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ScienceDirect

Acta Materialia 85 (2015) 107–111

Acta MATERIALIA

www.elsevier.com/locate/actamat

Thermal stability and the structure of vacancy–solute clusters in iron alloys

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Received 21 March 2014; revised 12 November 2014; accepted 12 November 2014

Abstract—Thermal stability and the structure of clusters formed by neutron irradiation are studied by means of positron annihilation spectroscopy of post-irradiation annealed FeCu, FeCuMnNi and FeMnNi alloys and rigid lattice calculations. While most of the vacancy–solute clusters dissolve in the temperature range between 650 K and 700 K, the presence of Ni and Mn solutes in vacancy–MnNi clusters provides an additional thermal stability and shifts the annealing stage corresponding to the dissociation of these clusters to higher temperature. Very good agreement between the measurements and calculations is obtained for vacancy–MnNi clusters of nanometric size, containing of about 25–50% of vacancies.

Keywords: Vacancy–solute clusters; Neutron irradiation; Positron annihilation; Iron alloys

1. Introduction

The structural properties of nanoclusters formed under neutron irradiation in iron-based alloys are essential for understanding embrittlement and hardening of reactor pressure vessel (RPV) steels. Even at nanometric sizes, the variety of solute, vacancy, and interstitial clusters, and their mutual complexes strongly affects the dislocation motion, causing macroscopic changes in the mechanical properties [1]. These changes, occurring in the RPV during service of a nuclear power plant (NPP), are of considerable importance to the safe operation and play a major role in the NPP life extension analyzes.

Despite the fact that a variety of nanoclusters were studied in irradiated iron alloys with different chemical complexity (e.g. pure iron, binary, ternary, quaternary alloys, and steels) [2,3], the ones that play a major role in the degradation of mechanical properties of RPV steels are not yet elucidated. The accumulated results so far showed that the main contribution to the hardening comes from copper-rich precipitates/clusters of a few nanometers in diameter that are easily formed under neutron irradiation due to the low solubility of Cu in Fe. Their structure reveals the synergy between all major solute atoms [3,4]. The existence of solute atom clusters in irradiated copper-free alloys and steels is confirmed by the atom probe tomography (APT) studies [5].

As the APT cannot detect lattice defects such as vacancies, and since most of the solute precipitates grow on the basis of vacancy mechanism [6], the full structure of such solute atom clusters, i.e. whether they contain the vacancies or not remains to be discussed.

Other defects formed under neutron irradiation such as small vacancy and interstitial clusters, and their mixture with light interstitials are usually very difficult to detect experimentally, leaving an open question of what type of defects are responsible for the material embrittlement and hardening in copper-free (or low-copper) steels.

In this study we analyze the properties of vacancy–solute clusters on the basis of their thermal stability. This is realized by performing the positron annihilation experiments in post-irradiation annealed neutron-irradiated FeCu, FeMnNi, and FeCuMnNi alloys. On the basis of comparison between the experiments and rigid lattice calculations, we confirm the existence of vacancy clusters enriched with Ni and Mn that exhibit a high thermal stability and large dissociation energy in comparison with other small vacancy(–solute) clusters that form in these alloys.

2. Materials

The materials used in this study are the polycrystalline iron alloys: Fe–Cu, Fe–Mn–Ni, and, Fe–Cu–Mn–Ni. The chemical composition of the investigated materials is given in Table 1. Neutron irradiation was performed in the Belgian Reactor (BR2) up 0.1 *displacement per atom*, *dpa*, (6.9×10^{19} n/cm^{-2}), at the temperature and pressure of about 300 °C and 150 bar, respectively. The details of the sample preparation and irradiation conditions are published in [7]. The post-irradiation isochronal annealing (0.5 h) was performed at various temperatures in the range between 573 K and 973 K.

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http://dx.doi.org/10.1016/j.actamat.2014.11.026
1359-6462/

Table 1. The nominal composition of investigated alloys.

Material comp. (wt.%)	Cu	Mn	Ni	C	Other sol.	Fe
FeCu	0.3	0	0	<0.005	<0.01	bal.
FeMnNi	0	1.09	0.75	<0.005	<0.01	bal.
FeCuMnNi	0.105	1.08	0.75	<0.005	<0.01	bal.

3. Positron annihilation experiment

The PAS experiments are performed with the Coincidence Doppler broadening spectrometer (CDB). The CDB spectra are measured using two Ge detectors. Details of the setup are described in [8]. The same two samples for each alloy are annealed and measured in a consecutive way. The CDB spectrum provides the momentum distribution of the core electrons, which can be used to determine the chemical environment of a positron–electron annihilation site [9]. The results are typically shown as the CDB ratio spectra, which correspond to the momentum distributions normalized to that of non-irradiated (defect-free) pure iron.

