Current Opinion in Solid State and Materials Science 20 (2016) 115–139

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

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

Radiation-induced solute segregation in metallic alloys

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ARTICLE INFO

Article history:
Received 13 July 2015
Revised 14 November 2015
Accepted 28 November 2015
Available online 12 December 2015

Keywords:
Radiation damage
Solute segregation
Diffusion
Clustering
Rate-theory kinetics
Computational modeling
Austenitic and ferritic stainless steels

ABSTRACT

The subject of radiation-induced solute segregation (RIS) in metallic alloys is reviewed. RIS manifests itself in several different ways, including diffusion to point-defect sinks (dislocations, grain boundaries, voids, etc.), which can induce precipitation in undersaturated alloys, as well as self-organization of solute clusters and precipitation in defect-free material. Diffusion in dilute and concentrated alloys is highlighted, as are theories of RIS that include new ideas on diffusion of complexes involving coupling between fluxes of point defects and of solute atoms. Many important experimental observations are presented, including up-to-date findings using atom-probe tomography, with special emphasis on solute segregation in austenitic and ferritic steels. Results from computational modeling and theory are also presented and discussed in light of experimental findings. Examples illustrating the factors affecting RIS are shown and some important outstanding issues that impact the current understanding of RIS are described and discussed.

1. Introduction

The irradiation of crystalline solids by energetic neutrons, ions or electrons subjects them to several kinds of radiation damage. Radiation damage begins with the production of atomic displacement damage, generally from collision cascades of various sizes that depend on the energy and mass of the bombarding species. The collisions produce vacancies and interstitial atoms in equal numbers, so-called Frenkel Pairs. Depending on the temperature of the materials the vacancy concentrations can far exceed their equilibrium values; the concentrations of interstitials are always far in excess of their equilibrium values, which are exceptionally small at all temperatures. A large fraction of the excess point defects recombine, eliminating the local radiation damage. In fact, it is fair to state that if recombination were perfect and all the vacancies and interstitials were eliminated by mutual annihilation, there would be no radiation damage at all except for transmutations that occur during neutron irradiation. But interstitials interact much more strongly than vacancies with both themselves and with pre-existing internal sinks for point defects, such as dislocations and grain boundaries, because of the large strain fields associated with the occupation of interstitial sites. Furthermore, interstitials are generally much more mobile than vacancies, so they have much shorter lifetimes. The interstitials that survive recombination interact with pre-existing sinks in a biased manner and leave behind the less mobile vacancies. Though vacancies are far less mobile than interstitials, they are nevertheless mobile enough to interact with each other, one serious consequence of which is the phenomenon of void swelling.

Interstitials and vacancies usually interact quite differently with the atomic species in an alloy. The interactions between atoms and point defects can be either attractive or repulsive, depending on factors such as size differences and electronic structure. Moreover, the diffusive fluxes of interstitials or vacancies toward point-defect sinks often produce concomitant preferential fluxes of atoms. Even in the absence of strong binding energies between the point defects and atoms it is possible for atom fluxes to be induced by point-defect fluxes, leading to radiation-induced redistribution of solute and solvent atoms. The longer-range radiation-induced solute redistribution (RISR) at point-defect sinks is generally referred to as radiation-induced segregation (RIS). When or if the concentration of solute atoms at a sink exceeds the limit of solubility in the alloy a new phase can nucleate and grow, leading to radiation-induced precipitation (RIP). It is also possible in many cases for irradiation to produce solute redistribution on a much shorter length scale, resulting for example in the long-range order of a previously compositionally disordered alloy.

The current state of knowledge of RIS constitutes the focal point of this review article. There have been several reviews of RIS over the past few decades [1–4] as well as review articles on radiation damage and reactor materials in general [5,6] and reactor steels

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http://dx.doi.org/10.1016/j.cossms.2015.11.001
1359-0286/

in particular [7], and the interested reader is encouraged to peruse these articles to appreciate how our understanding of this topic has evolved over time. At this writing it is fair to state that advances in the processing of alloys to produce microstructural features at the nano-scale, characterizing them and modeling their radiation-damage resistance warrant a current assessment of the progress in our understanding of RISR. We present a historical perspective on RIS, discuss some of the most recent advances and observations, describe the different approaches to modeling RIS and discuss recent models that endeavor to predict behavior. The influence of experimental variables (e.g. radiation temperature, the addition of trace elements) and microstructural parameters (e.g. grain boundary character) will be highlighted, particularly in steels, which are candidate alloys for use in Generation IV nuclear reactors [6]. The effects of RISR on alloy behavior, particularly high-temperature mechanical properties and resistance to corrosion and stress-corrosion cracking, are normally quite deleterious. These issues are discussed in comprehensive review articles by Fukuya [5] and Zinkle and Was [6] and therefore will not be addressed in this paper. The advent of atom probe tomography (APT) has been highly impactful in characterizing defects at the nano-scale, and we present numerous examples of new observations made using this technique, the limitations and advantages of which have been reviewed recently by Marquis [8].

