Effect of Nb Addition on Cu Precipitation in Ferritic Stainless Steel

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Formations of Cu-rich precipitate in 18%Cr-1.5%Cu stainless steels without and with 0.5%Nb have been examined mainly using transmission electron microscopy. The specimens solution-treated at 1250°C were isothermally transformed at various temperatures between 500 and 850°C. Fine spherical Cu-rich solute zones were nucleated in the steels in the beginning of aging. These Cu-rich zones exhibited bcc structure and then transformed into 9R structure with twins during aging. The spherical 9R-Cu particles changed into rod-shaped fcc-Cu particles after prolonged aging. Laves phase of Fe2Nb type started to form in the Nb-added steel almost after finishing nucleation and growth of Cu particles. Addition of Nb in the steel delayed the nucleation of the Cu-rich zones due to slow diffusion of Nb atoms in ferrite.

KEY WORDS: ferritic stainless steel; Cu precipitation; Nb addition; transmission electron microscopy (TEM).

1. Introduction

As for the Cu containing steels, it is well known that strength, high temperature strength and fatigue strength are improved by Cu precipitation. And, as well as a study about the Cu precipitation behavior, its effects to the texture and formability have been reported. According to the published phase diagrams of Fe–Cu binary system, the maximum solubility of copper in ferrite is 2.2 mass% at 850°C. The solubility of copper in ferrite, cα, is expressed as log[cα] = –4500/T+4.335, e.g. cα = 0.5 and 0.03 mass% at 700 and 500°C, respectively. Small solubility of Cu in ferrite leads to the formation of Cu particles during aging in Cu added steels. Process of Cu precipitation in ferrite has been reported as follows; (i) nucleation of the coherent spherical Cu-rich zones with bcc structure, (ii) transformation of bcc Cu-rich zones into multi-twinned particles with 9R structure, and (iii) transformation of 9R Cu-rich particles into fcc-Cu particles with shape change from sphere to rod. The shape change of Cu particle from sphere to rod is associated with coherency loss. Precipitation of Cu particles in stainless steels can also be found in the literature. Soylu and Honeycombe studied formation of Cu precipitates in a duplex stainless steel. They reported that first stage of Cu precipitation in ferrite was the formation of bcc coherent Cu-rich zones and bcc Cu-rich zones transformed to fcc Cu particles. Formation of Cu particles in a PH 15-5 stainless steel was studied in detail by Habibi Baiguirani et al. They showed that Cu-rich precipitation in a PH 15-5 began with the formation of coherent bcc clusters which subsequently transformed to twinned 9R, 3R and fcc-Cu particles. Murayama et al. reported that the chemical composition of the bcc Cu-rich clusters in a PH17-4 stainless steel has been found to be 55at%Cu, 30at%Fe, 10at%Cr and 5at%Ni. Rejection of Fe, Cr and Ni from Cu-rich cluster occurred during aging and concentration of coarsened fcc-Cu particles was almost 100at%Cu. Cu addition in stainless steels is also utilized from the viewpoints of corrosion resistance and antimicrobial activity. In addition, there is a case to add Nb to obtain superior corrosion resistance and mechanical properties in ferritic stainless steels. Niobium in ferritic stainless steels is known as a beneficial element to increase high temperature strength. Fujita et al. showed that an increase in 0.2% proof strength of a ferritic 19%Cr steel at 950°C by Nb addition is much greater than those by other elements such as Si, P, Ti, Mo, W, Hf and Ta. They suggested that increase in strength caused by Nb addition is mainly due to solid solution strengthening. Although there are many studies on the effects of Cu or Nb additions on the phase transformation and mechanical properties in steels, the effect of Nb addition on the formation of Cu precipitates in a ferritic stainless steel has not been well understood. The purpose of the present study, therefore, is to reveal the effect of Nb addition on Cu precipitation in a 18%Cr ferritic stainless steel.

