Scripta Materialia 140 (2017) 18–22

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

Quantitative evaluation of Cu particle dissolution in cold-worked ferritic steel

M. Asano [a,*], T. Masumura [b,c], T. Tsuchiyama [b,c], S. Takaki [b,c], J. Takahashi [d], K. Ushioda [e]

[a] *Graduate Student of Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*
[b] *Department of Materials Science and Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*
[c] *International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan*
[d] *Advanced Technology Research Laboratories, Nippon Steel and Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan*
[e] *Technical Development Bureau, Nippon Steel and Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan*

ARTICLE INFO

Article history:
Received 9 February 2017
Received in revised form 5 May 2017
Accepted 17 May 2017
Available online xxxx

Keywords:
Ferritic steels
Electrical resistivity/conductivity
Three-dimensional atom probe (3DAP)
Severe plastic deformation
Dissolution of precipitates

ABSTRACT

Aged Fe-2%Cu alloys containing precipitated Cu particles with different sizes (peak-aged and over-aged) were cold-worked by wire drawing to investigate the dissolution behavior of the Cu particles. Electrical resistivity measurements quantitatively revealed the increment of solute Cu concentration in the ferrite matrix during working. The peak-aged steel containing finer Cu particles experienced a more rapid dissolution compared with the over-aged steel. Work softening of the peak-aged steel was also found at strains between 3 and 5, because of the reduction in the particle dispersion-strengthening component from the total strength. Finally, further working resulted in the near complete solution of Cu.

Copper (Cu) particles precipitated in steel can effectively increase the yield strength similar to other precipitates such as carbides and nitride, although they are softer than the iron matrix due to their strong interactions with dislocations [1]. It is also known that Cu particles deform plastically during cold working then partially dissolve into the matrix in the higher strain regime [2]. This leads to a relaxation of stress concentration at particle/matrix interfaces and a retardation of void formation at the Cu particles [3]. Therefore, it is expected that the precipitated Cu particles have a lot of potential to become an ideal strengthening factor for steel without the deterioration of its formability. In our previous study [2], deformed Cu particles were experimentally demonstrated to partially dissolve into the iron matrix during cold rolling by means of high-resolution transmission electron microscopy (HR − TEM) and differential scanning calorimetry (DSC). Quantification of the dissolution process was also performed by X-ray diffractometry. However, due to the limited strain level achievable with cold rolling, the dissolution behavior of Cu particles under high strain was not evaluated. Further, the actual distribution of Cu atoms released from the deformed particles in the ferrite matrix is not clear. Here, wire drawing was employed to introduce a wider range of strain. In addition to the over-aged steel studied in previously [2], peak-aged steel was also adopted because of its practical importance. The evaluations of hardness, dislocation density, grain size, and electrical resistivity were conducted during straining to reveal the mechanical behavior associated with the deformation and dissolution of Cu particles. Moreover, the distribution of Cu atoms was clarified by atom probe tomography (APT).

Fe-2.0Cu-0.07Mn-0.01Si-0.001S-0.0069C (mass%) alloy was used in this study. This steel was solution-treated at 1173 K for 0.6 ks in the austenite single phase region, then water-quenched to obtain a massive ferritic structure with supersaturated Cu. The ferrite grain size of the solution-treated specimens was approximately 30 μm. This steel was then annealed at 873 K for 0.06 to 180 ks, followed by wire drawing to obtain a reduction in area up to 99.9% (true strain of 5.3). The microstructure was observed with a transmission electron microscope (TEM, JEOL JEM-2010) operated at 200 kV. TEM specimens were prepared by the twin-jet polishing method using a mixture of 20% perchloric acid and 80% ethanol at liquid nitrogen temperature (77 K). In addition, EBSD analysis using FE-SEM (Zeiss, SIGMA 500) was performed to observe the grain boundary distribution in the transverse section of the drawn specimens prepared by electrochemical polishing and ion milling.

