Research Article

Understanding Laves phase precipitation induced embrittlement of modified 9Cr–1Mo steel

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Abstract

Precipitation of Laves phase in steels is often identified as the primary cause for the degradation of mechanical properties. Analytical electron microscopy and thermodynamic modelling have been used in this study to understand the Lave phase precipitation induced damage initiation process in modified 9Cr–1Mo steel, exposed to high temperature for 10,000 h. The results have suggested that in addition to void nucleation at the interface and de-cohesion, the limited plasticity of the Laves phase is also a predominant mechanism for crack initiation in this material. The thermodynamic propensity of Laves phase precipitation around the carbides and the underlying role of local chemistry have also been studied. Binary Laves phases have been found to be stabilized by ternary additions.

Keywords Laves phase precipitation · Electron microscopy · Micromechanics · Steel · Fracture · Thermodynamic modelling

1 Introduction

The ceaseless increase in energy demands and stringent environmental regulations have fostered the use of modified 9Cr–1Mo or P91 heat resistant steels as structural materials, specifically in nuclear and thermal power, and in petro-chemical industries [1, 2]. The microstructure of the ASME grade P91 steel is commonly evolved by thermo-mechanical processing, and is reported to have an optimum combination of strength, toughness and other mechanical and electro-chemical properties [2], which are primarily attributed to the tempered martensite matrix with relatively high dislocation density, and precipitates of types: $M_{23}C_6$ (M = Cr, Fe, and Mo) carbides and finely dispersed MX-type (M = V, Nb and X = C, N) carbonitrides. The former is primarily located at the prior austenite grain boundaries (PAGBs) and the latter is within the laths [3]. Unfortunately however, it has been observed that the creditable properties rendered by the tailored microstructure do not span indefinitely [2]. Besides, embrittlement has been reported in most ferritic-martensitic steels, like this type, after exposure to higher temperatures over long durations. Well-agreed theories, which extend to explain this premature failure on aging, are (1) evolution and coarsening of carbides or and intermetallic phases, and (2) segregation of hydrogen and tramp elements (like P, As, Sn, etc.) to PAGBs [2]. Amongst these however, the major consensus view point has been the nucleation and growth of complex hard and brittle Laves phases (topologically close packed intermetallic compounds with AB_2 stoichiometry) [4, 5], on grain and lath boundaries [6].

Recent studies on aged modified 9Cr–1Mo steels have revealed that formation of Laves phase debilitates fracture toughness, while substantially increasing the ductile brittle transition temperature [2]. Decline in the solid solution strengthening component, and reduction in fatigue life from spawn of cavities/cracks, have also been noticed with

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the precipitation of Laves phases [7]. However, although the presence of Laves phases have been marked to be the major reason for overall degradation of fracture and deformation properties, a synergistic approach towards understanding its modus operandi is yet to be evolved.

Interestingly, in spite of the deleterious effects which come with it, Laves phase cannot be all-that devastating if the science that operates them is understood and properly addressed. For instance, the hard Laves phase particles can be effective, possibly the best precipitation hardeners should their size is well maintained in the fine regime [8]. Similarly, their complex crystal structure can offer absorption of massive quantities of deleterious elements such as phosphorous and hydrogen [7], which often acts to weaken the grain boundaries leading to premature failure of structures. Additionally, ductilization of the otherwise hard and brittle phase has been recorded possible by suitably controlling the chemistry and the defect structure [9–11]. Nevertheless, little practical knowledge has been elucidated from Laves phase study so far, particularly from a material of this kind.

The most commonly asked question about the Laves phase induced embrittlement in modified 9Cr–1Mo steel is on the role of crystal structure, crystal chemistry and the interfaces with the Laves phase precipitates, in the damage initiation mechanism. Further, the aspect of preferential nucleation of Laves phase precipitates in the vicinity of certain carbides is also not understood. Therefore, on the foundations of atomic scale observations, and thermodynamic approximations, the focus of this work is to arrive at an understanding of Laves phase induced embrittlement mechanisms in modified 9Cr–1Mo steel, so that the effects of interfaces, crystal structure and crystal chemistry of Laves phase could be correlated with the deterioration of fracture properties. A light is also shed on the revelation and explanation of the underlying mechanisms, which operate individually or in synergy to induce embrittlement in the system. The reported results evince to have a long reach in the field of structure–property correlation in structural steels, especially in case of Laves phase precipitation induced embrittlement.