2. Experimental Procedures

Ferritic stainless steel sheets marked with E1, E2 and E3, of 2 mm thick manufactured in the laboratory were used. The chemical compositions of the steels in mass% are shown in Table 1. The steels are based on a 18%Cr stainless steel with low impurities. The E1 and E2 steels contain 0.48%Nb and 1.53%Cu, respectively. Both 0.47%Nb and 1.57%C are contained in E3 steel. Specimens in 10 mm wide and 10 mm long were machined from the steels. They
were solution-treated at 1250°C for 0.6 ks and quenched into iced brine. Then, they were isothermally aged at various temperatures from 500 to 850°C for 0.01–86.4 ks. Thin foils for transmission electron microscopy (TEM) were prepared by twin-jet polishing technique using an electrolyte containing 90 vol% acetic acid and 10 vol% perchloric acid. They were examined in transmission electron microscopes, JEM100CX, JEM2100 equipped with energy dispersive spectroscopy (EDS) detector and JEM3010, operating at 100, 200 and 300 kV, respectively. Hardness measurements were carried out on both solution-treated and aged specimens at room temperature under 500 gf load. Average hardness was calculated from five measuring points.

3. Results

3.1. Vickers Hardness Measurements

The age-hardening curves at temperatures between 500 and 850°C are shown in Fig. 1. Circles, triangles and squares in Fig. 1 represent results for E1, E2 and E3 steels, respectively. Average values of Vickers hardness (Hv) for E1 and E2 steels after solid solution treatment (SST) were the same as 138, while that for E3 steel was 19 higher than those for the other steels. The Hv of E1 steel hardly changed during aging at all temperatures examined. The Hv of E2 and E3 steels, on the other hand, exhibited a large increase followed by a decrease during aging. The increase in Hv began more quickly at higher aging temperatures. Peak hardness during aging was decreased as increasing in aging temperature. Furthermore, the peak hardness in E3 steel is almost the same as that in E2 steel, indicating an increase in Hv in E3 by aging is smaller than that in E2. The age-

Table 1. Chemical compositions of the steels used in the present study (in mass%).

| No | C  | Si | Mn | P  | S  | Ni | Cr | Mo | Cu | Ti | Al | Nb | O  | N  |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| E1 | 0.002 | 0.04 | 0.01 | 0.01 | 0.0009 | 18.4 | 0.01 | 0.01 | 0.05 | 0.04 | 0.48 | 0.0036 | 0.004 |
| E2 | 0.001 | 0.03 | 0.01 | 0.01 | 0.0006 | 18.4 | 0.01 | 1.53 | 0.05 | 0.04 | 0.02 | 0.0085 | 0.004 |
| E3 | 0.002 | 0.06 | 0.01 | 0.01 | 0.0007 | 18.4 | 0.01 | 1.57 | 0.05 | 0.04 | 0.47 | 0.0057 | 0.004 |

Fig. 1. Vickers hardness change during aging at (a) 500, (b) 600, (c) 700, (d) 800 and (e) 850°C. Circles, triangles and squares represent the results for the E1, E2 and E3 steels, respectively.

Fig. 2. TEM micrographs for the E1 steel aged at 700°C for (a) 0.9 and (b) 14.4 ks, respectively. Arrows in (a) indicate formation of plate-shaped precipitates. (c) TEM micrograph for the E1 steel aged at 700°C for 86.4 ks. Selected area diffraction pattern taken from Fig. 2(c) is shown in (d). Key diagram of Fig. 2(d) is illustrated in (e). Solid circles and open circles in (e) correspond to diffraction spots of Laves phase and ferrite matrix, respectively. Subscript letters $\alpha$ and $L$ denote ferrite matrix and Laves phase, respectively. Cross marks indicate double or triple reflections.
hardening curve in E3 steel shifted to the longer aging time. It implies that Nb addition in a Cu-added ferritic stainless steel delays age-hardening behavior. Such the delay of increment in hardness by Nb addition in Cu-added ferritic stainless steel can be found in all the temperature range examined.

### 3.2. TEM Observations

Figures 2(a), 2(b) and 2(c) show the bright field images taken from E1 steels aged at 700°C for 0.9, 14.4 and 86.4 ks, respectively. Selected area diffraction pattern (SAD) taken from Fig. 2(c) is shown in Fig. 2(d). Key diagram of Fig. 2(d) is illustrated in Fig. 2(e). Plate-shaped particles indicated by arrows in Fig. 2(a) started to form in the matrix after aging for 0.9 ks. The particles were coarsened by prolonged aging as shown in Figs. 2(b) and 2(c). Analysis of SAD shown in Fig. 2(d) reveals that the particles are Fe2Nb type Laves phase. The crystallographic orientation relationship between the Laves phase (L) and the ferrite matrix (α) is analyzed as (112)α//(0001)L and (110)α//(0110)L.

