

# The formation and structure of Fe-Mn-Ni-Si solute clusters and G-phase precipitates in steels

D. J. M. King<sup>a,\*</sup>, P. A. Burr<sup>b</sup>, S. C. Middleburgh<sup>c</sup>, T. M. Whiting<sup>a</sup>, M. G. Burke<sup>d</sup>, M. R. Wenman<sup>a</sup>

<sup>a</sup> Centre for Nuclear Engineering, Imperial College London, South Kensington, London, SW7 2AZ, United Kingdom

<sup>b</sup> School of Electrical Engineering, University of New South Wales, Kensington, 2052, NSW, Australia.

<sup>c</sup> Westinghouse Electric Sweden AB, SE-721 63 Västerås, Sweden

<sup>d</sup> Materials Performance Centre, The University of Manchester, Sackville Street Campus, Manchester, M13 9PL, UK

\*Corresponding Author:

E-mail: [daniel.king@imperial.ac.uk](mailto:daniel.king@imperial.ac.uk)

Address: Flat 18, Crewkerne Court, Bolingbroke Walk, SW11 3NF, United Kingdom

Telephone: +447474031955

**Abstract.** Solute clustering and G-phase precipitation cause hardening phenomena observed in some low alloy and stainless steels, respectively. Density functional theory was used to investigate the energetic driving force for the formation of these precipitates, capturing temperature effects through analysis of the system's configurational and magnetic entropies. It is shown that enrichment of Mn, Ni and Si is thermodynamically favourable compared to the dilute ferrite matrix of a typical A508 low alloy steel. We predict the ordered G-phase to form preferentially rather than a structure with B2-type ordering when the Fe content of the system falls below 10–18 at. %. The B2 → G-phase transformation is predicted to occur spontaneously when vacancies are introduced into the B2 structure in the absence of Fe.

**Keywords:** density functional theory; RPV steels; duplex steels; ferritic; solute clustering

## 1. Introduction

An understanding of the behaviour of solute atoms within steel components is of great importance to many industries. This is especially true when the steels are exposed to elevated temperatures (573 – 773 K) for long periods of time (> 1 year), as intermetallic compounds are found to precipitate – some embrittling the alloy [1–3]. In the nuclear sector, austenitic stainless steels are commonly used for the primary coolant water pipes [4], reactor pressure vessel (RPV) cladding [5] and low alloy ferritic steels are used for the RPV themselves. The continued structural integrity of the RPV is vital for the extended and continued operation of light water reactors as it is unfeasible to replace them during the reactor's operational lifetime [6]. Solute clustering, due to prolonged neutron irradiation, is a known phenomenon that occurs in RPV steels and contributes to their embrittlement potentially limiting the life of the power plant [7]. However, a mechanistic understanding of the conditions and exact nature of their occurrence

is not agreed upon [8]. Further, debate continues as to whether current dose-damage relationships [9,10] already include the hardening from these clusters or if additional hardening terms may be required. Past studies have observed the clusters to consist of solute elements Cu, Mn, Ni and Si in the body-centred cubic (BCC) Fe matrix [11–13]. In efforts to avoid these features, the Cu content have been significantly reduced (as seen in A508 steels) [14]; however, Mn, Ni and Si are still observed to cluster. These clusters are sometimes termed as Mn-Ni-rich precipitates (MNPs) [15] or Mn-Ni-Si precipitates (MNSPs) [16]. However, there is some contention around their designation as “precipitates” due to the disagreement of their stability and structure [8]. The argument for their designation as a precipitate [17], suggests that the solutes form an  $Fm\bar{3}m$   $D8_a$  (ordered  $Th_6Mn_{23}$ ) intermetallic compound, commonly referred to as the G-phase [18]. This is quite plausible as in high alloy duplex stainless steels the G-phase is seen to precipitate in the ferritic phase, as a consequence of long thermal ageing (10,000 hrs at 673 K) [19,20]. Difficulties in confirming this hypothesis occur as experimental techniques commonly used to analyse the solute clusters, such as atom probe tomography (APT) [21] and small angle neutron scattering (SANS), do not sufficiently elucidate the clusters’ crystal structures. Publications using techniques better suited to crystal structure identification, such as, transmission electron microscopy (TEM) electron diffraction or high resolution TEM have not revealed evidence of the G-phase in irradiated RPV steels to-date.

The current study is concerned with the system at equilibrium. Density functional theory (DFT) is used to study the energetic preference for clustering, A2 disorder and partial ordering, analogous to B2 and  $D0_3$  (strukturbericht notation) of Mn, Ni and Si to occur in the BCC Fe lattice and the driving force for transformation to the G-phase.