2 Materials, experiments and modelling

2.1 Samples

In an earlier study [6] on modified 9Cr–1Mo steel, formation of Laves phase has been reported after an aging treatment of 10,000 h at 873 K (600 °C) and 923 K (650 °C). Therefore, two distinct samples, each from the respective aging treatment from the same steel, chemical composition of which is given in Table 1, have been used for this study. Sample 1,

Table 1 Chemical Composition of modified P91 steel

Element	Composition (wt%)
C	0.12
Mn	0.38
P	0.020
S	0.007
Si	0.470
Cr	9.420
Mo	1.00
Ni	0.13
Al	0.021
Nb	0.10
V	0.250
N	0.068
Fe	Balance

abbreviated as S1 hereafter, is 10% cold worked and aged at 873 K (600 °C) for 10,000 h. Sample 2, abbreviated as S2 hereafter, is 0% cold worked and aged at 923 K (650 °C) for 10,000 h.

2.2 Characterization techniques

Electron transparent samples from the steel with different thermal and deformation history were prepared by conventional technique. Transmission Electron microscope (Tecnai G2 F30 TEM) operated in the bright field (BF) image and selected area diffraction mode is deployed to outline the precipitates and strain fields. Elemental line profiling of the Laves phase and the carbide precipitates, as pictured through High angle annular dark field (HAADF) image, was performed using a line scan in X-ray energy dispersive spectroscopy (XEDS). Dislocation densities are visualized through HAADF images. The imaging data were quantified using a combination of Digital Micrograph and Tecnai Imaging and Analysis softwares.

3 Modelling

Thermodynamic phase stability of the intermetallic Laves phase, as a function of chemical composition and temperature is modelled using the CALPHAD (CALculation of PHAse Diagrams) approach. The model prediction grounds on the minimization of Gibbs free energy, and has been adopted through Thermocalc software, powered with TCFe6 database.

4 Results and discussion

4.1 TEM investigation

The degree of change in the chemistry and morphology of a microstructure is heavily dependent on the time and

temperature of ageing. Figure 1a, d illustrates the bright field images and diffraction patterns of S1 and S2; it must be recalled here that the ageing time of 10,000 h is common to either samples, it is on contrast, the heat treatment temperature, which is dissimilar. It is evident from the micrograph that extensive precipitation has occurred in both the tested samples during the entire course of ageing process. The size of the stable precipitates is bound to be coarsened as our observations are made at much higher exposure time; Laves phase in P91 grade may precipitate after 1000 h at 923 K (650 °C) or after 3000 h at 873 K (600 °C) [3, 12]. Nevertheless, readers must take a close account on the chemical composition of the steel as alloying elements can have a substantial effect on the phase stabilities and nucleation kinetics of the Laves phase [13, 14]. It is evident from the micrographs that a number of different precipitates have nucleated and coarsened during the exposure period. Therefore, to differentiate the precipitate-type, at first hand, a diffraction pattern is obtained across Laves phases and from the matrix in both the samples (Fig. 1b, d). Collation of the measured lattice parameter with standard values has been used as the basis

of precipitate identification. The high-lighted regions in the BF images, based on their lattice parameter values are tagged as Laves phases ($Fe_2(Mo,Nb)$). This correspondence reveals that the Laves phase chemistry can be highly sensitive to the steel composition, and could be multifarious: Fe_2Nb, Fe_2Mo or $Fe_2(Mo,Nb)$. Furthermore, it is interesting to observe, how quickly the intermetallic-Laves phase precipitates have coagulated into different morphologies. These results are in tune with previously reported studies [12]. Also noticeable from Fig. 1a, c are strain fields and dislocations, role of which on the Laves phase nucleation will be touched upon in the subsequent section.

