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10 **Direct observation of creep strengthening**
11 **nanoprecipitate formation in ausformed**
12 **ferritic/martensitic steels**

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21
22 **Abstract**

23 It is well known the effectiveness of ausforming on increasing the dislocation density
24 of fresh martensite. This work demonstrates, using Atom Probe Tomography, that this
25 increase in the dislocation density has a strong influence on the nucleation of
26 nanoprecipitates during tempering. Therefore, ausforming might be a powerful
27 processing route for the two-fold improvement of ferritic/martensitic steels where
28 creep resistance is of paramount importance. Firstly, ausforming refines the
29 martensitic microstructure (high strength and toughness), and secondly, it increases
30 the number density of thermally stable nanoprecipitates (creep resistance).

31 **Keywords:** MX nanoprecipitates; Atom probe Tomography; ausforming; creep
32 resistant steels; creep strength

The enhancement of energy efficiency in advanced nuclear reactors is based on the development of materials with improved properties to guarantee the safety, flexibility and economics of the system [1]. Ferritic/martensitic steels are candidates for nuclear advanced reactors because of their higher swelling resistance and thermal properties compared to austenitic steels [2]. One of the reference materials for those studies is the G91 steel grade, which chemical composition used in this work is Fe-8.76Cr-0.088C-0.317Si-0.597Mn-0.862Mo-0.186V-0.073Nb-0.038N. As it has been discussed elsewhere [3], the microstructure of these steels after austenitization and tempering consists of a ferritic matrix with a high number density of dislocations and two kinds of precipitates. One of these precipitates are the $M_{23}C_6$ carbides, where M are Cr, Fe and Mo, and the MX-nanoprecipitates, where M is V and Nb and X is C and/or N. The $M_{23}C_6$ carbides are mainly located along the prior austenite grain boundaries, block boundaries and lath boundaries, while the MX-nanoprecipitates are located within the laths [4]. These nanoprecipitates play an important role to control the creep resistance of these steels due to their location and their good thermal stability [5]. The MX-nanoprecipitates pin the dislocations during creep at high temperature and avoid the recovery and the degradation of the microstructure when the creep mechanism is dislocation motion controlled [5, 6]. For this reason, improving the distribution of these nanoprecipitates has received a lot of attention in the past to increase the operating temperature of these materials. One of the successfully applied routes consists in substituting the conventional heat treatment by an optimized thermomechanical treatment [7-12]. In this sense, the thermomechanical treatment modifies the austenite condition before its transformation to martensite. The deformation introduced in the austenite affects the austenite-martensite transformation, refining the martensitic microstructure generated during cooling to room temperature, and increasing the dislocation density.

The particular thermomechanical treatment investigated in this work is shown in Fig. 1a). This figure illustrates schematically the thermomechanical treatment performed in a 805 DIL Bahr plastodilatometer. These treatments have been carried out on 10 mm in length and 8 mm in diameter cylindrical samples. The samples have been heated at 5 °C/s and cooled at 50 °C/s. In the ausforming step, a deformation of 40 % at 0.1 s⁻¹ has been applied at 900 °C. Different interrupted by quenching cycles have been set to study the interaction between dislocation and MX formers elements

and the formation process of MX-nanoprecipitates: 1) at room temperature just after ausforming to obtain fresh martensite (Ausf_0); 2) after 5 minutes of tempering at 740 °C (Ausf_5); 3) after 25 minutes of tempering at 740 °C (Ausf_25) 4) and after 45 minutes of tempering at 740 °C (Ausf_45). Note that the tempering treatments are carried out in ferrite region after cooling to room temperature.

The thermomechanical treatment consists in three well differentiated steps. The first one is the austenitization where higher austenitization temperature than conventional processing is chosen. The goal of such a high austenitization temperature in the thermomechanical treatment shown in Fig. 1a) is to maintain in solid solution with as much MX former elements as possible for a subsequent precipitation. The objective of the second step (ausforming) is to generate a fresh martensite with a high dislocation density where the nucleation of MX-nanoprecipitates on dislocations can be promoted during the last step, i.e. the tempering step. In this way, the number density of MX nanoprecipitates in the final microstructure are increased.

