The Effect of C Concentration on Radiation Damage in Fe-Cr-C Alloys

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Abstract

Molecular dynamics simulations of the primary radiation damage by displacement cascades were performed in different Fe-Cr-C model alloys, using a recently developed analytical bond-order potential for the complete ternary system. Results obtained with this new potential were compared to previous studies employing potentials for the binary Fe-Cr and Fe-C systems. We analysed the effect of C concentration on the number of Frenkel pairs produced by the cascades, as well as on clustering of vacancies and self-interstitial atoms (SIAs), and on the Cr and C content in the defects. The effect of C concentration on defect production was negligible, except at very high concentrations of over 1 at.% C. The main effect was seen in the Cr content of clustered SIAs, which increased with increasing C concentration.

Keywords: steel, radiation damage, displacement cascade, primary defects, molecular dynamics

1. Introduction

One of the major challenges still facing commercial production of fusion and advanced fission power is the development of materials which can withstand the intense radiation environment in these reactors. Reduced activation ferritic-martensitic (RAFM) and oxide dispersion-strengthened (ODS) steels are current candidate materials for structural components due to their reduced swelling and helium embrittlement, and high recycling potential [1]. Although many issues remain unsolved, current development of RAFM steels with low activation levels, which at the same time resist irradiation embrittlement, has converged on high chromium steels such as EUROFER97 [2]. In addition to high levels of Cr,

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EUROFER97 also contains 0.5 at.% C, occurring partly in the form of carbide inclusions [3].

Development of optimal structural materials is made difficult by the current lack of testing facilities which could fully mimic the conditions in a working fusion power plant. Thus experimental results have to be extrapolated to the correct conditions. Correct predictions are dependent on a thorough understanding of the basic mechanisms occurring within the materialInsight into the atomic processes leading to swelling and embrittlement can be gained through multi-scale computer simulations.

An important step in the modelling process is given by molecular dynamics (MD) simulations of primary radiation damage in model alloys. Radiation effects have been extensively simulated in pure iron (Fe) [4], and some simulation studies have also been performed in binary systems such as FeC and FeCr. For instance, it is known that the presence of Cr has an effect on the behaviour of cascades in steels [5, 6], while, on the other hand, the presence of C by itself has not been observed to have an effect up to a concentration of 1 at.% C [7]. However, the mechanisms governing radiation damage in FeCrC have not previously been explored with molecular dynamics methods, mainly due to the lack of an inter-atomic potential describing the complete ternary system.

In this article we study the combined effect of Cr and C on primary cascade damage in bcc-Fe (ferrite), including concentrations of C up to 5 at.% Although the equilibrium solubility level of C in ferrite at 300 K is of the order of 10^{-12} wt% [8], non-equilibrium systems may contain higher concentrations. Hence, it is of interest to explore how higher concentrations affect the behaviour of radiation damage cascades. We examine how a recently developed inter-atomic bond-order potential for the ternary Fe-Cr-C system [9] describes the damage. The potential is developed for simulations in stainless steels and, e.g., reproduces the mechanical and thermodynamic properties of most Fe and Cr carbides as well as simple C and Cr defects in Fe.

2. Methods and analysis

Molecular dynamics simulations of cascades initiated by 1 keV and 5 keV recoils in Fe-x%Cr-y%C were carried out for all combinations of 5 and 10% Cr, with C concentrations between 0 and 5 at.%. For each case 50 cascades were simulated. In addition, 10 cascades each were also simulated in pure Fe, Fe-0.5%C and Fe-1%C, as well as 20 cascades in Fe5%C, for comparison to other potentials. The classical molecular dynamics [10] code PARCAS [11] was used for all simulations.

The analytical bond-order (ABOP) [12] potential used in this study was recently developed especially for simulating stainless steels. It uses previously existing, well-tested parametrizations for Fe-Fe [13, 14] and C-C [15, 16] interactions. New Cr-Cr, Fe-Cr, Fe-C and Cr-C potentials have been fitted to density-functional theory (DFT) and experimental results. Details of the fitting process and properties of the potential can be found in Ref. [9]. Amongst other things, the combined potential correctly reproduces the mixing energy curve for

2

Fe-Cr [17], in particular the negative mixing energies for low Cr concentrations. In addition, it gives a good description of all carbides considered to be important in stainless steels, in particular the thermal metastability of cementite.