## **2. Methodology**

### **2.1 Density functional theory**

A plane-wave density functional theory method was used, as implemented in the Vienna Ab initio Simulation Package (VASP) [22]. Developer provided pseudopotentials, using the projector augmented wave method (PAW) [23], were used to represent the electronic structure of each element. Semi-core  $p$

states were considered valence electrons for Fe (14), Ni (16) and Mn (13) and a standard number for Si (4).

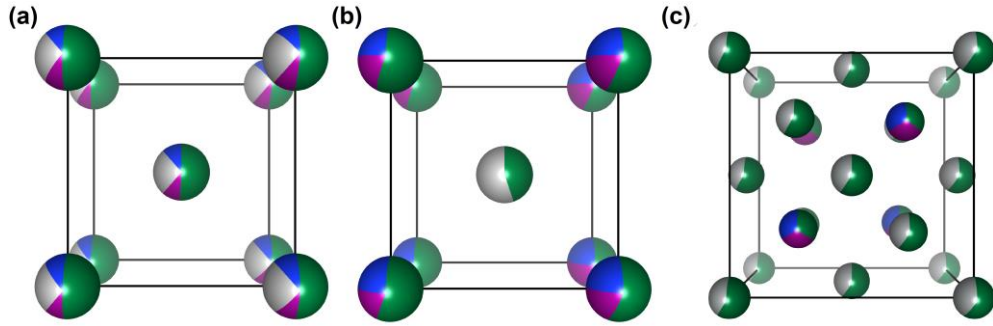
The  $k$ -points, cut-off energy and lattice parameters of all elements in their ground state structures (BCC-Fe, FCC-Ni,  $\alpha$ -Mn, diamond-Si) were converged and used as reference states. It was determined that a real space  $k$ -point density of  $< 0.02 \text{ \AA}^{-3}$  and a cut-off energy of 500 eV would provide accurate results, within  $10^{-3}$  eV, and were kept consistent throughout. The Methfessel Paxton [24] smearing method (width 0.1 eV) was used and full geometry relaxations were carried out under constant pressure for all calculations. Collinear spin polarisation effects were included. For the exchange-correlation functional, the generalised gradient approximation as developed by Perdew-Burke-Ernzerho [25] (GGA-PBE) was utilised. The convergence criterion for electronic convergence was  $10^{-6}$  eV and for geometry optimisation was  $10^{-4}$  eV.

To simulate disordered and partially ordered solute clusters, supercells of 128 atoms with BCC packing were created and the lattice sites were occupied by random selection of the elements allowed in that sublattice. E.g., in the B2 structure, Ni is restricted to one sublattice, Mn and Si are restricted to the other, and Fe pervades both. The randomisations were performed 10 times to produce 10 unique supercells of each composition providing a range of energies. This method has been used to much success in previous studies [26–28]. For the compositions analogous to the ferritic steel matrix of experimental specimens of A508 steels, single 250 atom supercells were used. For further methodology details please refer to a previous study [29].

### **3. Results and Discussion**

#### **3.1 Effect of concentration of Mn, Ni and Si in $\alpha$ -Fe**

In past experimental studies on RPV steels, through the use of APT, solute clusters are observed to evolve with increasing fluence [30]. To simulate this evolution, alloys with concentrations of 0, 50 and 66 at. % Fe, were investigated. The ratio of Mn:Ni:Si was fixed to 6:16:7 (stoichiometric G-phase). Three BCC packed structures, A2, B2 and D0<sub>3</sub> (Fig. 1), were investigated and compared to the G-phase intermetallic, which also had varying Fe contents. The D0<sub>3</sub> partial ordering was not found to differ from the fully disordered energies and therefore was not included in the results or investigated further.



**Fig. 1.** Visual representation of the 50 at. % Fe structures with coloured site occupancy fractions in (a) A2, (b) B2 and (c) D0<sub>3</sub> partially ordered structures where Fe, Mn, Ni and Si are represented by green, purple, grey and blue, respectively.