4.2 Thermodynamic modelling

Precipitation of the Laves phase between 873 K (600 °C) and 923 K (650 °C), as is apparent from the TEM investigation and quoted references [2, 3, 12], can be understandably reasoned through computational modelling predictions. Thermodynamic phase stability of the intermetallic Laves phase, as a function of chemical composition and temperature in the present work is predicted using CALPHAD (CALculation of PHAse Diagrams) approximation. As shown in Fig. 2a, b, isothermal sections at 873 K (600 °C) and 923 K (650 °C) are generated for Fe–Mo–Cr ternary phase diagram. It follows from the isothermal sections that the primary phase field of Laves phase-region of Laves phase stability- is cornered/localized over the Fe rich domain of the phase diagram. This finding further augment and supplement the precipitation of Laves phase in the temperature range of 873 K (600 °C) and 923 K (650 °C). It is thus right to conclude that precipitation of Laves phase in the given temperature range is a result of not a mere kinetic or temperature distribution phenomenon, but the stability of this phase, i.e. the Gibbs free energy of the Laves phase reaches its lowest over this temperature scale. It is thereby interpreted that Laves phase is a rather stable precipitate in this temperature regime, and not metastable as has been misconceived in the past [12]. It needs to be emphasized that as the ageing process continues, the material under consideration hops from one energy minima to another energy minima leading to a change in the microstructure [4]. Another intriguing observation, which the reader can draw from these isothermal sections, is the chemical composition of Laves phase. Historically, the composition of this intermetallic phase is reported to be Fe_2Mo. This speculation appears incorrect as the Laves phase primary phase field (Fig. 2a, b) is by and large affected by Cr content. It can be postulated that the composition of the Laves phase could have a variable chemistry. Therefore, while concluding Laves phase nucleation to be a thermodynamically driven phenomenon, we posit that Cr stabilizes the precipitate in the same way Si does as
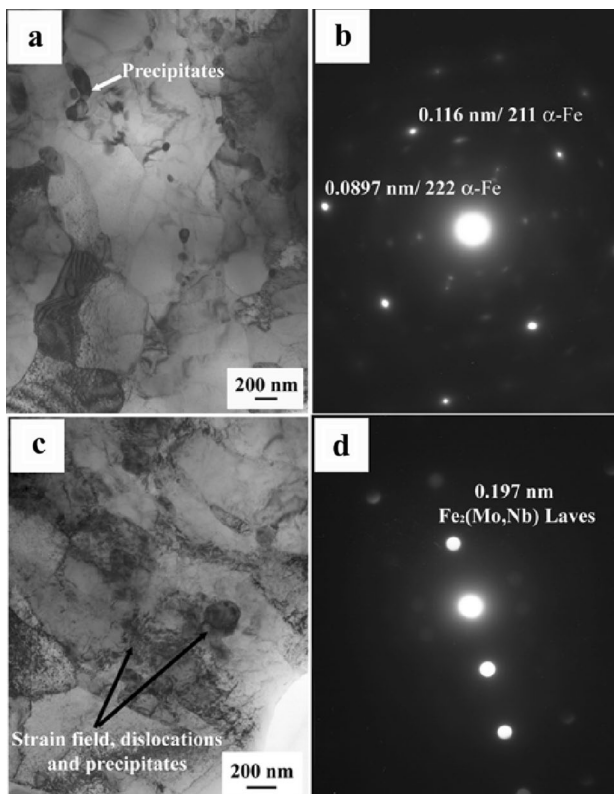
Fig. 1 **a** Bright field image and **b** selected area diffraction pattern of the 10% cold worked modified 9Cr–1Mo steel aged at 873 K (600 °C) for 10,000 h. **c** Bright field image and **d** selected area diffraction pattern of the 0% cold worked modified 9Cr–1Mo steel aged at 923 K (650 °C) for 10,000 h
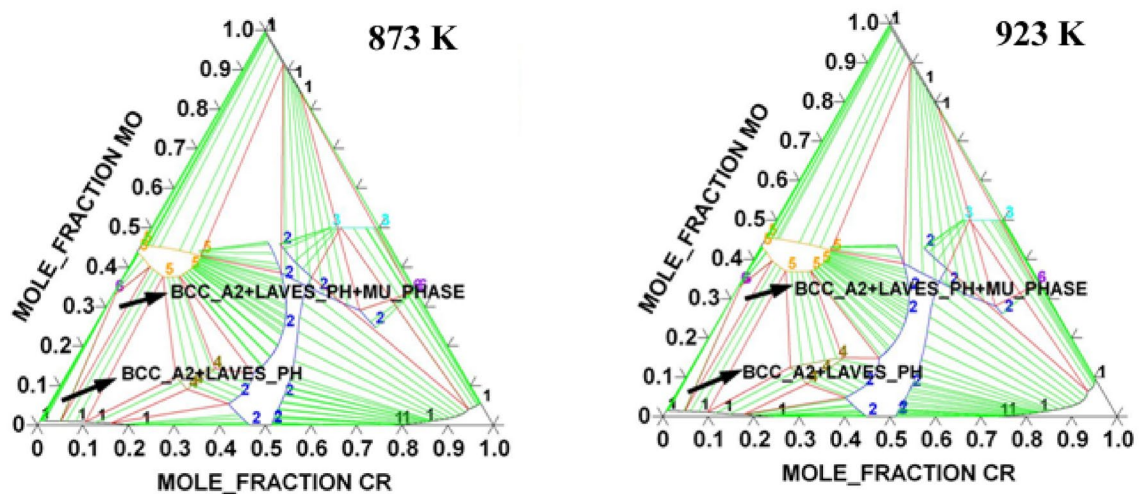
Fig. 2 Calculated isothermal section of Fe–Cr–Mo phase diagram at 873 K (600 °C) and at 923 K (650 °C). In both the isothermal sections primary phase field containing Laves phase is observed in the Fe rich side of the phase diagram