Figure 1b) is a TEM image that shows the distribution and size of these MX nanoprecipitates after the thermomechanical treatment applied in this work (Ausf_45).

Previous work demonstrated the effectiveness of ausforming on increasing the dislocation density in fresh martensite [13, 14] and the nanoprecipitates number density, allowing also the size reduction of these nanoprecipitates. As it was reported elsewhere [3], the number density of the MX-nanoprecipitates is boosted up to 3 orders of magnitude after ausforming and tempering compared to that obtained after the conventional treatment. The increase of austenitization temperature without subsequent ausforming (the so-called HAT treatment in Ref. [3]) results in a higher number density of nanoprecipitates after tempering than conventional treatment, but lower than that with ausforming and tempering [5]. This result has been corroborated by other authors that relate the improved creep resistance recorded with optimization of the thermomechanical treatment [15, 16].

While the effect of the austenitization temperature on precipitate dissolution [17, 18] and the effect of ausforming on the morphology and dislocation density of the ausformed fresh martensite have been widely studied [14, 19], the interactions of the MX elements formers and dislocations during tempering have not been discussed deeply. The motivation of this work is to study these interactions and find out why an

99 increased dislocation density in fresh martensite creates a higher number density of
100 MX nanoprecipitates after tempering. Therefore, attention must be paid to the role of
101 ausforming on generating an effective distribution of potential nucleation sites for
102 those nanoprecipitates. This is the goal pursued in this work, i.e. clarify the
103 mechanism of MX nanoprecipitate formation in dislocations that are responsible for
104 improving the creep performance [5, 7].

105 Nanoprecipitate analysis has been carried out by atom probe tomography (APT) using
106 a local electrode atom probe (CAMECA LEAP 4000X HR) in laser mode with a 50
107 pJ laser pulse energy, 200 kHz pulse repetition rate, a -243 °C base temperature, and a
108 collection rate of 0.005 ions per pulse. Several APT needles have been prepared
109 from each of the above mentioned conditions by means of a FIB-based site-selective
110 lift-out method [20] in locations inside martensite laths away from the boundaries.
111 Sections of the lift-out have been mounted onto a Si microtip array, sharpened using
112 30 kV annular milling, and cleaned with a 2kV Ga ion beam [21].

113 Elemental distribution maps from the APT analysis of the sample Ausf_0 are shown
114 in Fig. 2a). The Nb, V, NbN, VN, Cr, Mo and C ions are displayed individually and
115 each of the dots corresponds to the reconstructed position of each ion within the
116 needle. The Nb, V, NbN, VN, Cr, and Mo ion maps have a homogeneous distribution
117 throughout the volume, but there is a clear segregation of C filling a feature which
118 resembles a lath boundary. This can be explained by the dislocation density obtained
119 in the sample after Ausf_0. The dislocation density for the sample Ausf_0 was
120 reported by the authors in a previous work [3] to be $22 \pm 0.1 \times 10^{14} \text{ m}^{-2}$. Considering
121 uniform distributions of dislocations, an average dislocation-dislocation distance is
122 calculated to be 21 nm. Therefore, this boundary-boundary distance is much larger
123 than 21 nm and very close to the lath width, which is in the range over 200 - 400 nm.
124 The 1D concentration profile displayed in Figure 2b) only shows carbon segregation
125 in these linear martensitic defects. Similar segregation of C on lath boundaries in
126 quenched martensitic steels has been observed by APT in others works [22]. Remark
127 that, within the lath, no segregation of C or any element is observed suggesting that
128 only C diffusion takes place after ausforming upon martensite transformation on lath
129 boundaries and no on the dislocations.