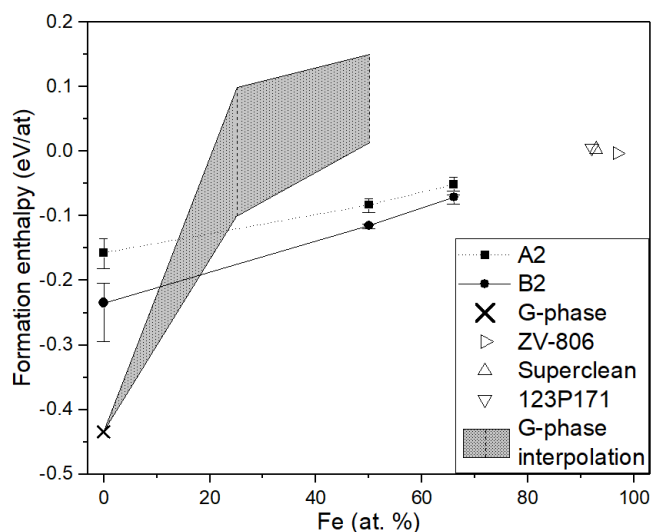
The dilute ferrite matrix of three A508 RPV steel analogues are also simulated for comparison: (1) a grade 2 steel with comparatively high amounts of Mn, Ni and Si “ZV-806”, (2) a grade 4N steel that omits Si “123P171” and (3) a grade 4N steel that omits Mn “Superclean”. These three compositions were modelled after experimental specimens of details found in references [31] and [32]; a summary of their compositions can be found in Table 1. It should be mentioned that the “omission” of Si and Mn in “123P171” and “Superclean”, respectively, is due to their low levels < 0.4 at. % of the alloying elements, which are therefore excluded from the 250 atom supercells.

Table 1. Experimentally measured base metal concentration of Mn, Ni, Si and other elements within the previously studied steels; where Fe is the remainder (units are atomic ppm).

Steel	Mn	Ni	Si	Other
A508 Gr 2 (ZV-806) [31]	116	143	26.2	329
A508 Gr 4N (123P171) [30]	54.9	758	2.9	501
Superclean A508 Gr 4N (118K001) [30]	3.8	717	0.971	524

In Fig. 2, it is seen that the formation enthalpy of each composition decreases (becomes more favourable) with the removal of Fe. It is evident that there is an energetic preference for the formation and enrichment of the solute clusters within the BCC configuration – an observation that supports the argument that the formation of solute clusters is radiation enhanced. The B2 partial ordering has a slight energetic preference (0.02 – 0.09 eV/at), which is increases with decreasing Fe, compared to the fully disordered A2 phase at 0 K. The G-phase is unstable at Fe contents of 25 and 66 at. % and a large degree of reconstruction occurs during geometry optimisation. The spread in energies of these structures is represented by a shaded region in Fig. 2. The G-phase is predicted to become energetically more stable

than the BCC packing below a threshold Fe content between 10 – 18 at. % corresponding well to experimental observations of ~13 at. % by Matsukawa in duplex stainless steels [20].

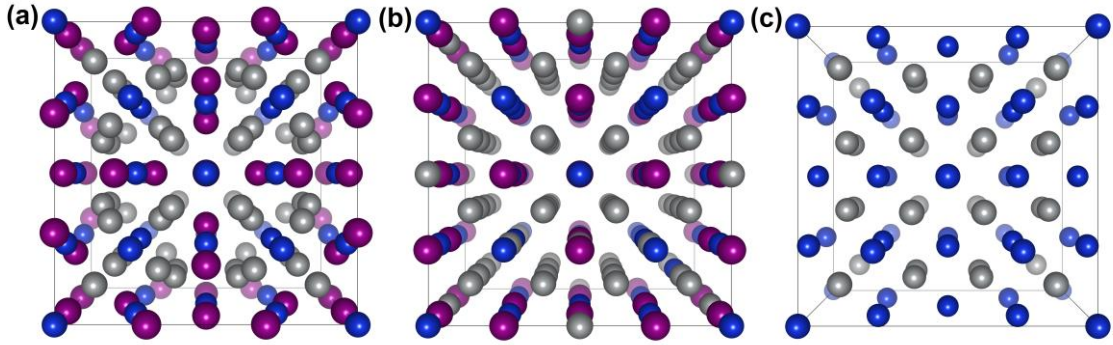


**Fig. 2.** Average formation enthalpies of the  $\text{Fe}_x\text{Mn}_6\text{Ni}_{16}\text{Si}_7$  A2 (filled squares) and B2 (filled circles) phases and their associated range in values (error bars), where  $x$  is varied from 0 – 66 at. %. The formation enthalpy of the G-phase, where  $x = 0$  at. % (cross), and spread in energies at  $x = 25$  and 66 at. % (dashed vertical lines) with the interpolated range of energies represented as a shaded region. Compositions indicative of the ferrite matrix of three experimentally characterised A508 specimens were also compared (open triangles).

It should be emphasised that the simulated fixed ratio of Mn, Ni and Si is idealised for ease of comparison to the stoichiometry of the G-phase and cluster compositions found in both duplex stainless steels and RPV steels can deviate significantly, as well as include other solute species [33,34].