a substitutional element in Fe_2Mo, as has been estimated by Alonso et al. [15] using the first principal calculations. It is theorized that Cr diffuses against its concentration gradient. This must be due to the take-up of a high amount of Mo in the Laves phase, and resulting depletion of Mo around it. This phenomenon of uphill diffusion plays an important role in growth of the Laves phase as already reported in regard with W by Zinkevich et al. [16]. Furthermore, since Cr atomic radius (1.28 Å) and electronegativity (1.7) matches closely with Fe (1.27 Å and 1.85), chances are that Cr is welcomed only in the first sublattice of Fe, and not in the second, which is constituted by Mo and/or Nb. Loss of Cr from the matrix can prove to be deleterious. Cr renders solid solution strengthening, oxidation and corrosion resistance to the steel -vital properties- and hence, any loss in its cleverly chosen concentration can degrade the steel during service.

4.3 XEDS investigation

To the best of the knowledge of the authors, crystal chemistry and crystallography of defects in Laves phases, so far, has not been completely understood. However, it has been reported in earlier literatures that chemistry strongly influences the defect structure, and in turn the mechanical properties and phase stability of the Laves phase. While no record of Cr could be found, extensive research has been carried out in the context of conceiving the roles of Mo [13], Si [15], Co [17], Cu [18], W [19] and C [19] on the precipitation and growth of Laves phase.

The focus of this section is to draw experimental evidence for elucidating the modelling outcomes: phase

stability and chemistry. Figure 3b displays the results of the elemental mapping, performed using a XEDS line scan on a randomly chosen precipitate; displayed on a HAADF image (Fig. 3a). Obvious at first sight is a significant compositional shift. At the precipitate, a spike in the concentration of the chromium content is recorded. This increase is accompanied with a steep fall in the iron concentration. Along with these, occurs a trivial increase in molybdenum content. From this hierarchical switch, it can be asserted that the characterized precipitate conform to a carbide (most-likely $M_{23}C_6$ ($Cr_{23}C_6$)). It needs to be noted that the absence of carbon signals follow from the incapability of XEDS to detect rays of low energies; those which are small enough to be absorbed by high atomic number elements in the sample or by the detector window.

