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Thermally promoted evolution of open-volume defects and Cu precipitates in the deformed FeCu alloys

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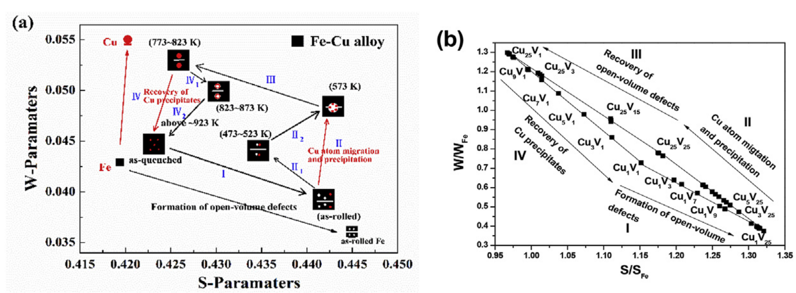
HIGHLIGHTS

- Cold rolling deformation led to the formation of defects.
- Annealing resulted in gradual recovery of open-volume defects and Cu precipitation.
- Annealing promoted the interaction between defects and Cu precipitates.
- S-W relationship revealed the interaction between defects and Cu precipitates.
- The trajectory of S-W points with temperature formed a closed “Parallelogram” shape.

GRAPHICAL ABSTRACT



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ABSTRACT

We have studied the effect of isothermal annealing on the evolution of the open-volume defect and the Cu precipitate in deformed Fe0.15Cu, Fe0.3Cu and Fe0.6Cu alloys. Using the coincidence Doppler broadening, positron annihilation lifetime and the S-W couples, the evolution of local electronic circumstance around the annihilation sites, open-volume defects and interaction between open-volume defects and Cu precipitates were measured as a function of the isothermal annealing temperatures. Cold rolling deformation induced an obvious increment in S parameters due to the formation of open-volume defects. Annealing not only resulted in gradual recovery of open-volume defects and Cu thermal precipitation, but also promoted the combination and interaction between defects and Cu precipitates. The interaction between open-volume defects and Cu precipitates was revealed clearly by the view point of S-W relationship. The S-W interaction for the different Cu_mV_n complexes was also calculated theoretically by MIKA-Doppler, which supports our experimental observations qualitatively. The results indicate that open-volume defects were formed first after cold rolling, followed by the Cu precipitation and recovery of open-volume defects, Cu precipitates recovered at the end. It is interesting that the trajectory of (S, W) points with increasing annealing temperature formed a similar closed “Parallelogram” shape. It is benefit for revealing the behavior of Cu thermal precipitation and their evolution in various Cu-bearing steels under thermal treatment. In addition, we also investigated the Cu content effect on the Cu precipitation in FeCu alloys, and the Cu precipitate phenomenon was enhanced in higher Cu content alloys.

1. Introduction

For the research of high strength Cu-bearing steels, the long-

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standing goal is to increase the strength while maintaining excellent yield strength, weld ability and low production costs [1]. It is well known that Cu addition to steels have some advantages, including the oxidation resistance, large strengthening and so on [2]. The Cu element addition is benefit for the low carbon steels with precipitation strengthening effect [1]. Commercially obtainable low carbon containing Cu steels have been successfully applied in the nuclear industry because of the excellent yield strength in the cold rolling and thermal treatment conditions [1,3–5]. When the steels is in the cold rolling and forging, open-volume defects (i.e., mainly the dislocations, vacancies and vacancy clusters) were introduced due to the deformation [6,7]. Subsequent annealing process will remove the vacancy defects and form the Cu precipitates. Cu precipitates are a major contributors to increase in hardness and embrittlement in nuclear reactor pressure vessels steels [8–10]. During the Cu precipitation process, the Cu-vacancy complexes gradually formed because of Cu atom occupation of open-volume defects. Thus, the Cu precipitate would interact with the defects during the annealing.

For the sake of avoiding the effect of other elements (C, Ni, Mn, V, B, N, Cr and so on) in low carbon Cu-bearing steels, the binary FeCu alloy is one of the most appropriate systems for investigating Cu precipitates and open-volume defects [5,11]. As we known, the nano-sized body-centered-cubic (bcc) Cu precipitate is initially fully coherent with the bcc Fe matrix [12,13]. Once reaching a critical size of about 4~6 nm, they would undergo a martensitic transformation from bcc to 9R structure, which is less coherent with the bcc Fe matrix [7]. Certainly, it is difficult to clearly extract the obvious Cu signal from a much stronger Fe matrix background by the common probes, such as x-ray, electron, neutron and so on [14]. What's more, the small Cu precipitates are also rather difficult to be observed directly by current high resolution TEM due to the resolution limit and the specimen high magnetism [13,15,16]. Onitsuka et al. studied the formation of Cu precipitates in Fe1.0% Cu alloy enhanced by deformation using positron annihilation technique, coincidence Doppler broadening, and the positron lifetime method. They found the migration and interaction of Cu atoms and open volume defects during cold rolling and annealing treatment [17]. The ultrafine Cu precipitation and evolution in as-rolled alloys have attracted considerable researches due to extensive application prospects in the Cu-bearing steels. Thus, we should focus on the thermal recovery of open-volume defects and thermally activated Cu precipitation for FeCu alloys under different thermal treatments in the present academic experiment.