### 3.2 B2 partial ordering of solute clusters in $\alpha$ -Fe

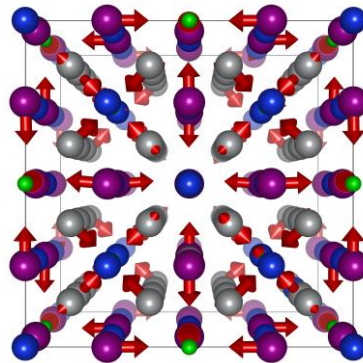
The similarity between the G-phase and B2 partial ordering is assessed within this section. Fig. 3 provides a visual representation of the similarities. Table S1 (supplementary material) explicitly states the location of the lattice matched sites. Interestingly, all the Si atoms and half the Ni sites are lattice matched, with all the Mn atoms experiencing reconstruction to form the G-phase.



**Fig. 3.** Atomic representation Mn (purple), Ni (grey) and Si (blue) in a cubic (a) G-phase unit cell, (b) B2 ordered (4x4x4) supercell and (c) their lattice matched atomic sites.

In contrast to the matching lattice sites between the cubic G-phase unit cell and the 4x4x4 B2 structure, there are 12 fewer atoms in the former. The coordinates of these discrepant atoms are also stated in Table S1. If the atoms at these locations are removed from the B2 supercell, prior to geometry optimisation in DFT – the G-phase is the resultant structure. The vectors (to scale) corresponding to the atomic displacements made as a result of the geometry optimisation within DFT can be seen in Fig. 4.

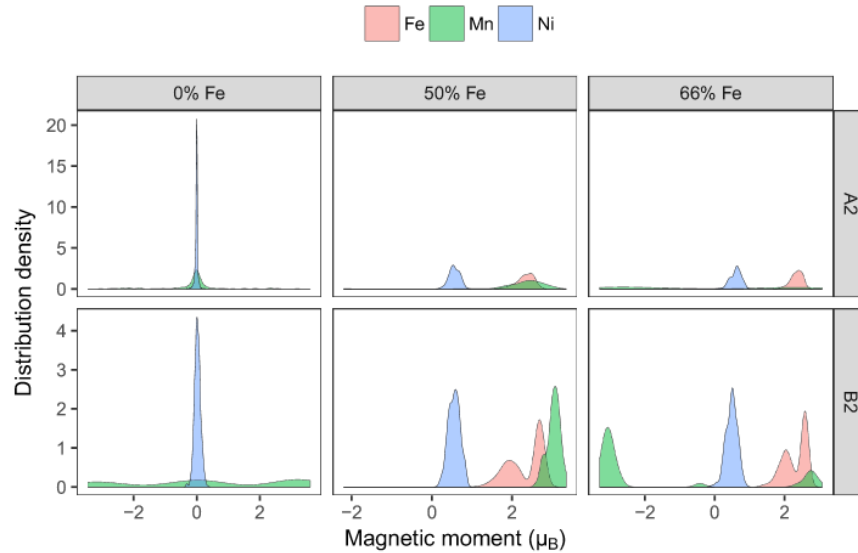
The spontaneous phase transformation, in the DFT energy minimisation, from a defective BCC packed structure to G-phase is a significant result as the transformation from BCC  $\rightarrow$  G-phase is hypothesised in experimental studies [20,35]. The current observation would suggest that the energy barriers for this transformation are dominated by the migration of the elements to their lattice matched sites and/or the formation of the twelve vacancies not the structural transformation itself, which is predicted to occur spontaneously once the preferred atomic ordering is present.



**Fig. 4.** Perfect B2 4x4x4 supercell with absences (green) and vectors (red) of the displacements predicted by DFT to obtain the G-phase.

### 3.3 Magnetic structure

Within this study, all simulations included spin polarisation effects, and as a result a significant degree of magnetic disorder was observed. The distribution of magnetic moments for each element can be seen in Fig. 5 for the simulated disordered systems.



**Fig. 5.** The distribution of magnetic moments of Fe (red), Mn (green) and Ni (blue) in the A2 and B2 phases with varying Fe content.