Co-existence of the chromium carbide precipitates alongside the Laves phase precipitates in our samples is in line with several previous studies [17, 20–22]. Isik et al. [20] have using atomic probe tomography (APT) described the preferential Laves phase precipitation at the micro grain boundaries of the chromium carbide precipitates, due to micro-segregation effects of select elements (such as Mo, Si, P). The elemental XEDS scans in this work agree well with the APT line scans in ref [20] and the absence of the Laves phases at the peripheries suggest that the local enrichment in the select elements, at the micro-grain boundaries and not peripheries is likely crucial for Laves phase nucleation. Nonetheless, the precipitation of chromium carbide is essential, given Laves phase nucleates only beyond 873 K (600 °C), after the $Cr_{23}C_6$ has precipitated.
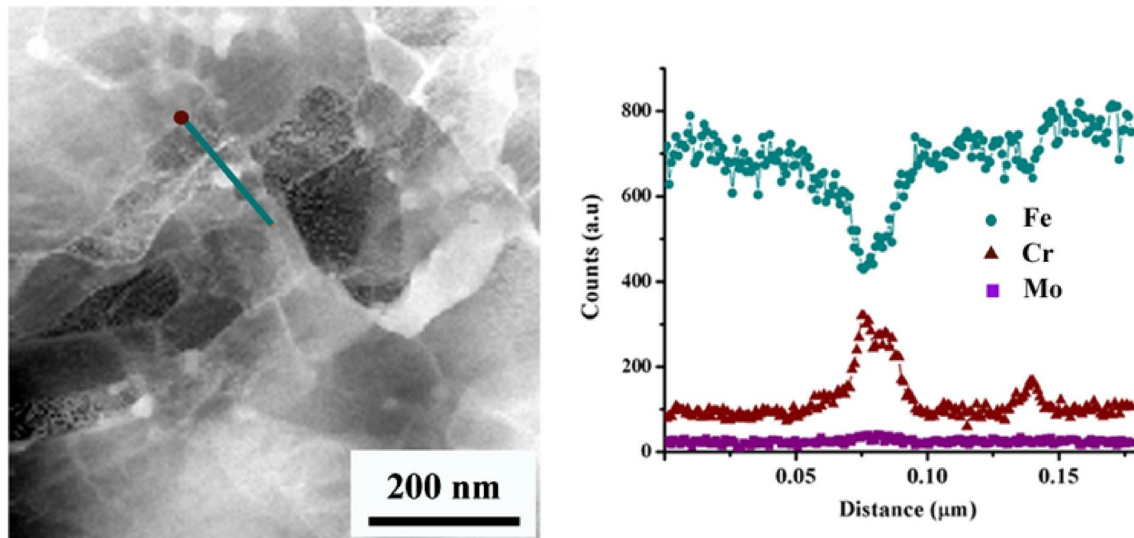
Fig. 3 HAADF image and XEDS line scan over a Cr rich precipitate which is 10% cold worked and aged at 873 K (600 °C) for 10,000 h. The line along which the beam was scanned is marked in the figure and the start point for scanning is marked on the line with a dot

4.4 HAADF investigation

Z contrast imaging generated by high angle annular dark field (HAADF) STEM can be an ideal characterization tool to the study of dislocation densities. It is well-established that precipitate-nucleation can be affected by factors of both thermodynamics and kinetics dispositions. Here we explore the effect of dislocations on the nucleation and growth kinetics of Laves phase.

As it is evident from Fig. 4a, in sample S2 (0% CW), no Laves phase precipitate is observed in a region of high dislocation density. Contrarily, in the case of sample S1 (10% CW) (Fig. 4b), Laves phase precipitates are evident and not necessarily all of them are at the regions of high defect density. This recording demonstrates that deformation history does not seemly contribute to the Laves phase nucleation. However, a more rigorous study is required to statistically quantify the precipitation across samples, and could be a future work.

