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Experimental and theoretical investigation of precipitate coarsening rate in Z-phase strengthened steels

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Abstract

Two Z-phase strengthened 12% Cr steels were investigated: they are similar in composition, however one steel contains Nb and the other contains Ta. Z-phase precipitates (CrMN, M=Nb or Ta) provide precipitation hardening for creep resistance at 650°C in these steels. Experimental data based on the transmission electron microscopy investigation of the size evolution of Z-phase precipitates during isothermal ageing at 650°C show that the Ta-based Z-phase benefits from a five times smaller coarsening constant compared to the Nb-based Z-phase. Theoretical calculations show that this is attributed to the smaller diffusivity of Ta compared to Nb in the steel matrix. Besides, comparing the size of the Ta-based Z-phase precipitates in the gauge and grip portion of a crept specimen, it is shown that Z-phase coarsens faster under stress.

Keywords: precipitate; coarsening rate; creep; electron microscopy; diffusivity.
1. Introduction

Increasing the steam temperature and pressure in fossil-fuel steam power plants leads to a higher thermal efficiency and a lower CO₂ emission and fuel consumption. The maximum allowed steam temperature and pressure are determined by the long-term creep and corrosion resistance of economically viable materials. The 9–12% chromium martensitic steels are used in the critical components of fossil fuel steam power plants such as main steam pipes and turbine rotors, due to their good corrosion and creep resistance, high thermal conductivity, and low thermal expansion coefficient [1, 2]. Precipitation hardening is regarded as the main mechanism to achieve long-term creep resistance and chromium is responsible for the corrosion resistance of these alloys. 

M₂₃C₆ (M=Cr, Fe), Fe₂(W, Mo), and MX (M=Nb, V, X=C, N) are the main precipitates contributing to the strength of the conventional 9–12% Cr steels for steam temperatures up to 600°C [1, 2]. In order to increase the steam temperature and pressure in such power plants to 650°C, Z-phase (CrMN, M=Nb or Ta) strengthened steels [3, 4] were recently developed. Z-phase strengthened steels combine a high chromium content to provide sufficient corrosion resistance, and a fine distribution of Z-phase precipitates to provide precipitation hardening for long-term creep resistance.

To evaluate whether or not a precipitate type can contribute to the strength of a material, one needs to study the nucleation, growth and coarsening behavior of the precipitates. Z-phase does not nucleate on its own and it was shown that Z-phase forms via indiffusion of Cr to the MX precipitates [5]. This process in conventional 12% Cr steel is very slow, so only a few Z-phase precipitates are formed. As Z-phase is the most stable nitride at the temperature of interest in these alloys, it grows rapidly at the expense of the relatively unstable MX precipitates. In Z-phase strengthened steels, a rapid transformation from MX to Z-phase leads to a fine distribution of Z-phase in the tempered condition or during the early stages of service. It was previously shown that such a fine distribution of Z-phase is achievable via stimulating the formation of Z-phase (high Cr and low C) for Nb-based Z-phase [6] and Ta-based Z-phase [3].

The precipitation behavior is not only affected by the high temperature but also by strain during creep. Hättestrand and Andrén [7] studied the influence of strain on the precipitation behavior of M₂₃C₆, VN and Laves-phase during creep of P92 at 600°C and 650°C. They reported an increase in the coarsening rate of M₂₃C₆ due to the effect
of strain. The number density of Laves-phase precipitates appeared to be higher in the crept specimens compared to the aged ones. There was no significant difference on the VN precipitates between the crept and the aged specimen.

In this paper, both experimental and theoretical calculations were employed to study the coarsening rate for two types of Z-phase: Ta and Nb based. Besides, the effect of strain on the coarsening behavior of Ta-based Z-phase is investigated.

2. Experimental methods

2.1 Materials

The trial steels investigated in this work were produced as 80 kg ingots by vacuum induction melting. The ingots were then hot rolled into 20 mm thick plates. The composition of investigated trial steels is provided in Table 1. These trial steels with either Nb (Z-Nb steel) or Ta (Z-Ta steel) contain a high Cr and a very low C concentration, in order to stimulate the formation of Z-phase and to achieve a fine distribution of stable Z-phase precipitates for precipitation hardening. A more detailed description of the alloy design is presented in Ref. [3, 4, 6]. Both trial steels were austenitized at 1150°C for 1 h and then cooled in air to room temperature. The steels were then aged for 1000, 3000, and 10,000 h at 650°C. Since Z-phase forms fastest at 650°C in 12% Cr steels [8], no extra tempering treatment was performed.

To study the effect of strain on the coarsening behavior of Z-phase, a crept specimen of Z-Ta steel was studied. This creep specimen had been austenitized at 1050°C for 1 h and tempered at 700°C for 7 h before creep testing at 80MPa/650°C for 6311 h. Specimens prepared from the grip and from the gauge portion (a region with approximately 1% reduction of area) of this crept specimen were investigated.