For APT analysis, we employed a three-dimensional atom probe (3DAP) with a large-angle reflectron (Oxford NanoScience) and a local electrode atom probe (LEAP, 4000XHR, Cameca). APT measurements with the 3DAP were performed under conditions where the specimen temperature was 50 K, pulse fraction was 20%, and the pulse repetition rate was 20 kHz. APT measurements with the LEAP were performed in laser mode under conditions where the specimen temperature was 50 K, laser pulse energy was 30 pJ, and the pulse repetition rate was 250 kHz. The pulsed-laser atom probe has a high yielding rate and thus

* Corresponding author.
E-mail address: asano14@takaki.zaiko.kyushu-u.ac.jp (M. Asano).

http://dx.doi.org/10.1016/j.scriptamat.2017.05.025
1359-6462/

was used for the wires with high drawing strains. Atomic datasets were analyzed using the commercial software IVAS (Cameca). Needle tip specimens for APT were fabricated directly from the wire samples using the standard two-stage electropolishing technique. The electrolytes used were 25% perchloric acid in acetic acid for the first stage, and 2% perchloric acid in 1-butoxyethanol for the second stage.

The dislocation density was measured by X-ray diffractometry using Cu-Kα radiation generated at 40 kV and 40 mA, where the Williamson-Hall method [4] was applied to convert the measured local strain to dislocation density. Electrical resistivity was measured with the four-point method [5] at liquid nitrogen temperature (77 K) using 50 mm long wire specimens, with each wire diameter depending on the area reduction from wire drawing. After keeping the specimens in liquid nitrogen for 1 min, the electrical resistivity was measured twice with two different current directions, and the average value was calculated. It is known that Matthiessen's rule (Eq. 1) holds for electrical resistivity (ρ_r).

$$\rho_r = \rho_\mathrm{L} + \rho_\mathrm{i} \tag{1}$$

where ρ_L stems from the lattice vibration and is temperature dependent. ρ_i represents the effects of solute atoms, defects, etc., and is not dependent on temperature. Therefore, by measuring in liquid nitrogen, the effect of ρ_L becomes nearly zero and the effect of solute Cu and dislocations on the electric resistance, ρ_i, can be extracted.

Fig. 1 (a) shows the change in hardness of the Cu steel during aging at 873 K as a function of time. Typical age hardening and over-aging softening behaviors are observed; the peak in hardness appears at 0.6 ks. Generally, it is thought that during the growth of Cu particles in the ferrite matrix, the particles change their crystal structure from bcc to fcc (ε-Cu), via an intermediate 9R structure [6,7]. Othen [7] et al. observed aged Fe-1.3 mass% Cu alloys with HR-TEM and reported that the bcc-Cu transformed to a 9R structure when the Cu particles ripened to 4–5 nm in diameter, and the fcc structure emerged at a Cu particle diameter of around 18 nm. Fig. 1 (b) shows a Cu atom map obtained by APT for the 0.6 ks-aged specimen (peak-aged steel), while Fig. 1 (c) presents a TEM image of the 180 ks-aged specimen (over-aged steel). Fine Cu particles with diameters of 4.4 nm were observed in the peak-aged steel. According to Othen's report [7], from their size, it is speculated that these particles would have bcc or 9R structures. On the other hand, in the over-aged steel, the approximately 35 nm Cu particles were confirmed to be fcc ε-Cu from the selected area diffraction analysis.