In absence of Fe, Ni exhibits negligible magnetisation, but with the addition of 50 and 66 at.% Fe, spin polarisation on the Ni atoms was observed. Following the trend seen in binary Fe-Ni alloys, Ni adopted a spin-aligned orientation relative to Fe with an average magnitude in magnetic moment smaller than that of a pure Fe-Ni alloy ( $\sim 1 \mu_B$ ) [36]. Mn exhibited a more varied behaviour with a broad distribution of magnetic moments from  $-3$  to  $3 \mu_B$  in both structures at 0 and 66 at. % Fe. There is clear localisation of the magnetic moment of Mn for the 50 at. % Fe content at  $2.5\text{--}3 \mu_B$  in both A2 and B2 but the B2 has a narrower distribution. It is well-known that Mn is highly susceptible to adopting a wide range of magnetic structures [37]; theoretical methods predict the local antiferromagnetic case to be more energetically favourable (in  $\alpha$ -Fe) [38]. Furthermore, there is a shallow energy landscape between the high and low spin-state for Mn [39] in  $\alpha$ -Fe. Indeed, within this study Mn is predicted to exhibit a large degree of disorder. The magnetic moment of Fe adopted a bimodal distribution in the B2 structures

whereby the lower magnitudes correspond to the Fe atoms located on the Ni occupied sublattice. This behaviour is to be expected as the magnetic moment of Fe, in  $\alpha$ -Fe ( $2.2 \mu_B$ ), deviates under the influence of solute atoms in their local environment [40].

### 3.4 Entropy

For highly alloyed mixtures of elements, the configurational entropy can contribute significantly to phase stability [41]. The vibrational and electronic components of entropy are predicted to contribute up to a maximum of half the magnitude of the configurational entropy [42,43]. When comparing two phases of the same packing and chemistry (with the only difference being site occupancies) the difference in vibrational entropy between the phases is expected to be small but non-negligible [44,45]. However, calculation of vibrational entropy for a large set of disordered systems is currently computationally unfeasible. For this reason, we consider configurational and magnetic entropy only.

The magnitude of the configurational entropy is proportional to the degree of disorder. Above some threshold temperature, a fully disordered case will become energetically favourable (providing that temperature is below the solidus). In the case of the modelled A2 and B2 solute clusters this threshold temperature was obtained by equating the calculated Gibbs free energy of the two phases:

$$T_{thr} = \frac{H_{A2} - H_{B2}}{S_{A2} - S_{B2}} \quad (1)$$

where  $H_{A2}$  and  $H_{B2}$  are the average calculated formation enthalpies of the disordered and partially ordered structures at 0 K, respectively, and  $S_{A2}$  and  $S_{B2}$  are the sum of the configurational and magnetic entropies of the disordered and partially ordered structures, respectively. The configurational entropy of the fully disordered structure was calculated using the equation for Gibbs entropy [46]:

$$S_{A2} = -nR \sum_{i=1}^N x_i \ln(x_i) \quad (2)$$

where  $n$  is the number of moles,  $R$  is the gas constant and  $x_i$  is the atomic fraction of element  $i$  in an  $N$  element system. To calculate  $S_{B2}$ , the sublattices were treated as separate alloys weighted by their contribution to one mole of the combined system:



$$S_{B2} = -R \left[ \sum_{k=1}^L n_k \sum_{\substack{i=1 \\ i \neq \alpha}}^N x_{i,k} \ln(x_{i,k}) \right] \quad (3)$$

where  $k$  is the sublattice in a system with  $L$  number of sublattices and  $\alpha$  denotes any element that does not appear on that specific sublattice. This method has been used to much success in the past [27,47].

Magnetic entropy is estimated in much the same manner as the configurational entropy term [48] and represents the number of magnetic states possible for each elemental species to exist within each structure [49]. These states are taken from the DFT calculations (Fig. 4).

$$S_{B2} = -R \left[ \sum_{i=1}^N n_i \sum_{s=1}^M X_{s,i} \ln(X_{s,i}) \right] \quad (4)$$

where  $X_{s,i}$  is the fraction of atoms of element  $i$  with the same magnetic moment,  $s$ , normalised to the total number of atoms of element  $i$  and  $M$  is the total number of atoms.

Within this study,  $X_{s,i}$  was calculated from the density distribution seen in Fig. 5, discretised into fix-width bins of  $0.03 \mu_B$  width. Due to the continuous nature of the magnetic moments the magnetic entropies were logarithmically proportional to the bin size used. However, the relative change in entropy between A2 and B2 phases is independent of bin size.

The predicted entropy contributions and threshold temperatures above which the disordered solute clusters become more favourable than their partially ordered counterparts, can be seen in Table 4.

Table 4. Calculated configurational entropy ( $S_{conf}$ ) and magnetic entropy ( $S_{mag}$ ) of B2 and A2 solute clusters and the threshold temperature ( $T_{thr}$ ) at which the two phases are in thermodynamic equilibrium ( $G_{A2}=G_{B2}$ ).