Positron annihilation is an ideal technique to detect the open-volume defects and Cu precipitates in binary dilute FeCu alloys. The S value of the Doppler broadening spectroscopy (DBS) could detect the open-volume defects; while the W parameter can convey Cu precipitation information around the annihilation sites. Positron annihilation lifetime spectroscopy (PALS) could characterize the defect size and density, which is reflected by analyzing positron lifetime and its intensity. Coincidence Doppler broadening (CDB) measurement determines the high momentum distribution of electrons annihilated with positrons by detecting the local electronic circumstance at the positron annihilation sites. It can differentiate the Cu atoms definitely around open-volume defects by decreasing the background of high momentum contributions [18]. In the current study, we reported the thermally promoted evolution of the open-volume defects and Cu precipitates in deformed Fe0.15Cu, Fe0.3Cu and Fe0.6Cu alloys studied by PALS and CDB spectra. And, DBS mainly focused the interaction between open-volume defects and Cu precipitates investigated by the view of S-W relationship.

2. Experimental details

As the experiment alloys, Fe0.15Cu, Fe0.3Cu and Fe0.6Cu (wt.%) alloys were melted from iron powder (99.99%) and copper powder (99.999%) in a high-frequency induction furnace at 1873K. The solution treatment of these alloys was carried out at 823 K–973 K for 32 h. And then the samples were tempered at 773 K/10 h and were cooled by furnace. The bulk materials were cut into 10 mm × 10 mm × 0.4 mm square sheets. For a better dissociation of Cu atoms in the matrix, the FeCu alloys were well-annealed at 1173 K for 2 h in vacuum, keeping the temperature and then quenching in ice water immediately. Mainly open-volume defects were introduced in the already prepared samples by cold rolling to 30% reduction in thickness, and then the isochronal annealing were carried out for 0.5 h in a vacuum. The annealing temperatures were in the range of 373 K–973 K with an increment step of 50 K.

CDB technique was used to measure the high momentum distribution of core electrons come from Fe and Cu atoms in the present work. The shape of the spectrum in high momentum region (13×10^{-3} $m_oc < |P_L| < 30 \times 10^{-3}$ m_oc, where c is light speed and m_o indicates electron rest mass) exhibits characteristic signals from the positron annihilation with core electrons [15]. The low momentum region ($|P_L| < 3 \times 10^{-3}$ m_oc) exhibits characteristic signals from the positron annihilation at defects. The ratio curves of the CDB spectra for FeCu alloys with respect to pure Fe reference were aim to extract positron annihilation information with the Cu core electrons.

In the DBS, the S and W parameters are defined as the ratio of central low momentum area (510.2 keV–511.8 keV) and two wing high momentum regions (503.34 keV–507.17 keV and 514.83 keV–518.66 keV) to total region, respectively. S results from positron annihilation with valence electrons, which conveys the defect information in matrix. W origins from the positron annihilation with core electrons (such as Cu 3d electrons), and it can estimate the Cu atom density around positron annihilation sites.

PALS analysis was carried out with the fast–slow coincident system, and the time resolution is 197 ps. The ^{22}Na positron source was placed in the middle of two samples (i.e., sample–^{22}Na source–sample), and the positron lifetime spectra were acquired by two detectors. In order to reduce the statistical error, each lifetime spectrum was counted up to a total of 2×10^6. Before analyzing the defect information in the deformed specimens, the source and background components should be subtracted. And then the lifetime spectrum L(t) could be decomposed into the short lifetime τ_1 and long lifetime τ_2:

$$L(t) = (I_1/\tau_1)\exp(-t/\tau_1) + (I_2/\tau_2)\exp(-t/\tau_2) \quad (1)$$

where τ is the lifetime and I is the corresponding intensity. τ_2 originates from vacancies and micro-voids, whereas the τ_1 mainly indicates the dislocation information in the deformation alloys [16].

3. Results and discussion

3.1. CDB results and evolution of Cu precipitates

Typical ratio curves of deformed Fe0.15Cu, Fe0.3Cu and Fe0.6Cu alloys annealed isochronally with the range of 373 K–973 K to well annealed pure Fe are shown in Fig. 1a, b and 1c. As the references, the ratio curves for pure Cu, as-quenched FeCu alloys, as-rolled pure Fe and as-rolled FeCu alloys normalized to pure Fe are also shown in Fig. 1. For the pure Cu, the Cu characteristic signal is the broad peak around 24×10^{-3} m_oc. For the as-quenched FeCu alloys, the ratio curve is close to 1, which is consistent the value of pure Fe. It suggests that most of positrons annihilated with the Fe electrons. Quenching made the Cu atoms evenly dispersed and isolated in the