Bright field images of E2 steel aged at 700°C for 0.03, 0.3, 1.8 and 86.4 ks are shown in Figs. 3(a) to 3(d), where the incident electron beam was adjusted to nearly parallel to the [111]α direction. Enlarged images of Figs. 3(a) and 3(b) are inserted in each figure. Fine spherical zones less than 10 nm in diameter as indicated by arrows were observed in Fig. 3(a). The spherical zones exhibited uniform contrast in the bright field image. Only diffraction spots from ferrite matrix could be detected in the SAD taken from Fig. 3(a). Growth of the spherical zones was observed in Fig. 3(b). Some of the spherical particles exhibited striped contrast parallel to [110]α direction in the matrix as indicated by an arrow. Coarsening of spherical particles was observed in Fig. 3(c). Some of spherical particles started to change their shape into rod as indicated by arrows in Fig. 3(c). After aging for 86.4 ks, all particles became coarse rod-shaped as shown in Fig. 3(d). The SAD taken from a dotted circle area in Fig. 3(d) is shown in Fig. 3(e). Key diagram of Fig. 3(e) is illustrated in Fig. 3(f). Analysis of the SAD revealed that the rod-shaped particles exhibited fcc structure with near Kurdjumov-Sachs (K-S) orientation relationship with the matrix. The fcc-Cu particle analyzed in Fig. 3(d) exhibited {111} fcc twin variants, which can be known from stereographical analysis of Fig. 3(f). Condensation of copper was detected by composition analysis of the rod-shaped particles by EDS. Therefore, formations of the spherical zones, the spherical

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**Fig. 3.** TEM micrographs for the E2 steel aged at 700°C for (a) 0.03 and (b) 0.3 ks, respectively. TEM micrographs for the E2 steel aged at 700°C for (c) 1.8 and (d) 86.4 ks, respectively. Selected area diffraction pattern taken from a dotted circle area in Fig. 3(d) is shown in (e). Key diagram of Fig. 3(e) is illustrated in (f). Solid circles and open circles in (f) correspond to diffraction spots of fcc-Cu phase and ferrite matrix, respectively. Two Cu phase variants are observed and exhibit twin relationship. Subscript letters α and Cu denote ferrite matrix and fcc-Cu phase, respectively. Cross marks indicate double or triple reflections.

**Fig. 4.** (a) High resolution TEM image for the E2 steel aged at 700°C for 0.03 ks. (b) the Fourier transformed pattern of (a).

