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On the thermal stability of late blooming phases in reactor pressure vessel steels: An atomistic study

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ABSTRACT

Radiation-induced embrittlement of bainitic steels is the lifetime limiting factor of reactor pressure vessels in existing nuclear light water reactors. The primary mechanism of embrittlement is the obstruction of dislocation motion produced by nanometric defect structures that develop in the bulk of the material due to irradiation. In view of improving the predictive capability of existing models it is necessary to understand better the mechanisms leading to the formation of these defects, amongst which the so-called "late blooming phases". In this work we study the stability of the latter by means of density functional theory (DFT) calculations and Monte Carlo simulations based on a here developed quaternary FeCuNiMn interatomic potential. The potential is based on extensive DFT and experimental data. The reference DFT data on solute–solute interaction reveal that, while Mn–Ni pairs and triplets are unstable, larger clusters are kept together by attractive binding energy. The NiMnCu synergy is found to increase the temperature range of stability of solute atom precipitates in Fe significantly as compared to binary FeNi and FeMn alloys. This allows for thermodynamically stable phases close to reactor temperature, the range of stability being, however, very sensitive to composition.

1. Introduction

Radiation-induced embrittlement of bainitic steels is the lifetime limiting factor of the irreplaceable reactor pressure vessels (RPV) in existing nuclear light water reactors (LWR). The primary mechanism of embrittlement is the obstruction of dislocation motion produced by nanometric defect structures that develop in the bulk of the material due to irradiation. Two classes of nano-structural features are considered as the main contributors to the embrittlement of RPV steels, both hardly visible in the electron microscope: (a) clusters of solute atoms such as Cu, Ni, and Mn, generally catalogued as precipitates; and (b) the so-called 'matrix damage', generally interpreted in terms of clusters of point-defects [1–3].

In the first class of features, one can further distinguish between Cu-rich precipitates (CRPs) [2] and Mn–Ni-rich precipitates (MNPs) [4]. The formation of the latter, which might also not contain Cu, is favoured by low(er) temperature and high Ni (and Mn and Si) content [3]. MNPs without Cu are detected only at sufficiently high neutron fluence, not only in (low-Cu) RPV steels [5,6], but also in FeMnNi model alloys [6,7]. Moreover, based on simplified thermodynamic-kinetic models briefly recalled below, there is a belief that precipitates rich in Mn and Ni, once nucleated, will rapidly grow to large volume fractions [3]. For these reasons, they are more commonly denoted as *late blooming phases* (LBP), or confused with them. Their appearance has been associated with the possibility of a sudden and unexpected increase of embrittlement above a certain dose, that cannot be predicted by current commonly used empirical correlations [2,3], thereby posing a question mark on the possibility of extending the lifetime of existing LWR.

In view of improving the predictive capability of existing models it is necessary to understand better the mechanisms leading to the formation of these so-called LBPs, to investigate their stability and to assess their strength as obstacles to dislocation motion. The possibility of forming Cu free MNPs was put forward for the first time in [8], based on regular solution theory calculations and equilibrium lattice Monte Carlo simulations, parameterized purely on the basis of thermodynamic considerations [2–4,9]. These early simulations led to the conclusion that it is thermodynamically favourable for Mn, Ni and Si to precipitate and form clusters at the interface around a core of Cu. Moreover, the results of the simulations suggested that lower temperature and lower Cu content, or higher Mn, Ni and Si content, would favour Mn, Ni and Si

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enrichment of these clusters. The model did not include, however, any description of the mechanisms of precipitation by diffusion, nor any detail about solute/point-defect interaction. It was indeed explicitly assumed that MNPs, as well as CRPs, are stable thermodynamic phases, the formation of which is enhanced under irradiation, and would be more frequently found in low-Cu steels, especially if temperature is low (265 °C versus the usual 288 °C) and dose is fairly high [2,4,8,9].

In a recent study [10], a more advanced simulation methodology was used to investigate the physical mechanism of formation of LBPs. Namely, an atomistic kinetic Monte Carlo model parameterized on electronic structure calculations data was used to study the formation and evolution under irradiation of solute clusters in FeMnNi ternary and FeCuMnNi quaternary alloys. Two populations of clusters were observed to form, which can be discriminated by whether or not the solute atoms are associated with self-interstitials and their clusters. MnNi-rich clusters, that invariably contained a large majority of self-interstitials, were observed to form at a very early stage of the irradiation in both modelled alloys; the quaternary alloys contained also self-interstitial-free, Cu-containing clusters. MnNi-rich clusters nucleated very early via a self-interstitial-driven mechanism, earlier than Cu-rich clusters; the latter, however, grew in number much faster than the former, helped by the strong thermodynamic driving force to Cu precipitation in Fe, thereby becoming dominant in the low dose regime. The kinetics of the number density increase of the two populations was thus significantly different. The somewhat provocative conclusion of that work was that the so-called *late blooming phases* might well be neither *late*, nor *phases*. Indeed, a specific feature of the model used in [10] was that the precipitation of Ni and Mn due to thermodynamic driving forces was implicitly excluded, as a consequence of the fact that the density functional theory (DFT) calculations used to parameterize the model predicted repulsion between Ni and Mn pairs in Fe. Even so, Ni and Mn clusters did form, at very low doses, catalysed by the presence of self-interstitials, thereby showing that the thermodynamic stability of these clusters as phases is *not a necessary condition* for their appearance under irradiation. The intimate relationship between solutes and self-interstitials also casts some doubts on the physical justification of distinguishing between "precipitates" and "matrix damage" as two separate classes of embrittling features.