Simulations were performed in cubic samples of 42 lattice unit cells to a side, with periodic boundaries. The cells were constructed by creating a perfect bcc lattice of Fe, then randomly changing Fe atoms to Cr with a probability corresponding to 5 or 10% Cr. C interstitials were randomly added to octahedral sites, the defect configuration with lowest formation energy, to achieve the desired C concentrations. For each cascade a different cell was created, then thermally equilibrated for 10 ps at 300 K. The cell was held at zero pressure during equilibration, using Berendsen pressure control [18].

After equilibration an Fe primary knock-on atom (PKA) was picked near the centre of the cell, and given a velocity corresponding to the desired 1 or 5 keV recoil energy, in a random direction. Cascades from 1 keV PKAs were allowed to evolve for 15 ps, while 5 keV cascades were run for 20 ps. The simulation cell was held at constant volume during the cascade, and the temperature of the atoms within 3 Å of the boundaries was scaled using Berendsen temperature control [18], with a time constant of 100 fs. Previous studies [19] show that temperature scaling at the borders does not affect results as compared to methods which do not employ scaling.

In addition, the edges of the cell were monitored for atoms with energy above 10 eV, to guarantee that the cascades did not overlap with themselves. In the event of an atom with kinetic energy greater than 10 eV reaching a cell boundary, the simulation was aborted and a different PKA further away from that side was given the same velocity, in the same direction, and the cascade was redone. For recoils of 5 keV roughly one third of all runs were redone, while all 1 keV cascades stayed well within the cell borders.

No electronic stopping was used for consistency with previous simulations [19, 6].

The evolution of cascades was studied by analysing snapshots taken at 0.1 ps intervals for the first 2 ps, and at longer intervals for the rest of the run. Defects were calculated by centering a Wigner-Seitz (WS) cell on each lattice site, and counting the number of atoms within each cell. A multiply occupied cell was interpreted as a self-interstitial configuration, while an empty cell indicated a vacancy. All C atoms were disregarded in the initial defect analysis.

In the cases with 3% or 5% C and 10% Cr, a small number of isolated Frenkel pairs were produced during equilibration. This indicates that, at least within the current interatomic potential, the lattice starts to locally destabilize when high C and Cr concentrations are in close vicinity of each other. This implies that the "Frenkel pair" numbers obtained for the 3 at.% and 5 at.% C cells are not a reliable measure of the number of point defects, but rather reflect an effective measure of the volume of materials subject to a phase transition (in a similar manner as Wigner-Seitz analysis can be used to estimate the volume of amorphized material in semiconductors [20]). However, the cascade simulations described below show that overall the lattice is still stable, as most of the initial damage recombines. The numbers were on average 56 ± 0.5 and 31 ± 2 Frenkel

pairs in 3% and 5% C, respectively. These amounts were subtracted from the final damage count for the concentrations in question.

A defect was considered as belonging to a cluster if it was within a certain cut-off radius from at least one other atom in the cluster. The bcc second nearest neighbour distance was used as the cut-off radius for SIA clusters, while clustering of vacancies was calculated using the third nearest neighbour distance as cut-off. These cut-off radii conform to those used in previous studies of damage in FeCr [5, 19, 6].

The Cr content in SIAs was determined by counting the number of Cr atoms out of all atoms found in multiply occupied WS cells. This fraction was then divided by the percentage of Cr in the matrix, giving the Cr concentration relative to the stoichiometry of the cell. The amount of Cr in clustered defects was calculated in the same way, counting only atoms contained in clusters of 5 defects or more. This analysis was done on the final atom configuration, and included all defects, also those appearing during equilibration.

The amount of C in defects was calculated as the fraction of vacancies, and of Fe and Cr SIAs, which were adjacent to C atoms out of the total number of vacancies and SIAs, respectively. Again, this was divided by the concentration of C in the matrix, for a relative C concentrationA defect was counted as being adjacent to a C atom if one or more C atoms were within nearest neighbour distance from the centre of the WS defect cell.

3. Results and discussion

3.1. Collision cascades

In order to determine whether simulation times of 15 ps was enough for 1 keV cascades, 6 test runs were performed for 30 ps. The results showed no change in defect numbers, within the statistical uncertainties, between the times of 15 ps and 30 ps.