**Fig. 5.** (a) High resolution TEM image for the E2 steel aged at 700°C for 0.3 ks. (b) the Fourier transformed pattern of (a). (c) a simulated diffraction pattern of ferrite, α, and two 9R-structure variants. (d) a diffraction pattern illustrated by taking into account the occurrence of double reflections in (c).
particles with striped contrasts and rod-shaped particles should be related to copper condensation, i.e. Cu precipitation. **Figure 4**(a) shows a high resolution TEM image of a spherical zone observed in Fig. 3(a). Figure 4(b) shows a Fourier transformed (FT) pattern of Fig. 4(a). The incident electron beam was parallel to the \([1\bar{1}1]_\alpha\) direction. It was confirmed that the spherical zone had bcc structure and was coherent with the matrix. **Figure 5**(a) is a high resolution TEM image of a spherical particle with striped contrast shown in Fig. 3(b). The incident electron beam was parallel to the \([1\bar{1}1]_\alpha\) direction. A dotted circle indicates the interface between the spherical particle and the matrix. Atomic arrangements of the spherical particle exhibited a herringbone type contrasts corresponding to multi-twinning. Twin planes were almost parallel to \([1\bar{1}0]_\alpha\). **Figure 5**(b) shows a FT pattern of Fig. 5(a). **Figure 5**(c) shows simulated diffraction patterns of ferrite and two variants of 9R-structure with orientation relationship between ferrite and a 9R-structure variant as \([\bar{1}1\bar{1}]_\alpha//([\bar{1}1\bar{1}])_{R-Cu}\) and \(([\bar{1}1\bar{1}]_\alpha//([\bar{1}1\bar{1}])_{R-Cu}\). The diffraction simulation was carried out using the software, Desktop Microscopist, by the Lacuna Laboratories. In the diffraction simulation the 9R-structure variants hold twin relationship whose twin plane is \((\bar{1}1\bar{4})_{R-Cu}//(110)_\alpha\). By taking account of double reflections in **Fig. 5**(c), a diffraction pattern in **Fig. 5**(d) is obtained. All spots (intensities) in the FT pattern in **Fig. 5**(b) can be explained by referring to **Fig. 5**(d). Thus, the particle in **Fig. 5**(a) is of 9R structure with twins whose twinning plane is parallel to \((\bar{1}1\bar{4})_{R-Cu}//(110)_\alpha\). The 9R-Cu particles and the ferrite matrix were related by the orientation relationship: \([\bar{1}1\bar{1}]_\alpha//([\bar{1}1\bar{1}])_{R-Cu}\) and \((\bar{1}1\bar{4})_\alpha//([\bar{1}1\bar{4}])_{R-Cu}\) which was found in the previous studies.17,18,23)

**Figures 6**(a) and 6(b) are the bright field images of E3 steel aged at 700°C for 0.3 and 1.8 ks, respectively. Spherical Cu-rich zones finely dispersed in the matrix can be found in **Fig. 6**(a), where the maximum hardness was obtained in E3 steel. Coarsening of Cu particles was observed in **Fig. 6**(b). Rod shaped particles were found in
E3 steel aged at 700°C for 86.4 ks as shown in Fig. 7(a). The SAD taken from Fig. 7(a) is shown in (b), revealing the rod shaped particles were fcc-Cu particles with near K-S orientation relationship to the ferrite matrix. Shape change of Cu particles from sphere to rod was also observed in E3 steel. Homogeneous nucleation of Laves phase\textsuperscript{(23)} in the matrix can be found in Fig. 7(c). The SAD taken from Fig. 7(c) is shown in (d). Key diagram of Fig. 7(d) is illustrated in Fig. 7(e). The crystallographic orientation relationship between Laves phase and the matrix is as follows; (112)\textsubscript{α}/\textsubscript{(0001)}\textsubscript{h}, and (110)\textsubscript{L}/\textsubscript{(0110)h}, which is the same as that found in Fig. 2(d). Heterogeneous nucleation of Laves phase on Cu particles was also found as shown in Figs. 8(a) and 8(d). The SAD taken from Figs. 8(a) and 8(d) are shown in Figs. 8(b) and 8(e), respectively. Key diagram of Fig. 8(b) is illustrated in Fig. 8(c). The Laves phase particles nucleated on the edge or the side of rod-shaped Cu particles.

4. Discussion

4.1. Hardness Change during Isothermal Aging

The Hv of E1 and E2 steels after SST were the same as 138. The Hv of a binary Fe–18%Cr alloy after SST was measured separately as 121. Therefore, the amounts of solid solution hardening by 0.48%Nb in E1 steel and 1.53%Cu in E2 steel were 17 Hv. Increment in hardness by 0.48%Nb (=0.28at%Nb) addition in a 18%Cr steel (E1 steel) after SST was the same as that in a 18%Cr steel with 1.53%Cu (=1.33at%Cu) (E2 steel). The amount of Nb atoms, 0.28 at%, in E1 steel is about one fifth of that of Cu atoms, 1.33 at%, in E2 steel, implying that the effect of solid solution hardening by Nb atoms is five times greater than that by Cu atoms. Since the amount of solid solution hardening by additions of both 0.47%Nb and 1.57%Cu into a 18%Cr steel (E3 steel) was 36 Hv, the effect of simultaneous addition of Nb and Cu atoms on Hv seems to almost follow additivity rule. This implies that solute Nb and Cu atoms in E3 steel exist in the ferrite matrix independently.