Fe content (at. %)	$S_{B2}$ ( $\times 10^{-5}$ eV/at/K)		$S_{A2}$ ( $\times 10^{-5}$ eV/at/K)		$T_{thr}$ (K)
	$S_{conf}$	$S_{mag}$	$S_{conf}$	$S_{mag}$	
0	4.13	1.87	8.57	1.36	1971
50	7.22	2.84	10.1	2.52	1202
66	6.36	2.56	8.37	2.62	985

The magnetic contribution, to the total entropy, are of relatively similar magnitudes between the A2 and B2 structures; it is the configurational entropy that is predicted to have the greatest impact on phase stability.

The quoted values for  $T_{thr}$  are calculated using the *average* formation enthalpies of the A2 and B2 structures. By using a combination of minimum enthalpy of A2 and maximum enthalpy of B2, and vice-versa, a range in  $T_{thr}$  values are obtained: 524 – 4228 K, 711 – 1891 K and 679 – 1019 K for 0, 50 and 66 at. % Fe, respectively. For the 0 at. % Fe structures, it is reasonable to assume that this large degree of uncertainty arises due to the metastability of the BCC phase and that the threshold temperature is unphysical. For the structures with 50 and 66 at. % Fe, these results suggest that the B2 type ordering may be stable in the solute clusters at operating temperatures of the steel components. In experimental terms, it should be possible to identify such ordering using TEM. However, below the lower bounds of the estimated  $T_{thr}$  values the kinetics may be insufficient for ordering to occur.

#### 4. Conclusions

The enrichment of solute species Mn, Ni and Si is energetically preferable over the dilute ferrite matrix of a typical low alloy steel. Between 10 – 18 at. % Fe, the G-phase is predicted to be more stable than BCC packing, in agreement with past experimental observations on duplex stainless steels.

The energy barrier for transformation from BCC packing to G-phase is expected to exist in the vacancy production and migration of solute species. When ~10% of vacancies are introduced into the BCC structure (12 vacancies in a 128-atom supercell), and elemental site occupancies are lattice matched, the transformation from between the BCC → G-phase is expected to occur spontaneously.

At 0 K the B2 partial ordering is more energetically favourable than the A2 configuration at all Fe contents of the solute clusters. When considering the configurational and magnetic entropy, the A2 structure will become energetically favourable at composition specific threshold temperatures. Magnetic entropy is determined to be significantly less important than configurational entropy in the order/disorder transition of A2/B2.

## Acknowledgements

Mark Wenman and Daniel King were funded by EPSRC grant no. EP/P005101/1. M. Grace Burke is funded by grant no. EP/P003591/1. Thomas Whiting acknowledges support through the CDT in nuclear energy grant no. EP/L015900/1 and funding from Rolls-Royce Plc. This research was undertaken with the assistance of resources provided by the Australian National Computational Infrastructure supported by Intersect Australia Ltd (Raijin) and Imperial College Tier 2 computing (Cx1 and Cx2).

