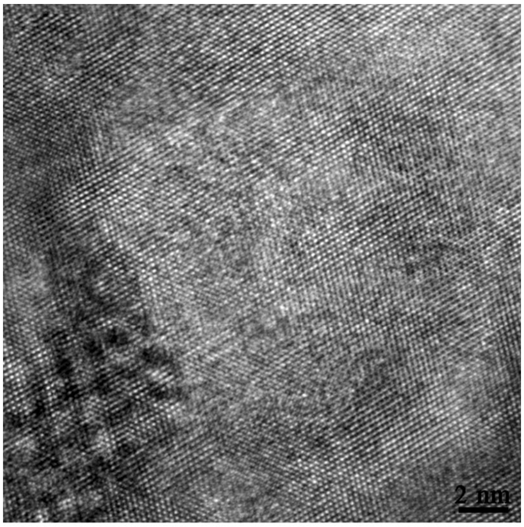


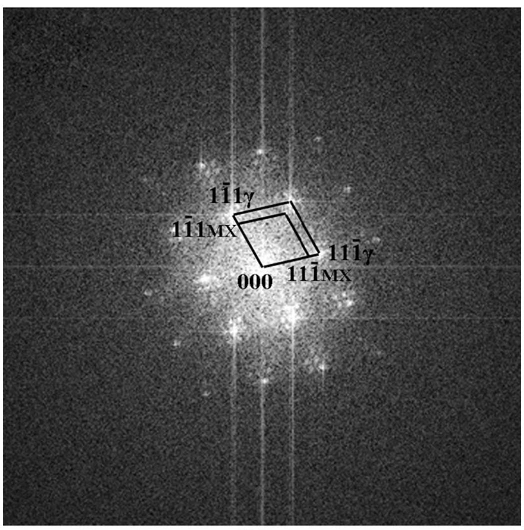
Fig. 4—TEM micrographs of Nb-rich MX phases precipitating at a Cu-rich particle (*a*) and EDS result of the Cu-rich particle (*b*).

interface between the Cu-rich phase and austenitic matrix due to a relatively high concentration of Nb and C atoms at the interface.

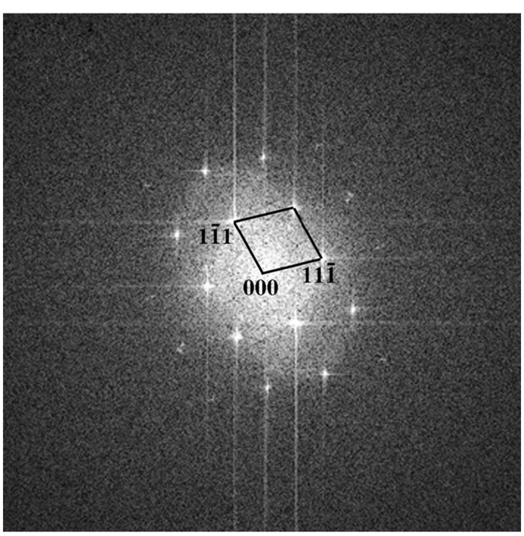
Moreover, the nanosized Nb-rich MX phases with the morphology of Moiré fringes were often observed to precipitate on dislocations, as shown in Figures 6(a) and (b). Figure 6(a) clearly shows that the nanosized cubical-shaped Nb-rich MX with the morphology of char-



(a)

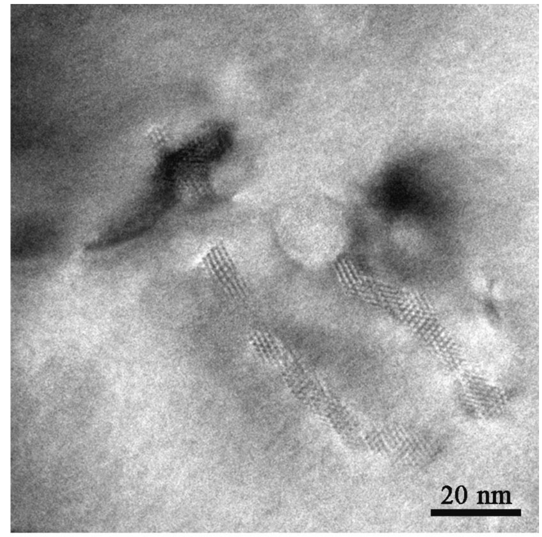


(b)

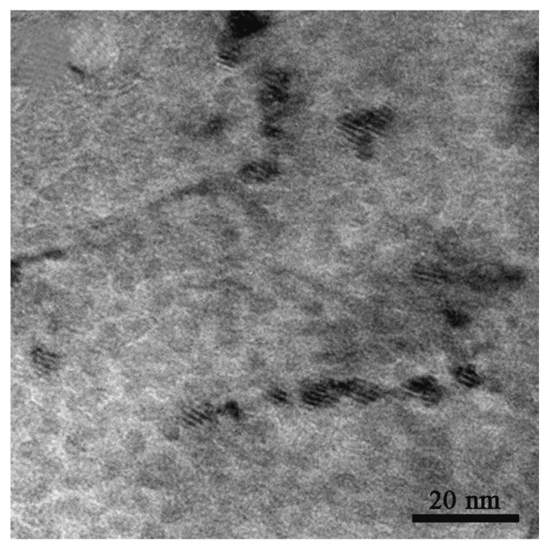


(c)

◀Fig. 5—HRTEM micrograph of Nb-rich MX phase with morphology of characteristic Moiré fringes precipitating at a Cu-rich particle taken along the [011] direction (*a*), the corresponding FFT diffractogram of Nb-rich MX phase (*b*), and the corresponding FFT diffractogram of Cu-rich particle (*c*).



(a)



(b)

Fig. 6—TEM micrographs of Nb-rich MX phases precipitating along dislocations in the austenitic matrix (*a*, *b*).

acteristic Moiré fringes precipitates along a dislocation, which is pinned by a Cu-rich particle. This is because small interstitial C and N atoms are usually clustered at dislocation cores during creep at high temperature and Nb-rich MX phases easily nucleate on dislocations. The above TEM observations indicate that the incoherent Nb-rich MX phases and coherent Cu-rich phases with a nanosized diameter densely precipitate and effectively impede dislocation movement in the austenitic matrix of the steel. The nanosized Nb-rich MX and Cu-rich precipitates are stable and the growth rate is low during creep at high temperature because of their low interfacial energies with the austenitic matrix.[4,12] Therefore, the dense incoherent Nb-rich MX phases and coherent Cu-rich phases with a nanosized diameter contribute excellent precipitation strengthening effect and creep resistance in the Super304H austenitic steel.

In summary, a large amount of precipitates with a nanosized diameter were observed by TEM in the austenitic matrix of the Super304H steel after creep test under 250 MPa at 923 K (650 °C) for 447 hours. The nanosized and cubical-shaped precipitates with the morphology of characteristic Moiré fringes are identified as incoherent Nb-rich MX phases. The precipitation of the nanosized Nb-rich MX phases were often observed at the coherent Cu-rich phases with a nanosized diameter in the austenitic matrix. In addition, the nanosized Nb-rich MX phases were found to precipitate easily on dislocations during creep. It is concluded that the dense incoherent Nb-rich MX and coherent Cu-rich precipitates with a nanosized diameter contribute excellent creep resistance in the Super304H austenitic steel.

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