On the other hand, Fig. 3a) shows the elemental distribution maps of VN, NbN, Nb and V for the Ausf_5 sample. In contrast to the previous sample (Ausf_0), segregation of Nb, V and N atoms can be clearly identified in the APT dataset where N field evaporates predominately as NbN and VN ions. The isoconcentration surface of 1 at.-% V shown in Fig. 3b) reveals that these segregated regions are observed as curved lines suggesting that these features are dislocations. The 1D concentration profile displayed in Figure 3b) shows that the concentration of solute in dislocations for V, Nb, N is 5.71 ± 0.6 at.-%, 2.15 ± 0.3 at.-% and 4.1 ± 0.5 at.-% on the peak concentration, respectively. Together with the segregation of these elements, Cr segregation was also detected to be 13.9 ± 0.8 at.-%. Note that trajectory aberrations could limit the accuracy of these compositions due to mixing from the matrix.

The segregation of V, Nb, N and Cr along dislocations indicates an early stage of formation of the MX-nanoprecipitates and demonstrates that dislocations can act as nucleation sites for MX-nanoprecipitates.

Besides, a comparison between the APT atom maps for Ausf_0 (autotempered), Fig. 2a) and Ausf_5 (5 minute temper., Fig. 3a) demonstrates a segregation of elements such as Nb, V and Cr to dislocations only during tempering, not during ausforming. This is consistent with the work of Takahashi *et al.* [23] where the presence of a “Nb-Cottrell atmosphere” was revealed for the first time using atom probe tomography. This particular strong attraction of Nb to dislocation cores is related to the large atom size of Nb with regard to Fe [24], which finds a more relaxed position inside the expansive strain field of the dislocation.

As it has been mentioned above for the case of Nb, the attractive interaction between large atoms (Nb) and dislocations is due to their ability to find a more relaxed position in the crystal structure. As Nb, Cr and V (which have higher atomic size than that for Fe [24]) segregate to dislocations they become pinned due to the low diffusivity of Nb, V and Cr at tempering temperatures, inhibiting its movement during tempering. Therefore, Nb, V and Cr additions retard dislocation recovery at high temperatures. A similar phenomenon has been reported by other authors [25] and has highlighted the retardation effect on dislocation recovery at high temperature [26]. This fact means that the dislocation annihilation is retarded during tempering and, consequently, a high density of nucleation sites for the MX nanoprecipitates are conserved during

tempering. Overall, the higher dislocation density that has been introduced during ausforming contributes to the nucleation of MX-precipitates during tempering by segregation of Nb, V and Cr atoms. The segregation of Nb, V and Cr atoms also maintains the dislocation density during tempering, and therefore, preserves the nucleation sites for MX-precipitates.

Figure 4a) shows 2.5 at.-% V isoconcentration surfaces used to visualize and identify the segregated areas for the sample Ausf_25. The spherical-like shape indicates that the segregated areas are nanoparticles. Differentiation of clusters or nanoprecipitates from nanoparticles is a complex problem in APT because the main distinction between clusters and nanoprecipitates is based on their crystallographic arrangements and this technique does not show crystallographic information. Clusters are characterized as a preferential segregation of atoms in the matrix without an own crystal structure, whereas nanoprecipitates have their own crystal structure apart from the preferential segregation of atoms. In the case of 9Cr ferritic/martensitic steels MX nanoprecipitates are defined as nanoparticles dispersed within the laths with a composition rich in V and Nb, but without Fe [10]. In the present work, clusters are differentiated from nanoprecipitates according to their chemical composition, defining the clusters as nanoparticles with high content of Fe.

The corresponding 1D concentration profile along one of the nanoparticles observed in the sample Ausf_25 is shown next to the isoconcentration surface image and is used to quantitatively determine the solute partitioning between the matrix and the nanoparticles. The partitioning of Nb, V, N and Cr to the nanoparticles is evident. Values of 1.0 ± 0.3 at.-% in Nb, 10.6 ± 0.9 at.-% in V, 6.7 ± 0.8 at.-% in N and 14.41 ± 1.1 at.-% in Cr in the nanoparticles are determined on the peak concentration. Notice that the nanoparticles also contain a significant amount of Fe (63.4 ± 1.5 at.-%). This high concentration of Fe suggests that these nanoparticles can be identified as clusters, which are formed prior to MX nanoprecipitates.