Although precipitation of Laves phase in E1 steel was observed during aging, age-hardening was hardly observed in E1 steel. Since formation of Laves phase consumes solute Nb atoms, an increase in hardness by the formation of Laves phase should accompany a decrease in hardness by loss of solution hardening by solute Nb atoms. For E1 steel, the effect of precipitation hardening was cancelled out by chance due to the solute depletion in the matrix. According to another experiment by authors, the change of Hv during aging at 700°C in a 18%Cr steel with 0.87%Nb was also measured and age hardening by precipitation of Laves phase was detected. It can be said that the balance between solid solution hardening and precipitation hardening will determine age-hardening processes of Nb added stainless steels.

Large increase in Hv during aging was observed in E2 and E3 steels due to formation of fine Cu-rich zones. The maximum hardness in E2 and E3 steels decreases with increasing in aging temperature, implying that volume fraction of Cu precipitates decreases or inter-particle distance of Cu precipitates increases with increasing in aging temperature. Since solubility of Cu in ferrite increases with increasing temperature,\textsuperscript{(9,10)} volume fraction of Cu precipitates in E2 and E3 steels should be decreased in the higher temperature range. After onset of a decrease in Hv, the Cu particles having 9R-structure were started to observe. This implies that the decrease in Hv could be related to not only an increase in the distance between the Cu-rich zones by coarsening but also structural change of the zones from bcc to 9R-structure. Deformation mechanism of the steels is expected to change from the cutting of the zones to the Orowan-type or cross-slip around 9R-Cu particles. The change of Hv by the formation of Cu-rich precipitates is governed by various factors, i.e., precipitate size, volume fraction, concentration and structure of the Cu-rich zones/particles, which will be examined in future. It should be noted that onset of increase in Hv by the formation of Cu-rich zones is retarded in E3 steel. Since the Laves phase was not observed in the early stage of formation of Cu-rich zones in E3 steel, it is considered that solute Nb atoms suppressed the formation of Cu-rich zones.

4.2. Retardation of Cu precipitation by Solute Nb Atoms

Retardation of nucleation of Cu-rich precipitates by solute Nb atoms was detected in all temperature ranges examined (by reference to Fig. 1). The Cu precipitation began with the formation of Cu-rich solute zones in both E2 and E3 steels. The effect of solute Nb atoms on the formation of Cu-rich solute zones will be discussed as follows.

The atom probe studies have shown that bcc Cu-rich zones in binary Fe–Cu alloy contained substantial amount of Fe.\textsuperscript{(14,33)} Goodman et al. reported that nanometer sized Cu-rich zones contained approximately 50%Fe.\textsuperscript{(14)} In commercial steels containing Ni, Mn and Al bcc Cu-rich zones in nanometer size contained relatively large amounts of Fe, Ni and Al.\textsuperscript{(39)} Furthermore, the computer simulation with Cahn–Hilliard diffusion equation revealed that a nucleus of Cu-rich precipitate contained large amount of Fe in the early stage of Cu precipitation.\textsuperscript{(36)} Therefore, bcc Cu-rich spherical zones observed in the early stage of aging in E3 steel might contain substitutional constitutive element, such as Fe, Cr and Nb. However, the inclusion of Nb atoms in the Cu-rich zones seems to be unfavorable and Nb atoms should diffuse outward from the zones during nucleation of the zones for the following reasons. The interaction parameter, L, of thermodynamic expression for regular solutions in a binary system indicates how two different atoms will interact in each other. The L in X–Y binary system is defined as

\[ L = \frac{2N_A(E_{XY} - E_{XX} - E_{YY})}{N_{XX} + N_{YY}} \]