4. Computation method

To compute the dissociation energy of a single vacancy to vacancy solute cluster (VSC) we used the rigid lattice calculation. The dissociation energy of a vacancy from a VSC, $E_d = E_b + E_m$, is calculated in the standard approximation [10] as the sum of the binding energy of a single vacancy to a VSC, $E_b(V_mS_n) = E(V_{m-1}S_n) + E(V) - E(V_mS_n) - E(Fe)$, and the vacancy migration energy in *bcc* Fe. The latter was taken to be E_m=0.65 eV, following available density function theory (DFT) data [11]. The $E(V_{m-1}S_n)$ and $E(V_mS_n)$ denote the total energy containing a $V_{m-1}S_n$ and V_mS_n cluster, respectively, $E(V)$ is the total energy containing one vacancy, and $E(Fe)$ is the total energy of the perfect Fe crystal. The rigid lattice model is based on pair interactions up to the second nearest neighbor distances, $E = \sum \epsilon^{(i)}_{k,l}$, where the sum runs over the first and second nearest neighbor pairs, k and l denote the species of the lattice sites including Fe, vacancy, Cu, Mn and Ni atoms. All pair interactions were derived from DFT data on the point defect properties [12]. The calculations were performed in the periodic body centered cubic *bcc* crystals containing 54,000 atoms, which was proven sufficient to remove any box size effect (calculation with larger box sizes provided the exact same values). The VSCs were constructed in the most compact way such that the vacancy cluster is at the center of the VSC, consistently with Monte Carlo simulations [13]. Each cluster composition was sampled 100 times to reduce the standard error down to 20 meV. All analyzed cluster compositions are summarized in Table 2.

5. Results and discussion

The CDB spectra of FeCu, FeMnNi, and FeCuMnNi alloys annealed at various temperatures are shown in Fig. 1(a)–(c), respectively. All irradiated materials have enhancement in the low momentum region, indicating that positrons are trapped and annihilate in the open volume defects induced by irradiation such as vacancies and voids. The broad peak centered at about 25×10^{-3} m_0c, see Fig. 1(a) and (c) is observed only in alloys containing Cu. It can be attributed to the annihilation of positrons and 3d electrons of Cu atoms, and is consistent with other studies [14,16]. By increasing the annealing temperature, the CDB spectra of all three alloys gradually change, with a tendency to reach the pure Fe spectrum in the temperature range from 873 K to 973 K (600–700 °C). At a temperature of about 973 K only FeCuMnNi alloy is fully annealed. In FeMnNi and FeCu alloys the high-T spectra deviate from the straight line, which indicates that small amounts of defects might still remain in the samples. This deviation probably originates from the small deformation induced during the sample preparation prior irradiation or after dismantling of irradiation capsule [17,18]. The materials containing Cu, namely FeCu and FeCuMnNi alloys, exhibit an increase of the CDB signal in the high momentum region (around 25×10^{-3} m_0c), up to an

Table 2. The cluster compositions (at.%) used in the calculations.

V	Cu	Mn	Ni	MnNi (Relative to each other)	CuMnNi (Relative to each other)
				25–75	75–12.5–12.5
25	75	75	75	50-50	50–25–25
				75–25	
				25–75	75–12.5–12.5
50	50	50	50	50–50	50–25–25
				75–25	
				25–75	75–12.5–12.5
75	25	25	25	50–50	50–25–25
				75–25	

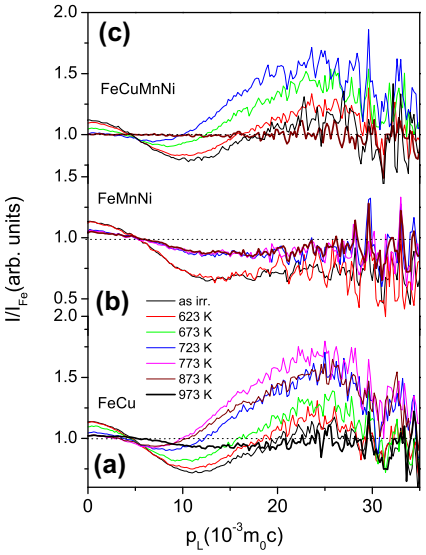

Fig. 1. Doppler broadening spectra of (a) FeCu, (b) FeMnNi, and (c) FeCuMnNi alloys.