The end of the tempering stage reveals some features that are interesting to highlight. Figure 4b) shows the 2.5 at.-% V isoconcentration surfaces used to visualize the segregation areas for the sample Ausf_45 (45 min of tempering) and the 1D concentration profile along one of these areas. As it was observed in the sample

Ausf_25, these areas present a spherical-like shape, therefore, can be defined as nanoparticles.

The number density of these nanoparticles is considerably lower than that observed for the nanoparticles in the sample Ausf_25. However, the sizes of these particles are approximately the same size (5-10 nm) as those observed in the Ausf_25 sample (25 min of tempering), and are in good agreement with the TEM results for the same sample shown in Fig. 1b). However, a comparison between the 1D concentration profile shown in Figs. 4a) and 4b) exhibit an important change in the chemical composition. The nanoparticles after 45 min of tempering (Fig. 4b)) contain a significantly higher amount of Cr (17.2 ± 1.0 vs. 14.41 ± 1.1 at.-%), Nb (4.45 ± 0.6 vs 1.0 ± 0.3 at.-%), V (32.9 ± 1.3 vs. 10.6 ± 0.9 at.-%) and N (23.3 ± 1.2 vs 6.7 ± 0.8 at.-%) and a lower amount of Fe (16.4 ± 1.0 vs 63.4 ± 1.5 at.-%) than their counterpart after 25 min of tempering (Fig. 4a)). Note that the particles have similar sizes and the needle radii are similar in those regions, so the composition measurements are comparable despite the trajectory aberrations, particularly because the measured compositional difference between them is large.

The nanoparticles found in the sample Ausf_45 are thought to be the MX nanoprecipitates due to the tempering time and their chemical composition, which content low concentration of Fe. These concentration of Fe is explained by the trajectory aberrations and ion crossing in the APT dataset, which is caused by the irregular shape of the APT needle from different evaporation fields between the matrix and the precipitates [27, 28]. The degree of compositional mixing between the matrix and nanoparticles becomes more severe as the particle size becomes smaller, as the ion crossing occurs at the interface, and the evaporation field difference between the matrix and precipitate becomes larger. The particles studied here are >5 nm, which would minimize, but not eliminate, this effect.

The presence of Cr in the clusters and nanoprecipitates contrasts with the common reported composition of the MX nanoprecipitates, where the main elements are Nb, V, C and N. Nevertheless, Yinzhong Shen et al. reported in their work [29] similar Cr concentration in MX nanoprecipitates after tempering in a 9Cr ferritic/martensitic steel. Also, These nanoprecipitates contained similar V and N concentrations indicating that these MX nanoprecipitates are mainly nitrides. Long-term creep tests

will be performed in the future in order to study the stability of these nanoprecipitates, rich in Cr and N, and their effect on the creep strength.

It is worth noting the very low concentration of C in these nanoparticles after 45 min of tempering (1.3 ± 0.3 at.-%), supporting the work previously cited [29]. This fact can be explained because most of the C is consumed by the precipitation of $M_{23}C_6$ carbides, which have a C content around 20 at.-% as it has been reported in previous works by APT [30]. Herbig *et al.* [31] studied the segregation of carbon in some features with different misorientation angles within the ferrite matrix. They observed an evident trend of increasing C-excess with increasing misorientation angle. This fact may explain the preferential nucleation of $M_{23}C_6$ carbides on lath, block and prior austenite grain boundaries where the misorientation is higher than in dislocations. This is consistent with our observations where N is strongly segregated to dislocations as compared with C.