## References

- 
- [1] H.J. Beattie, F.L. VerSnyder, A new complex phase in a high-temperature alloy, *Nature*. 178 (1956) 208–209.
  - [2] J.M. Vitek, G-phase formation in aged type 308 stainless steel, *Metall. Trans. A*. 18 (1987) 154–156.
  - [3] K.H. Lo, C.H. Shek, J.K.L. Lai, Recent developments in stainless steels, *Mater. Sci. Eng. R Reports*. 65 (2009) 39–104.
  - [4] M.K. Miller, J. Bentley, APFIM and AEM investigation of CF8 and CF8M primary coolant pipe steels, *Mater. Sci. Technol*. 6 (1990) 285–292.
  - [5] F. Gillemot, Overview of reactor pressure vessel cladding, *Int. J. Nucl. Knowl. Manag.* 4 (2010) 265–278.
  - [6] S.J. Zinkle, G.S. Was, Materials challenges in nuclear energy, *Acta Mater*. 61 (2013) 735–758.
  - [7] S.J. Zinkle, J.T. Busby, Structural materials for fission & fusion energy, *Mater. Today*. 12 (2009) 12–19.
  - [8] R. Ngayam-Happy, C.S. Becquart, C. Domain, L. Malerba, Formation and evolution of MnNi clusters in neutron irradiated dilute Fe alloys modelled by a first principle-based AKMC method, *J. Nucl. Mater*. 426 (2012) 198–207.
  - [9] J.F. Knott, C.A. English, D.R. Weaver, D.P.G. Lidbury, Views of TAGSI on the effects of gamma irradiation on the mechanical properties of irradiated ferritic steel reactor pressure vessels, *Int. J. Press. Vessel. Pip.* 82 (2005) 929–940.
  - [10] G.R. Odette, T. Yamamoto, D. Klingensmith, On the effect of dose rate on irradiation hardening of RPV steels, *Philos. Mag.* 85 (2005) 779–797.
  - [11] P. Pareige, J.C. Van Duysen, P. Auger, An APFIM study of the microstructure of a ferrite alloy after high fluence neutron irradiation, *Appl. Surf. Sci.* 67 (1993) 342–347.
  - [12] J.M. Hyde, A. Cerezo, T.J. Williams, Statistical analysis of atom probe data: Detecting the early stages of solute clustering and/or co-segregation, *Ultramicroscopy*. 109 (2009) 502–509.
  - [13] M.K. Miller, K.A. Powers, R.K. Nanstad, P. Efsing, Atom probe tomography characterizations of high nickel, low copper surveillance RPV welds irradiated to high fluences, *J. Nucl. Mater*. 437 (2013) 107–115.
  - [14] ASTM International, Standard Specification for Quenched and Tempered Vacuum-Treated Carbon and Alloy Steel Forgings for Pressure Vessels BT - Standard Specification for Quenched and Tempered Vacuum-Treated Carbon and Alloy Steel Forgings for Pressure Vessels, in: World Trade Organization TBT Committee, West Conshohocken, PA, 2017.
  - [15] G.R. Odette, G.E. Lucas, Recent progress in understanding reactor pressure vessel steel embrittlement, *Radiat. Eff. Defects Solids*. 144 (1998) 189–231.
  - [16] H. Ke, P. Wells, P.D. Edmondson, N. Almirall, L. Barnard, G.R. Odette, D. Morgan, Thermodynamic and kinetic modeling of Mn-Ni-Si precipitates in low-Cu reactor pressure vessel steels, *Acta Mater*. 138 (2017) 10–26.
  - [17] G. Odette, B. Wirth, A computational microscopy study of nanostructural evolution in irradiated pressure vessel steels, *J. Nucl. Mater*. 251 (1997) 157–171.
  - [18] X. Yan, A. Grytsiv, P. Rogl, V. Pomjakushin, X. Xue, On the crystal structure of the Mn–Ni–Si G-phase, *J. Alloys Compd.* 469 (2009) 152–155.
  - [19] S. Li, Y. Wang, X. Wang, F. Xue, G-phase precipitation in duplex stainless steels after long-term thermal aging: A high-resolution transmission electron microscopy study, *J. Nucl. Mater*. 452 (2014)