From the time development of defects shown in Figure 1, one can see that the cascades develop and recombine, as is usual for metals [20]. In particular, recombination can be seen to occur with the same time profile at all levels of C included in this study, although the remaining defects are more numerous at higher concentrations. The number of defects fluctuates strongly in Fe-10%Cr-5%C, but these fluctuations are evened out when averaged over different runs. An average over 20 cascades is also shown in Figure 1.

The sequence of snapshots in Figure 2 shows a slice of the simulation cell during a 5 keV cascade in Fe-5%Cr-0.3%C. One can see development of the initial heat spike, and subsequent recombination of the lattice, with a few defects remaining. The larger darker spheres represent Cr, while the smallest darkest spheres are C.

3.2. Primary damage
3.2.1. Defect numbers

Figure 3 shows the number of surviving Frenkel pairs as a function of C concentration. Results from Refs [19] and [6] for FeCr have been added for
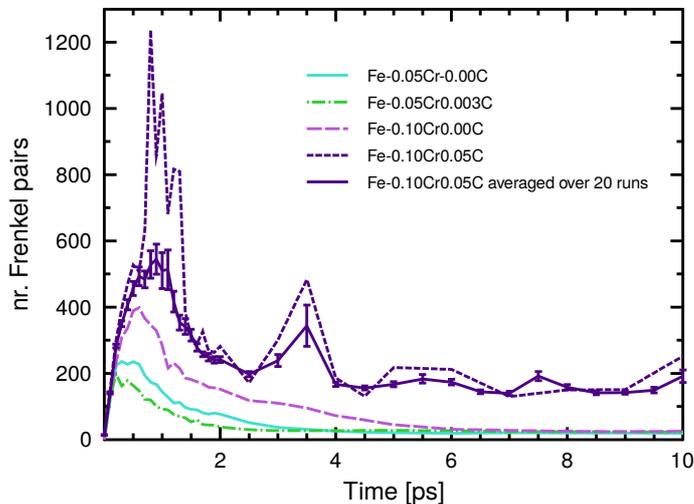
Figure 1: (Color online) The number of Frenkel pairs occuring during a selection of 5 keV cascades as a function of time. Defects are calculated from single cascades. In addition the average over 20 cascades in Fe-10%Cr-5%C is also shown.

direct comparison. For the binary FeCr system with 5% Cr, recoils at 1 and 5 keV produce defect numbers in accordance with the earlier results. Also the number of Frenkel pairs produced in Fe-10%Cr at 1 keV are consistent with previous results. On the other hand, with this potential a clear increase (about a factor of three) in defect numbers with increasing Cr concentration is seen in 5 keV cascades, contrary to previous results [6], which showed no increase in defects up to 15% Cr. It should, however, be mentioned, that tests of 15% Cr not included here showed a slight destabilization of the lattice, an effect likely related to the potential.

The addition of C in octahedral positions for concentrations up to 1 at.% has no significant effect on the number of defects, which is in agreement with previous results for the binary FeC system [7].There is no amorphization of the metal up to 1 at.% C, although C in solution is thermodynamically unstable at these concentrations, and in the longer term ought to form cementite precipitates. This, however, does not fully destabilize the lattice, as can be seen from the strong recombination in Fig.1. However, at concentrations above 1 at.% of C there is a clear and fairly strong increase in defect numbers, since the bcc lattice destabilizes locally.

The number of surviving Frenkel pairs in the binary FeC system shows no increase with increasing C concentration, and is in full agreement with previous

results [7].

3.2.2. Defect clusters

Formation of vacancy clusters is shown in Fig. 4, where results from Ref. [6] have been added for direct comparison. Vacancy cluster formation in binary FeCr is seen to be independent of Cr content, and similar to that attained in previous studies [5, 19, 6] for 1 keV recoils, within the statistical uncertainties. However, results from 5 keV recoils show a much lower level of vacancy clustering for all concentrations of C and Cr.

SIAs created by 1 keV cascades consist mostly of point defects spread throughout the cascade area, as can be seen in Fig. 5 from the low clustered fraction. However, in 5 keV cascades, clusters of SIAs start to form due to the more intense heat spike. No clear effect of C concentration can be seen.