In summary, the dislocation density increase introduced by ausforming in martensite can be taken advantage of to increase the population of MX-nanoprecipitates, and refine their size [5, 9, 11, 15]. This is possible because of the strong interaction that exists between dislocations and the MX-former elements. The APT results have shown strong segregation of Nb, V, Cr and N to dislocations during tempering, which retards the annihilation of dislocations and, consequently, retains potential nucleation sites for MX-nanoprecipitates during tempering. This is because the segregated atoms drag the dislocation motion during tempering due to the low diffusivity of these atoms at the tempering temperatures. Concerning the formation process of MX-nanoparticles, different stages have been identified for the interrupted tempering times investigated. After quenching, and before tempering (Ausf_0), only C segregation takes place on lath boundaries and no segregation of C or any element was observed on dislocations. In the early stage of tempering (Ausf_5) V, Nb, Cr and N are segregated to dislocations, which proves that dislocations act as nucleation sites for these nanoprecipitates. As the tempering time increases (Ausf_25), nanoparticles (5-10 nm in size) enriched in Nb, V, N, Cr and Fe are observed. Finally, at the end of tempering (Ausf_45), nanoparticles with a similar size of those found in the sample Ausf_25 are detected, but with higher amounts of Nb, V, Cr, N and less Fe. The nanoparticles found in the sample Ausf_25 are thought to be clusters due to their high Fe content. These clusters develop during tempering in the MX nanoprecipitates observed in the

sample Ausf_45. The clusters evolve into precipitates by consuming neighboring clusters, which is supported by the lower number density of clusters in the sample Ausf_25 compared to that for the MX nanoprecipitates in the sample Ausf_45.

The M/X ratio for these nanoparticle is different to the expected ($M/X=1$) for the MX nanoprecipitates. This deviation might be caused by local magnification effects and trajectory aberrations during APT measurements, which also explains the low amount of Fe in these particles. These nanoparticles are the MX-nanoprecipitates that are distributed with a high number density after the thermomechanical treatments, and are thought to be responsible for the increase in creep strength in these steels.

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References

- [1] R.L. Klueh, A.T. Nelson, Journal of Nuclear Materials 371(1–3) (2007) 37-52.
- [2] F. Masuyama, ISIJ International 41(6) (2001) 612-625.
- [3] J. Vivas, C. Capdevila, E. Altstadt, M. Houska, D. San-Martín, Scripta Materialia 153 (2018) 14-18.

286 [4] F. Abe, *Current Opinion in Solid State and Materials Science* 8(3–4) (2004)
 287 305-311.

288 [5] J. Vivas, C. Capdevila, E. Altstadt, M. Houska, M. Serrano, D. De-Castro, D.
 289 San-Martín, *Materials Science and Engineering: A* 728 (2018) 259-265.

290 [6] M. Tamura, H. Sakasegawa, A. Kohyama, H. Esaka, K. Shinozuka, *Journal of*
 291 *Nuclear Materials* 321(2–3) (2003) 288-293.

292 [7] J. Vivas, C. Capdevila, J. Jimenez, M. Benito-Alfonso, D. San-Martin, *Metals* 7(7)
 293 (2017) 236.

294 [8] J. Vivas, C. Celada-Casero, D. San Martín, M. Serrano, E. Urones-Garrote, P.
 295 Adeva, M.M. Aranda, C. Capdevila, *Metallurgical and Materials Transactions A*
 296 47(11) (2016) 5344-5351.

297 [9] R.L. Klueh, N. Hashimoto, P.J. Maziasz, *Scripta Materialia* 53(3) (2005) 275-280.

298 [10] L. Tan, J.T. Busby, P.J. Maziasz, Y. Yamamoto, *Journal of Nuclear Materials*
 299 441(1–3) (2013) 713-717.

300 [11] R.L. Klueh, N. Hashimoto, P.J. Maziasz, *Journal of Nuclear Materials* 367–370,
 301 Part A(0) (2007) 48-53.

302 [12] J. Hoffmann, M. Rieth, L. Commin, P. Fernández, M. Roldán, *Nuclear Materials*
 303 *and Energy* 6 (2016) 12-17.

304 [13] M. Zhang, Y.H. Wang, C.L. Zheng, F.C. Zhang, T.S. Wang, *Materials Science*
 305 *and Engineering: A* 596 (2014) 9-14.