where \( z \) is coordination number, \( N_A \) is Avogadro’s number and \( E_{XY} \) is bond energy per atom pair between X and Y atoms, \( E_{XX} \) and \( E_{YY} \) are also defined as that of \( E_{XX} \) and \( E_{YY} \). If \( L < 0 \), the atoms in the solution prefer to be surrounded by atoms of the opposite type, while if \( L > 0 \), the atoms prefer to be surrounded by atoms of their own kind. The interaction parameter of bcc phase in Fe–Cu system, bcc\textsubscript{Fe–Cu}, was reported as bcc\textsubscript{Fe–Cu} = \( (41033-0.622t) \) J/mol, where \( t \) is temperature.\textsuperscript{(77)} Another bcc\textsubscript{Fe–Cu} parameter was also suggested as bcc\textsubscript{Fe–Cu} = \( (39257.976-1.498304t) \) J/mol.\textsuperscript{(38)} Therefore, the values of bcc\textsubscript{Fe–Cu} at 700°C in each case are calculated as 35174 and 35220 J/mol, respectively. On the other hand, interaction parameter of bcc phase in Nb–Cu system, bcc\textsubscript{Nb–Cu}, was reported as 49480.18 J/mol.\textsuperscript{(39)} Since the bcc\textsubscript{Nb–Cu} is much larger than the bcc\textsubscript{Fe–Cu}, the existence of Nb atoms in the Cu-rich zones is more unfavorable.
than the case of Fe atoms. Furthermore, since inclusion of Nb atoms in a Cu-rich zone would increase the strain energy for nucleation of the zones, Nb atoms should be away from the zones. Atomic radii in angstrom of Fe, Cr, Cu and Nb atoms are 1.241, 1.249, 1.278 and 1.426, respectively.\(^{40}\) The atomic radius of Nb is much larger than those of the others. Since atomic radius of Cu is a little larger than that of Fe, lattice parameter of the bcc Cu-rich zone would be larger than that of the matrix which consists of mainly Fe atoms, resulting in a misfit strain at the interface. If Nb atoms were included in the bcc Cu-rich zone, lattice parameter of the zone would be more increased and strain energy barrier for the zone nucleation should increase. Therefore, it has been shown that inclusion of Nb atoms in the bcc Cu-rich zones is not preferable for the zone nucleation from the two points of view, i.e., the interaction parameter, \(L\), and the strain energy for nucleation of the zones.

In the process of Cu-rich zone formation, therefore, outward diffusion of Nb atoms is needed to occur. The outward diffusion of Nb atoms from the Cu-rich zones should lead to formation of Nb-rich zones around them. Actually, the Nb-rich Laves phase nucleated on the Cu-rich precipitates as shown in Fig. 8. The diffusion coefficient of Nb in ferrite is substantially smaller than that of Cu in ferrite.\(^{41}\) For example, according to the diffusion coefficients of Cu and Nb atoms in ferrite, migration distances of Cu and Nb atoms by a random walk at 700°C for 10 s will be 18 and 4 nm, respectively. The migration distance of Nb atoms is about one-fifth of that of Cu atoms. The slow diffusion of Nb atoms would retard the nucleation of the Cu-rich zones. Outward diffusion of Fe and Cr atoms from the Cu-rich zones would also occur. Since their diffusions in E2 and E3 steels are expected to be almost the same in terms of diffusion rate, they are little relation to the retardation of the zone formation.

5. Conclusions

The formations of Cu precipitate in 18%Cr-1.5%Cu stainless steels without and with 0.5%Nb are summarized as follows.

1. Formation of Cu precipitates in ferrite began with nucleation of bcc Cu-rich spherical zones. The bcc Cu-rich zones first transformed into multi-twinned 9R structure and then changed to fcc structure associated with shape change into rod.

2. The initial increase in Hv during aging was caused by the formation of fine spherical Cu-rich zones. The decrease in Hv after the increase in Hv was probably due to not only coarsening of the Cu-rich zones but also structural change of the zones from bcc to 9R-structure. The onset of increase in Hv by the formation of Cu-rich zones was retarded by solute Nb atoms.

3. Solute Nb atoms delayed formation of Cu-rich zones in a ferritic stainless steel. Since the inclusion of Nb atoms in the Cu-rich zones is unfavorable, outward diffusion of Nb atoms from the zones is needed for nucleation of the zones. Since the diffusion of Nb atoms in a ferrite matrix is substantially slower than that of Cu atoms, the formation of the Cu-rich zones is delayed by slow diffusion of Nb atoms.

4. Laves phase, Fe\(_2\)Nb, formed in Nb added ferritic stainless steels during aging. Some of Laves phase particles nucleated on Cu-rich precipitates, implying that outward diffusion of Nb atoms from Cu-rich zones occurred.

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