3.3. Cr concentrations in defects

Figure 6 shows the Cr content in SIAs, which increases slightly with increasing energy. No effect of C content can be seen. The Cr content in SIA clusters is shown in Figure 7. Only clusters of 5 or more were considered, for consistency with previous studies [6]. At 1 keV almost no clusters of this size were formed, so results are given only for 5 keV cascades.With 5 % Cr in the matrix, there is a less than stoichiometric level of Cr in the defect clusters, while with 10 % Cr the cluster Cr content reaches the same level as that of the surrounding matrix.

3.4. C concentrations in defects

The C content in defects after 5 keV cascades can be seen in Figure 8Many vacancy sites were occupied by C atoms, but an even stronger affinity of C towards Fe and Cr SIAs can be seen, especially at a lower concentration of Cr in the matrix. The content of C in defects is clearly above stoichiometric levels for all concentrations of C, both for vacancies and SIAs. This supports earlier results for the binary FeC system [7]. The level of C content in defects relative to the stoichiometry is the same for all C concentrations, within the statistical uncertainties. A possible effect of Cr concentration can be seen on the C content in both vacancies and SIAs, with a lower C content in vacancies and higher in SIAs at 5% Cr compared to 10% Cr.
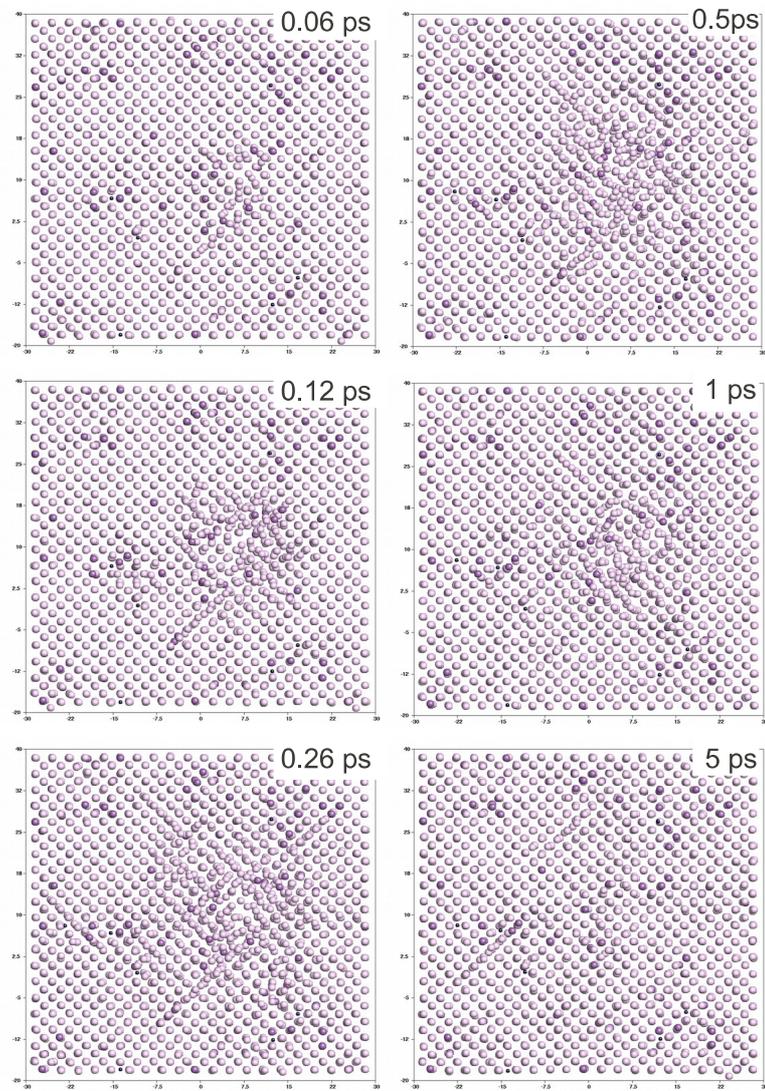
Figure 2: (Color online) Snapshots of a slice from a simulated 5 keV cascade in Fe-5%Cr-0.3%C. The larger darker spheres represent Cr, while the smallest darkest spheres are C, and the rest are Fe.
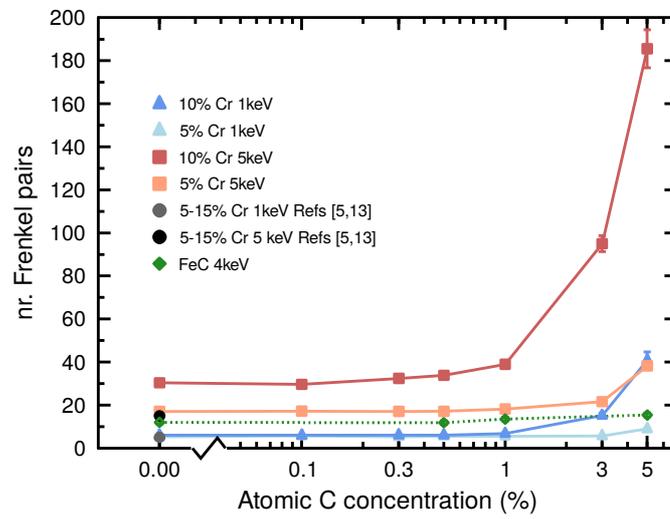
Figure 3: (Color online) The average number of surviving Frenkel pairs for cascade energies of 1 keV and 5keV in Fe with 5% and 10% Cr, as a function of atomic C concentration.
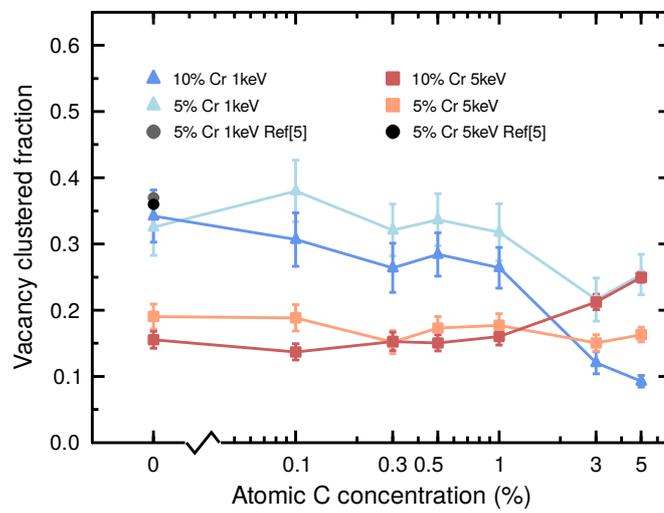
Figure 4: (Color online) The fraction of clustered vacancies obtained from 1 keV and 5 keV cascade simulations in Fe with 5% and 10% Cr, given as a function of C concentration. The error bars are 1σ errors of the average.
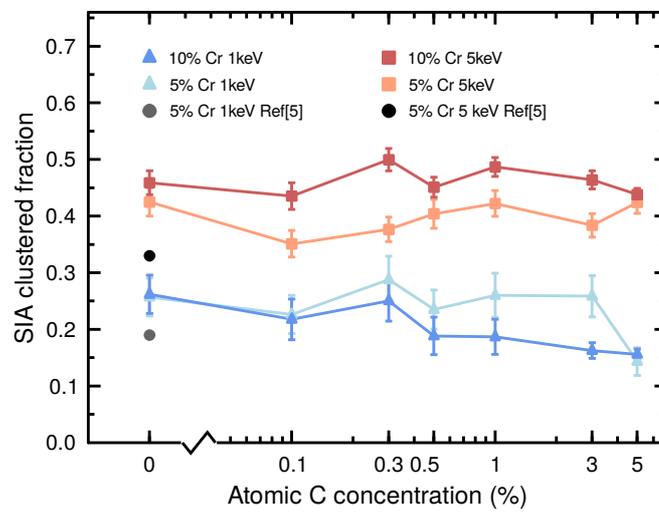
Figure 5: (Color online) The fraction of clustered SIAs obtained from 1 keV and 5 keV cascade simulations in Fe with 5% and 10% Cr, given as a function of C concentration. The error bars are 1σ errors of the average.
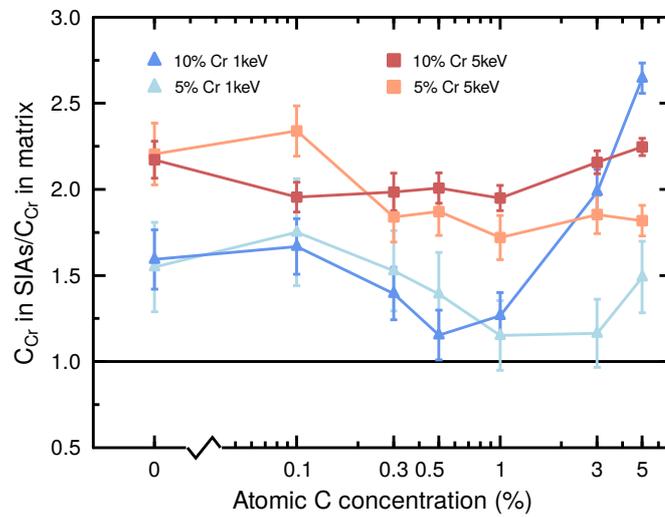
Figure 6: (Color online) Cr content in SIAs relative to the stoichiometric Cr content in the matrix, obtained from 1 keV and 5 keV cascade simulations in Fe with 5% and 10% Cr, given as a function of C concentrationThe error bars are 1σ errors of the average.
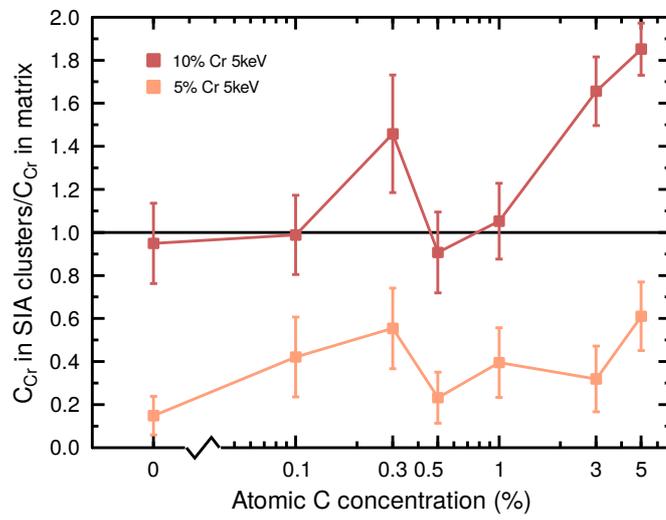