5 Failure mechanisms

The aftermaths of Laves phase precipitation embrace degradation of physical, chemical and mechanical properties [2, 3]. Overall, it has been observed that after a long exposure period, the condition of the steel gets jeopardized from all metallurgical facets. Although, the downfall in chemical and physical properties has already been discussed in the previous sections, priority needs to be attached to the mechanical properties; the decline in the latter can single-handedly stimulate catastrophic failure.
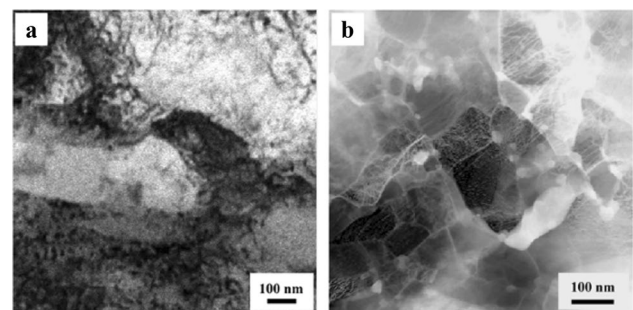
Fig. 4 HAADF image of modified 9Cr–1Mo steel: **a** 0% cold worked and aged at 650 °C (923 K) for 10, 000 h, and **b** 10% cold worked and aged at 873 K (600 °C) for 10,000 h. In **a** no Laves phase precipitate is observed in a region of high dislocation density. In **b** clusters of Laves phase precipitates are observed, not necessarily all of them are at the regions of high defect density

For instance, Dimmler et al. [21] reported stunted fatigue resistance of the steel due to Laves phase precipitation. In the same line, Sathyanarayanan et al. [6] reported a drop in dynamic fracture toughness with the precipitation of Laves phase. Dimmler et al. [23] have attributed this to be a result of massive nucleation and growth of cracks/voids at low strain values on regions adjacent to the Laves phase. On a comparison scale, it was concluded that the void density across Laves phase tends to be much greater than that could be attributed to any other precipitate. Figure 5 illustrates different mechanisms that may contribute individually or synergistically to multiply the propensity for fracture in steel from Laves phase precipitation. Mechanism 1, as plotted in red scribble, describes piling of dislocations over the hard non-deforming Laves phase. Such stacking
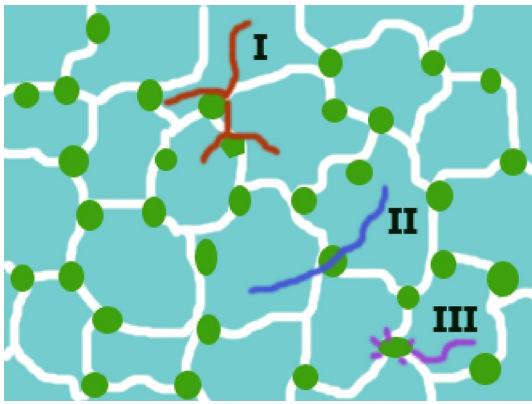
Fig. 5 Schematic representation of different mechanisms that may contribute to the enhanced propensity for fracture in modified 9Cr–1Mo steel after ageing at elevated temperature and Laves phase precipitation

Fig. 6 **a**–**d** HAADF micrographs of the modified 9Cr–1Mo steel-10% cold worked and aged at 873 K (600 °C) for 10,000 h. Note the absence of dislocations entanglement and voids around the Laves phase precipitate

leads to build up of high stresses, which act to micro-void/cavity nucleation. These voids consequently develop into self-propagating cracks, which induce brittle mode of fracture. Mechanism 2, represented in blue line -smearing through the precipitate-, operates on cleavage of the otherwise brittle Laves phase. Mechanism 3, pictured as a purple scribble, like Mechanism 1 is a consequence of the absence of coherence between the matrix and the Laves phase precipitate. The immense interfacial strain energy between the abutting Laves phase and matrix contributes to spawn of a number of voids, which are well capable of transforming into cracks.