Nonetheless, the work in [10] left open the question of whether or not NiMn(Si) clusters may or not be regarded as thermodynamic phases and, if so, under which conditions and with which range of stability. As a matter of fact, considering the FeMn and FeNi binary alloys separately, the respective phase diagrams indicate that the solubility limits of Mn and Ni in α-Fe at 300 °C are approximately 3 and 4 wt% respectively [11–14], i.e., significantly higher than the typical Ni and Mn content in RPV steels. Nonetheless, the solubility limit provided for the *ternary* FeMnNi alloy (TCFE5 database) by the *Thermocalc* software [15] (0.64 at.% and 0.2 at.% at 300 °C for Mn and Ni, respectively [7]) is significantly lower, denoting a strong synergy between Ni and Mn in Fe. *Thermocalc* uses an experimental database of thermodynamic functions, extrapolated whenever the available data are insufficient, to calculate the phase diagram of most alloys, based on free energy functions of temperature and concentration and common tangent construction (Computer Coupling of Phase Diagrams and Thermochemistry: Calphad database and formalism). Quite clearly, extrapolation to temperatures for which it is difficult to obtain experimental calorimetric data is always uncertain. In particular, the data for the MnNi interaction used in Calphad originate from an extrapolation of experiments realized by Dinsdale at temperatures ~400 °C [16]. The difference between the results of the DFT-informed model in [10] and the *Thermocalc* results arises from the nature of the MnNi interaction, which is attractive in the Calphad database, while it is repulsive according to so far available DFT calculations [17]. Thus, there seems to be a discrepancy between DFT and Calphad and a good part of the present work is devoted to investigating whether this discrepancy is real or not and whether it can be removed and, if so, how.

This is done by performing new DFT calculations to be used, together with experimental phase diagram indications, to develop a thermodynamically consistent interatomic potential for the FeCuNiMn system. We show that, even though DFT calculations predict instability of Ni–Mn pairs and triplets, Ni–Mn clusters become stable above a certain size. By informing the interatomic potential to this new insight, as well as to other experimental reference data, it becomes possible to use it as a reliable tool to study phase stability in the FeCuNiMn system. The use of appropriate Metropolis Monte Carlo techniques to build the phase diagram of the quaternary alloy from the potential allows us in this work, therefore, to give a reasonable *ab initio*, rather than experimental, estimate of the range of temperature and concentration in which MnNi(Cu) precipitates in Fe can be considered as thermodynamically stable phases, as well as the expected equilibrium concentration of Ni and Mn in those phases.

The advantage of fitting an interatomic potential over building a purely thermodynamic model is that the former can also be fitted, up to a certain extent, to reproduce the interaction of solute atoms with point-defects and their clusters. This is done and partly tested in the present work, opening the way to the study of complexes composed of both point-defects and solute atoms. The ultimate objective is that the interaction of these nanofeatures with dislocations can be investigated quantitatively. As a matter of fact, irrespective of whether solute clusters in RPV steels are or are not thermodynamically stable phases, their association (or not) with point-defect clusters, especially self-interstitial clusters, will influence not only their kinetics of formation and stability, but also, and more importantly, the strength that they oppose as obstacles to dislocation motion.

2. Methods and formalisms

2.1. Density functional theory calculations

The DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [18,19]. VASP is a plane-wave DFT code that implements the Projector Augmented Wave (PAW) method [20,21]. Standard PAW potentials supplied with VASP were used, with exchange and correlation functional described by the Perdew–Wang parameterization [22] in the Generalised Gradient Approximation (GGA), with a Vosko–Wilk–Nusair interpolation [23]. For Fe, Cu, Ni and Mn pseudo potentials with 8, 11, 10 and 7 valence electrons were used, respectively.

Finite temperature smearing was obtained following the Methfessel–Paxton method with a smearing width of 0.3 eV. The plane-wave cut-off energy was set to 300 eV, which proved sufficient for convergence of the binding and migration energy of the selected configurations. Brillouin zone sampling was performed using the Monkhorst–Pack scheme, where meshes of $3 \times 3 \times 3$ k-points proved sufficient for convergence. The total energy was calculated in periodic bcc supercells containing 128 atoms in a fixed volume set to the equilibrium volume of Fe.

For the defect-solute and solute–solute interactions the total binding energy of a configuration containing n objects ($i = 1...n$) X_i is defined as,

$$E_b(X_1 \ldots X_n) = \sum_i E(X_i) - \left[E\left(\sum_i X_i \right) + (n-1) E_{ref} \right], \quad (1)$$

where E_{ref} is the energy of the supercell without any objects (pure bcc Fe), $E(X_i)$ is the energy of the supercell containing the single