306 [14] S.W. Seo, G.S. Jung, J.S. Lee, C.M. Bae, H.K.D.H. Bhadeshia, D.W. Suh,
 307 *Materials Science and Technology* 31(4) (2015) 436-442.

308 [15] S. Hollner, B. Fournier, J. Le Pendu, T. Cozzika, I. Tournié, J.C. Brachet, A.
 309 Pineau, *Journal of Nuclear Materials* 405(2) (2010) 101-108.

310 [16] S. Li, Z. Eliniyaz, F. Sun, Y. Shen, L. Zhang, A. Shan, *Materials Science and*
 311 *Engineering: A* 559(0) (2013) 882-888.

312 [17] C. Pandey, A. Giri, M.M. Mahapatra, *Materials Science and Engineering: A* 657
 313 (2016) 173-184.

314 [18] P. Yan, Z. Liu, H. Bao, Y. Weng, W. Liu, *Materials Science and Engineering: A*
 315 597 (2014) 148-156.

316 [19] G. Miyamoto, N. Iwata, N. Takayama, T. Furuhashi, *Acta Materialia* 60(3) (2012)
 317 1139-1148.

318 [20] M.K. Miller, R.G. Forbes, *Materials Characterization* 60(6) (2009) 461-469.

- [21] K. Thompson, D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, B. Gorman, Ultramicroscopy 107(2) (2007) 131-139.
- [22] Y.J. Li, D. Ponge, P. Choi, D. Raabe, Scripta Materialia 96 (2015) 13-16.
- [23] J. Takahashi, K. Kawakami, J.-i. Hamada, K. Kimura, Acta Materialia 107(Supplement C) (2016) 415-422.
- [24] D. Raymond Chang, P. Kenneth Goldsby, Chemistry, McGraw-Hill Education 2015.
- [25] K.Y. Xie, T. Zheng, J.M. Cairney, H. Kaul, J.G. Williams, F.J. Barbaro, C.R. Killmore, S.P. Ringer, Scripta Materialia 66(9) (2012) 710-713.
- [26] S.L. Shrestha, K.Y. Xie, S.P. Ringer, K.R. Carpenter, D.R. Smith, C.R. Killmore, J.M. Cairney, Scripta Materialia 69(6) (2013) 481-484.
- [27] M.K. Miller, M.G. Hetherington, Surface Science 246(1) (1991) 442-449.
- [28] S. Dhara, R.K.W. Marceau, K. Wood, T. Dorin, I.B. Timokhina, P.D. Hodgson, Data in Brief 18 (2018) 968-982.
- [29] Y. Shen, H. Liu, Z. Shang, Z. Xu, Journal of Nuclear Materials 465 (2015) 373-382.
- [30] M.I. Isik, A. Kostka, V.A. Yardley, K.G. Pradeep, M.J. Duarte, P.P. Choi, D. Raabe, G. Eggeler, Acta Materialia 90 (2015) 94-104.
- [31] M. Herbig, D. Raabe, Y.J. Li, P. Choi, S. Zaefferer, S. Goto, Physical Review Letters 112(12) (2014) 126103.

Figures

Figure 1. a) Thermomechanical treatments investigated in this study and b) distribution of MX nanoprecipitates within the laths after thermomechanical treatments.

348 Figure 2. a) Atom maps of Cr, Mo, C, Nb, NbN, V and VN and b) 1D concentration
349 profile perpendicular to the defect denoted by the black arrow for the Ausf_0 sample.

350

351 Figure 3. a) Atom maps of Nb, NbN, V and VN and b) 1 at.-% V isoconcentration
352 surface and 1D concentration profile perpendicular to the dislocation denoted by the
353 black arrow for the Ausf_5 sample.

354

355 Figure 4. 2.5 at.-% V isoconcentration surfaces and the corresponding 1D
356 concentration profile along the nanoparticles denoted by black arrows a) for the
357 Ausf_25 sample and b) for the Ausf_45 sample.