2. Manifestations of radiation-induced solute redistribution

Okamoto and Wiedersich [9] were the first to observe and identify both RIS and RIP, which was manifested by precipitation of the intermetallic compound Ni_3Si (with the ordered $L1_2$ Cu_3Au crystal structure) at the surfaces of radiation-induced voids in an austenitic stainless steel. Okamoto and Wiedersich postulated that undersized Si atoms would preferentially populate the concentration of interstitial atoms. Since intersitials as well as vacancies diffuse toward void surfaces, which are very strong point-defect sinks, the precipitation of Ni_3Si would occur once the solubility limit of this phase was exceeded. Shortly afterwards, Barbu and Ardell [10] observed the precipitation of Ni_3Si in a Ni–4 at.% Si alloy irradiated by Ni^+-ions at 500 °C. Since the solubility of Si in Ni exceeds 10 at.% at temperatures above 600 °C [11], it is evident that the 4% Si alloy is highly undersaturated at 500 °C. Moreover, the lattice constant of Ni–Si solid solutions decreases with increasing Si content [12], hence Si is clearly undersized in the binary alloy. One of the radiation-induced microstructures observed by Barbu and Ardell [10] is shown in Fig. 2.1; the segregation of Si to interstitial dislocation loops and precipitation on them is evident. The RIP of Ni_3Si in undersaturated Ni–Si alloys at grain boundaries, coherent twin boundaries and free surfaces was observed later by Janghorban and Ardell [13]; examples are shown in Fig. 2.2. The idea that RIS and RIP were due to a preferential interstitial population of undersized Si atoms was reinforced by the results of experiments by Rehn et al. [14] on binary Ni alloys containing 1 at.% Si, Al, Ti or Mo, the latter three of which are oversized. Using Auger spectroscopy, Rehn et al. found that Al, Ti and Mo segregated away from the free surface of their specimens; only Si segregated toward the free surface.

Radiation-induced solute redistribution over shorter length scales is manifested in several different ways. We mention three examples here. The first is the introduction of long-range order in a disordered solid solution, exemplified by the discovery by Weaver and Ardell [16] of Pd_8W in an undersaturated alloy of Pd–18 at.% W irradiated by protons at 600 °C. The ordered Pd_8W phase is stable, but to this day does not appear in the equilibrium Pd–W phase diagram. An example of this phenomenon is shown in Fig. 2.3. Other examples of isostructural Pd_8X phases induced by irradiation are Pd_8Mo [17] and Pd_8V [18]. Another well-known example of RISR over short length scales is the amorphization of crystalline alloys, especially ordered intermetallic compounds. Lesueur [19] reported the first observation of radiation-induced amorphization of a neutron-irradiated Pd–Si alloy, and Thomas et al. [20] later observed a similar result in near-equiatomic NiTi alloys irradiated by high-voltage electrons. Numerous examples of radiation-induced amorphization have since been observed in many different ordered intermetallic compounds under a wide variety of bombarding species and irradiation temperatures. The third manifestation of RISR is the crystallization of an amorphous alloy. Early examples were reported by Parsons and Balluffi [21] and Azam et al. [22] and similar findings have been reported in many other amorphous alloys. The literature on RISR over short length scales is therefore quite large, so to keep the size of this review manageable, we will keep the focus on solute redistribution over longer diffusive length scales.

The earliest observations of Okamoto and Wiedersich [9] have been augmented by many other observations of RIS. Their conjecture of a preferential association between undersized atoms and radiation-produced interstitials is by now indisputable. It was noted as long ago as 1983 by Rehn and Okamoto [23] that the *depletion* of an undersized solute at a point defect sink had never been observed; we believe that this is still the case today. It is also true, for the most part, that oversized solute atoms tend to become depleted at point defect sinks as a consequence of radiation

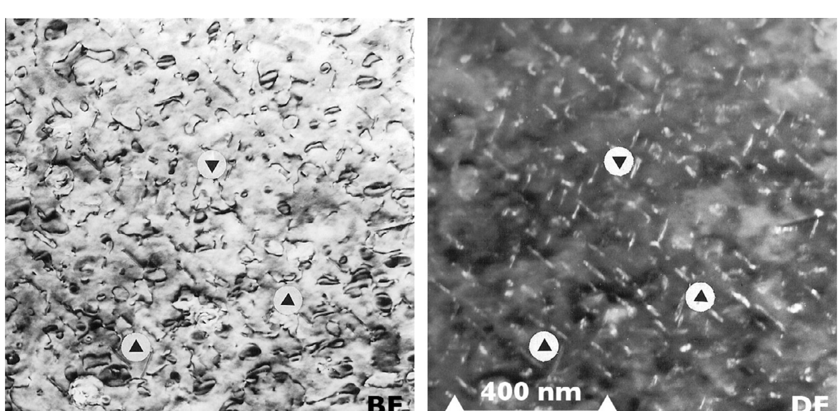

Fig. 2.1. Bright field (BF) and dark field (DF) transmission electron micrographs of the same area (see arrowheads) in a Ni–6 at.% Si alloy irradiated at 500 °C to a dose of 10 dpa using Ni^+ ions [10]. The precipitation of ordered Ni_3Si is evident at the dislocation loops in the DF image, taken using a (100) superlattice reflection.