In order to characterize the Z-phase precipitates in the trial steels, an FEI Titan 80-300 transmission electron microscope (TEM) equipped with an EDAX X-ray detector and a TIA energy dispersive X-ray (EDX) software were employed. High angle annular dark field (HAADF) and bright field (BF) in the scanning transmission electron microscopy (STEM) mode were used to image the precipitates. EDX was used to
analyze the chemical composition of individual precipitates in the trial steels. Atom probe tomography (APT) was employed to measure the solubility of Nb and Ta in the steel matrix of specimens aged for 10,000 h at 650°C.

To prepare TEM specimens, discs 3 mm in diameter were cut from the steels with different heat treatment conditions and mechanically ground to the thickness of 100 μm. The electron transparent specimens were prepared by electropolishing in 10% perchloric acid + 90% methanol at -30°C and a bias voltage of 10V using the twin-jet Struers Tenupol 5.

2.2 Diffusivity calculation

Using the Thermo-Calc software [9], with the thermodynamic database TCFE8 [10] and the mobility database MOBFE3 [11], the chemical diffusivity and the influence of Co on the diffusivity of Ta and Nb in the Fe bcc matrix at 650°C were calculated.

2.3 Creep testing

For creep testing, specimens austenitized at 1150°C/1h and tempered at 650°C/24h were used. The creep rupture testing was performed in accordance with Standard EN ISO 204:2009. The creep rupture tests were carried out at 650 °C under a constant load corresponding to 120, 100 (Z-Nb only), or 80 MPa using specimens of 7 mm in diameter, 50 mm in gauge and 135 mm in length. The creep tests were done on the specimens austenitized at 1150°C/1 h and tempered at 650°C/24 h.

3. Results and discussion

3.1 Creep testing at 650°C

Figure 1 shows the creep rupture strength of both trial steels at 650°C. The creep strength of the Z-Ta steel is higher than that of the Z-Nb steel tested for all stress levels. The data for Z-Ta at 100 MPa is missing. However, we have creep data at 100 MPa for a different heat treatment of Z-Ta, austenitizing at 1050°C/1h and tempering at 700°C/7h. This gave a rupture time at 650°C of approximately 4300 h, which is in accordance with the data in the diagram.
3.2 Characterizing Z-phase

Figure 2 shows an STEM-EDX elemental mapping taken from the Z-Nb and Z-Ta steels aged for 3000 h. The Cr and Nb map in the Z-Nb steel and the Cr and Ta map in the Z-Ta steel show Z-phase precipitates. The W map shows Laves-phase precipitates in both steels. Laves-phase contains approximately 16 at. % Cr [12], which is slightly higher than the Cr content in the matrix (approximately 13 at.%), which gives some contrast in the Cr maps. Typical EDX spectra from such precipitates are also provided in Figure 2. Although STEM images yield similar contrast for Z-phase and Laves phase, EDX analysis can identify the two phases unambiguously.

Z-phase precipitates are mainly found in a blade-like morphology, since Z-phase grows in specific orientations with the steel matrix. A typical example of such a morphology taken from Z-Ta steel aged for 10,000 h, together with the schematic drawing of Z-phase precipitates, are shown in Figure 3. The projection of wide and narrow surfaces of the Z-phase precipitates are shown in Figure 3 a. Similar morphology was also reported previously by Cipolla [5] for Nb and V based Z-phase.

There are two commonly used methods to measure the size of precipitates in 9–12% Cr steels. The first approach [13], known as particle diameter (PD), is the average of the longest dimension and the dimension perpendicular to the longest dimension of the precipitates. The second approach, known as equivalent circle diameter (ECD) [7, 13], is to measure the area of the precipitates using image-processing software and calculate the equivalent circle diameter. These techniques are commonly used for spherical particles or for bulky particles with irregular morphology. Zhu et al. [14] showed that these two approaches provide similar results for M_{23}C_{6} carbides. Thus, the PD approach was used as one of the methods to measure the size of the Z-phase precipitates.

Another method was also employed in the present study, i.e. the equivalent sphere radius (ESR) of the precipitates, since Z-phase precipitates are formed in the blade-like morphology. The obtained data from the PD method, \( d_{\text{max}} \) and \( d_{\text{min}} \), were treated the following way: the \( d_{\text{max}} \) was considered as the length of the precipitates. If \( d_{\text{min}}/d_{\text{max}} > 0.5 \), then \( d_{\text{min}} \) was considered as the width of the precipitates, otherwise \( d_{\text{min}} \) was considered as the thickness. The length, width and thickness of approximately 100
precipitates were measured. ESR was calculated based on the average volume of the precipitates:

\[ L \times T \times W = \frac{4}{3} \pi r^3 \]  
Equation 1

where \( L \), \( T \), and \( W \) are the average length, thickness, and width of the \( Z \)-phase precipitates. The obtained data from ESR and the radius measured via the PD method were then compared.

3.3 Experimental coarsening rate of \( Z \)-phase

Figure 4 shows the evolution of \( Z \)-phase precipitates in the trial steels during ageing at 650°C for 1000, 3000, and 10,000 h. Both Nb and Ta-based \( Z \)-phase precipitates were found with the blade-like morphology in the 1000 h-aged specimens, and they kept the same morphology over ageing up to 10,000 h. In Figures 4 a and b, \( Z \)-phase precipitates are oriented in such a way that the wide surfaces of most precipitates are shown, while in Figures 4 c and e, the narrow surfaces of most precipitates are displayed, and in Figure 4 f, both the wide and narrow surfaces of \( Z \)-phase precipitates are projected.