Fig. 2 (a) shows the change in hardness with wire drawing of the three specimens, solution-treated, peak-aged, and over-aged steels, as a function of equivalent strain. The hardness of the solution-treated steel monotonously increases with increasing strain. Since there are no Cu particles in this specimen, dislocation strengthening primarily contributes to the hardening, though the effect of grain refinement strengthening would be valid in the high strain regime. In the case of over-aged steel, the hardness changes similarly to that of solution-treated steel in the low strain regime up to 2. In the higher strain regime, though, the hardening rate of over-aged steel is accelerated and the hardness overtakes that of the solution-treated steel and finally reaches 4.0 GPa. This result indicates that the dispersed Cu particles enhanced dislocation accumulation [8] and/or slowed the dynamic recovery process. As with the other specimens, work hardening occurs in the peak-aged steel with increasing strain, though this originally has a much higher hardness meaning that particle-dispersion strengthening and dislocation strengthening can work simultaneously. However, after reaching peak hardness by straining at approximately 3, the hardness tends to slightly decrease, i.e., work softening appears. After further straining above 5, it is interesting that the hardness approaches that of the solution-treated specimen. Fig. 2 (b) shows the dislocation density, ρ_d, measured by X-ray diffractometry for the deformed specimens. The change in dislocation density with strain almost corresponds to that of the hardness of the solution-treated and over-aged steels. The grain boundary distribution was also observed by EBSD for the drawn specimens. Fig. 2 (d) represents orientation imaging maps of the solution-treated, peak-aged, and over aged specimens which are drawn at a strain of 5.3. The grain boundaries are indicated with black lines (misorientation angle >5°). The density of the grain boundary is significantly increased by severe wire drawing; however, almost all boundaries are oriented parallel to the drawing direction. There was no significant difference in the grain refinement behavior during wire drawing among specimens. These measurements revealed that the complicated work hardening and softening behavior of peak-aged steel cannot be explained only by the dislocation and grain boundary densities, suggesting that the work softening is derived from another factor, that is, the reduction of particle dispersion strengthening in the high strain regime due to dissolution of dispersed Cu particles.

In order to estimate the amount of dissolved Cu during deformation, electrical resistivity measurements were conducted for the deformed specimens (Fig. 2(c)). It is well known that the electrical resistivity goes up with increasing concentration of lattice defects such as interstitial atoms, dislocations and grain boundaries [9–11]. Therefore, if we could deduct the effects of accumulated dislocations and strain-induced grain boundaries from the measured electrical resistivity, the amount of

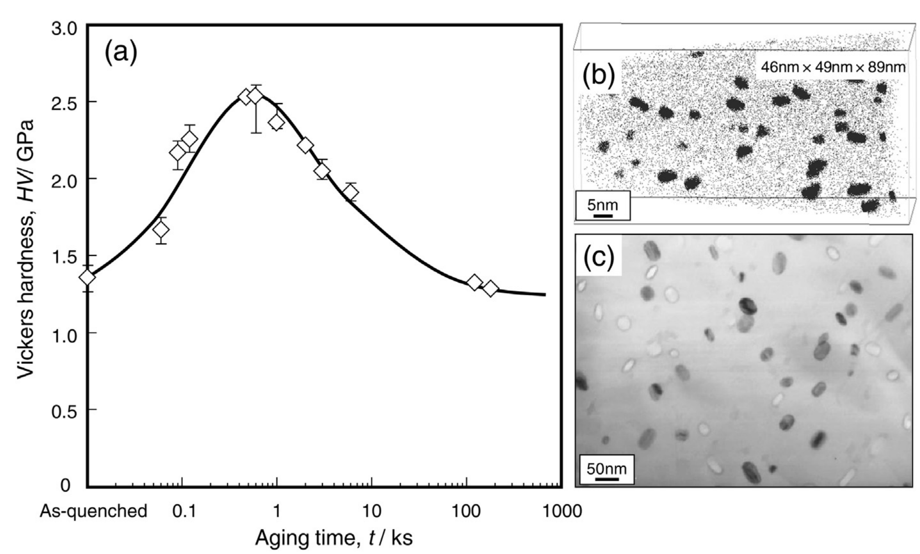

Fig. 1. Change in hardness during aging treatment at 873 K for the Fe-2%Cu alloy as a function of aging time (a), 3D Cu maps of the 0.6 ks-aged specimen obtained with the 3D atom probe (3DAP) (b), and a TEM bright-field image of the 180 ks-aged specimen (c).