Figure 7: (Color online) Cr content in clusters of SIA larger than 5, from 5 keV cascade simulations in Fe with 5% and 10% Cr. Results are given relative to the stoichiometric Cr content in the matrix.The error bars are 1σ errors of the average.
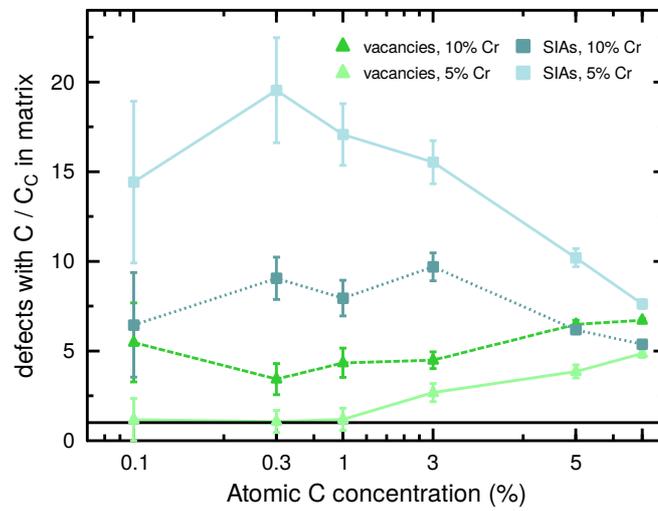
Figure 8: (Color online) Fraction of vacancy and SIA defects with C within nearest neighbor distance, divided by concentration of C in matrix. Results from 5 keV cascade simulations in Fe with 5% and 10% Cr. The error bars are 1σ errors of the average.

4. Conclusions

In conclusion, a slight difference can be seen in cascade damage simulated with the potential applied here, compared to earlier potentials. The effect of Cr was found to be more pronounced than previous studies have reported.

The results show that that the presence of C has a negligible effect on damage production in FeCrC alloys up to a C concentration of 1 at-%. At higher concentrations clear effects of C on the damage production are visible (likely related to onsets of phase transitions), but it is difficult to envision any stable ferritic steels where this high C concentrations would be relevant.

Comparison of the effects of Cr with previous simulations indicate that potential reliability remains an issue for quantitative prediction of damage production in FeCr alloys.

Acknowledgements

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15