The question that must now be raised is which among these three, is the mechanism that primarily contributes to the deterioration of mechanical properties of the material after ageing at temperatures between 873 (600 °C) and 923 K (650 °C).

Observations of HAADF micrographs of a failed P91 steel sample (Fig. 6a–d), show that that dislocation clustering is not an identifiable trait of Laves phase. While some regions abutting Laves phase reflect dislocations pile-up (Fig. 6d), majority of Laves phase peripheries (Fig. 6a–c) are devoid of the dislocations clutter; Laves phase is not pre-stressed by dislocations. Furthermore micro-voids or cavities around the peripheries of the Laves phase precipitates are absent. This implies mechanisms 1 and 3, which operate on de-cohesion of phases, perhaps, do not significantly contribute to the fracture. In better terms, Laves phase are not the nucleating sites for dislocations. Mechanism 2, therefore seems to appear more apparent. Since the Laves phase is not pre-stressed by the dislocations, which add to creep, the brittle disposition, which is compositional dependent coupled with the loss of matrix solid solution strengthening must therefore be the
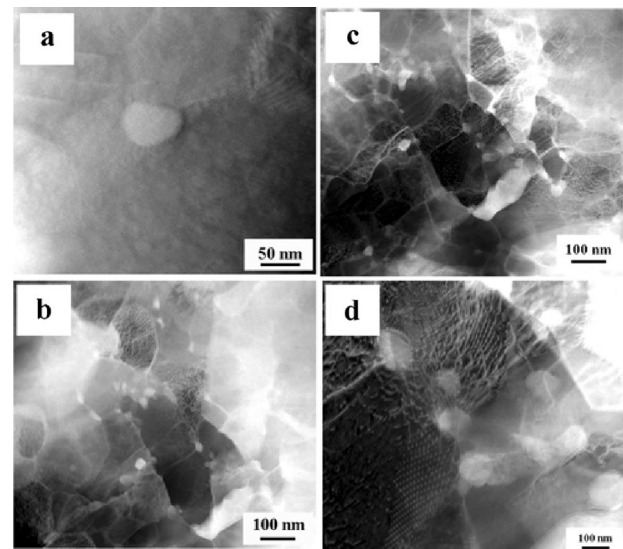
predominant causes for failure. It needs to be emphasized that the non-appearance of solid Laves phase with cavities around it must not be mistaken for the complete absence of mechanisms 1 and 3. Both these mechanisms contribute to creep through creating stress concentrations; a much needed condition for mechanism 3 to come to life.

This finding now opens doors for a more directional and constructive research towards combating the premature failure of P91 steel based components; a strategy targeting ductilization of the Laves phase. One most promising way of doing this is by bringing the synchro-shear mechanism in effect [9–11], i.e. tailoring the defect structure via materials chemistry. These mechanisms corroborate substantially to account for the unprecedented failure of the modified P91 steel components at temperatures between 873 (600 °C) and 923 K (650 °C).

6 Conclusions

This study was carried out with intentions of deciphering and describing the predominant cause for the failure of creep resistant modified 9Cr–1Mo steel -an unparalleled material for steam generators in thermal and nuclear power plants, at temperatures between 873 (600 °C) and 923 K (650 °C).

On the basis of atomic scale observations and thermodynamic approximations, the following conclusions are drawn:

1. Laves phase precipitation in the temperature regime of 873 K (600 °C) and 923 K (650 °C), is the primary cause of embrittlement in modified 9Cr–1Mo steel.

2. The crystal chemistry of the Laves phase is not strictly Fe_2Mo. It could accept ternary or even quaternary additions which further stabilizes the phase and changes the defect structure.

3. Laves phase in modified 9Cr–1Mo is a thermodynamically stable phase between temperatures 873 K (600 °C) to 923 K (650 °C), and not meta-stable, as considered in literature.

4. Thermodynamic calculation shows that chromium depletion around the carbides, makes it thermodynamically possible for Laves phase to nucleate around the carbides.

5. Limited plasticity of the Laves phase coupled with the loss of solid solution strengthening effect has been identified to be responsible for the embrittlement phenomenon.

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