- 382–388.
- [20] Y. Matsukawa, T. Takeuchi, Y. Kakubo, T. Suzudo, H. Watanabe, H. Abe, T. Toyama, Y. Nagai, The two-step nucleation of G-phase in ferrite, *Acta Mater.* 116 (2016) 104–113.
- [21] B. Gault, M.P. Moody, J.M. Cairney, S.P. Ringer, *Atom probe microscopy*, Springer Science & Business Media, 2012.
- [22] G. Kresse, J. Furthmüller, *Software VASP, vienna (1999)*, *Phys. Rev. B.* 54 (1996) 169.
- [23] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B.* 59 (1999) 1758.
- [24] M. Methfessel, A.T. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Phys. Rev. B.* 40 (1989) 3616.
- [25] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [26] S.C. Middleburgh, D.M. King, G.R. Lumpkin, M. Cortie, L. Edwards, Segregation and migration of species in the CrCoFeNi high entropy alloy, *J. Alloys Compd.* 599 (2014) 179–182.
- [27] D.M. King, S.C. Middleburgh, L. Edwards, G.R. Lumpkin, M. Cortie, Predicting the Crystal Structure and Phase Transitions in High-Entropy Alloys, *Jom.* 67 (2015) 2375–2380.
- [28] D.J.M. King, S.C. Middleburgh, A.G. McGregor, M.B. Cortie, Predicting the formation and stability of single phase high-entropy alloys, *Acta Mater.* 104 (2016) 172–179.
- [29] D.J.M. King, P.A. Burr, E.G. Obbard, S.C. Middleburgh, DFT study of the hexagonal high-entropy alloy fission product system, *J. Nucl. Mater.* 488 (2017) 70–74.
- [30] P.B. Wells, T. Yamamoto, B. Miller, T. Milot, J. Cole, Y. Wu, G.R. Odette, Evolution of manganese–nickel–silicon-dominated phases in highly irradiated reactor pressure vessel steels, *Acta Mater.* 80 (2014) 205–219.
- [31] M.G. Burke, R.J. Stofanak, M. Hyde, C.A. English, W.L. Server, Microstructural aspects of irradiation damage in A508 Gr 4N forging steel: Composition and flux effects, in: A. Grossbeck, ML and Allen, TR and Lott, RG and Kumar (Ed.), *Eff. Radiat. Mater. 21st Int. Symp., AMERICAN SOCIETY TESTING AND MATERIALS, 2004*: pp. 194–207.
- [32] M.G. Burke, R.J. Stofanak, J.M. Hyde, C.A. English, W.L. Server, Characterisation of irradiation damage in A508 class 2 and class 4 forging steels, in: G.S. Was, L. Nelson (Eds.), *10th Int. Symp. Environ. Degrad. Mater. Nucl. Power Syst. React.*, 2002.
- [33] T. Takeuchi, J. Kameda, Y. Nagai, T. Toyama, Y. Matsukawa, Y. Nishiyama, K. Onizawa, Microstructural changes of a thermally aged stainless steel submerged arc weld overlay cladding of nuclear reactor pressure vessels, *J. Nucl. Mater.* 425 (2012) 60–64.
- [34] T. Takeuchi, Y. Kakubo, Y. Matsukawa, Y. Nozawa, T. Toyama, Y. Nagai, Y. Nishiyama, J. Katsuyama, Y. Yamaguchi, K. Onizawa, Effects of thermal aging on microstructure and hardness of stainless steel weld-overlay claddings of nuclear reactor pressure vessels, *J. Nucl. Mater.* 452 (2014) 235–240.
- [35] T. Hamaoka, A. Nomoto, K. Nishida, K. Dohi, N. Soneda, Accurate determination of the number density of G-phase precipitates in thermally aged duplex stainless steel, *Philos. Mag.* 92 (2012) 2716–2732.
- [36] M.F. Collins, J.B. Forsyth, The magnetic moment distribution in some transition metal alloys, *Philos. Mag.* 8 (1963) 401–410.
- [37] D. Hobbs, J. Hafner, density functional study of phase stability and noncollinear magnetism in Mn, *J. Phys. Condens. Matter.* 13 (2001) L681–L688.
- [38] H. Akai, M. Akai, J. Kanamori, Electronic structure of impurities in ferromagnetic iron. II. 3d and 4d impurities, *J. Phys. Soc. Japan.* 54 (1985) 4257–4264.
- [39] B. Drittler, N. Stefanou, S. Blügel, R. Zeller, P.H. Dederichs, Electronic structure and magnetic properties of dilute Fe alloys with transition-metal impurities, *Phys. Rev. B.* 40 (1989) 8203.
- [40] A. Ayuela, N.H. March, The magnetic moments and their long-range ordering for Fe atoms in a wide variety of metallic environments, *Int. J. Quantum Chem.* 110 (2010) 2725–2733.
- [41] D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, D. Raabe, Ab initio thermodynamics of the CoCrFeMnNi high entropy alloy: Importance of entropy contributions beyond the configurational one, *Acta Mater.* 100 (2015) 90–97.
- [42] A. van de Walle, G. Ceder, The effect of lattice vibrations on substitutional alloy thermodynamics, *Rev. Mod. Phys.* 74 (2002) 11–45.
- [43] A. Benisek, E. Dachs, The vibrational and configurational entropy of disordering in Cu<sub>3</sub>Au, *J. Alloys Compd.* 632 (2015) 585–590.
- [44] T. Hickel, B. Grabowski, F. Körmann, J. Neugebauer, Advancing density functional theory to finite temperatures: methods and applications in steel design, *J. Phys. Condens. Matter.* 24 (2011) 53202.
- [45] F. Körmann, Y. Ikeda, B. Grabowski, M.H.F. Sluiter, Phonon broadening in high entropy alloys, *Npj Comput. Mater.* 3 (2017) 36.

- [46] R. Swalin, *Thermodynamics of Solids*, in: Wiley, New York, 1991: p. 21.
- [47] C. Niu, A.J. Zaddach, A.A. Oni, X. Sang, J.W. Hurt, J.M. LeBeau, C.C. Koch, D.L. Irving, Spin-driven ordering of Cr in the equiatomic high entropy alloy NiFeCrCo, *Appl. Phys. Lett.* 106 (2015) 161906.
- [48] M.S. Ghiorso, Thermodynamic analysis of the effect of magnetic ordering on miscibility gaps in the Fe–Ti cubic and rhombohedral oxide minerals and the Fe–Ti oxide geothermometer, *Phys. Chem. Miner.* 25 (1997) 28–38.
- [49] B. Fultz, Vibrational thermodynamics of materials, *Prog. Mater. Sci.* 55 (2010) 247–352.