Figure 5 shows the size distribution (PD approach) of \( Z \)-phase precipitates in the Z-Ta and Z-Nb steels. It is obvious that Z-Ta benefits from a much smaller precipitate size compared to Z-Nb. After 1000 h ageing at 650°C, precipitates in Z-Ta distributed in a very narrow size range (with smaller average size) compared to those in Z-Nb, which can explain for the very different creep strength of the steels at the high stress level (120 MPa). Ageing up to 3000 h gave a bimodal distribution of precipitate size for both trial steels. The bi-modal size distribution shifted to larger precipitate size after 10,000 h ageing, which was more pronounced for the Nb-based \( Z \)-phase compared to the Ta-based \( Z \)-phase. Even though, no quantitative data is reported on the number density of the \( Z \)-phase precipitates in two steels, it is worth mentioning that the number density of Ta-based \( Z \)-phase appears to be higher than that of for Nb-based \( Z \)-phase. Number density and size of the precipitates are of two important parameters defining their contribution to the strength of the materials.
Figure 6 shows the size evolution of Z-phase precipitates in both trial steels measured via the PD and ESR methods. As can be seen, both methods show similar results. Apparently for larger precipitates in the Z-Nb steel aged for 10,000 h, the difference between the two methods increases. The measured ESR of the Nb-based Z-phase is 18.7±0.8, 27.5±1.1, and 38.2±1.4 nm for specimens aged for 1000, 3000, and 10,000 h, respectively. The ESR of the Ta-based Z-phase is 5.1±0.2, 18.6±0.6, and 23.8±0.8 nm for specimens aged for 1000, 3000, and 10,000 h, respectively.

In Z-Nb steel, previous APT investigation on the specimen aged for 24 h at 650°C [5] showed the presence of precipitates rich in Cr, N and Nb. These precipitates had some fluctuations in the composition, which was attributed to the ongoing dissolution and phase transformation from NbN to Z-phase. For Nb-based Z-phase, it was also shown that the in-diffusion of Cr to the NbN precipitates continues up to 3000 h, when Z-phase reaches its equilibrium composition all over the precipitate [6]. The same behavior is also expected for the Ta-based Z-phase. The fluctuation in the composition of the precursor precipitates to Z-phase and dissolution and transformation of precipitates is probably the main reason for the rapid increase in the size of the precipitates from 1000 h aged specimens to 3000 h aged ones. Thus, it was assumed that the increase in the size of the precipitates in this period belongs to the growth stage. Therefore, in order to exclude the growth stage, the experimental coarsening rate for Z-phase precipitates is measured for the precipitate size evolution (based on ESR) in the aged specimen for 3000 h to 10,000 h based on the well-known Ostwald ripening equation:

\[ r^3 - r_0^3 = K_P \cdot t \]  \hspace{1cm} \text{Equation 2}

where \( r \) is the precipitate radius at time \( t \) (10,000 h in this investigation) and \( r_0 \) is the precipitate radius at time zero (3000 h in this investigation). The coarsening constant \( K_P \) was determined to 1.4×10^{-30} and 2.8×10^{-31} (m^3 s^{-1}) for the Nb-based and Ta-based Z-phase, respectively. Thus at 650°C the measured coarsening constant for Nb-based Z-phase is a factor of 5 larger than that for Ta-based Z-phase.

The coarsening constant for Ta-based Z-phase is in the same order of magnitude as that of the VN precipitates in the P92 steel. The coarsening constant was calculated for VN precipitates from the experimental data presented by Hätestrand and Andrén [7] for the P92 steel aged at 650°C for up to 10,000 h. The radius of VN precipitates was 17.5 (as-
tempered condition) and 21.5 nm (10,000 h aged at 650°C), which give a coarsening constant of $1.3 \times 10^{-31}$ (m$^3$s$^{-1}$).

### 3.4 Calculated coarsening rate of Z-phase

At present the Nb-based Z-phase has been thermodynamically assessed in the database TCFE8, but not the Ta-based Z-phase. This means that a full kinetic modeling of Z-phase coarsening (using e.g. DICTRA, the diffusion model in Thermo-Calc) cannot be made for Z-Ta, and neither can the equilibrium solubilities of Ta and N be calculated. However, calculations of the coarsening constant using the model by Ågren et al. [15] can be made, if the diffusivity calculations for Nb and Ta in the matrix are combined with estimates of interfacial energies from DFT calculations and measured composition data from APT.

#### Diffusivity of Nb and Ta in the matrix

Using the Thermo-Calc software, the chemical diffusivity of Ta in the Z-Ta steel and Nb in the Z-Nb steel at 650°C was calculated to be $6.81 \times 10^{-19}$ m$^2$s$^{-1}$ and $6.91 \times 10^{-18}$ m$^2$s$^{-1}$, respectively. Thus, Ta diffuses one order of magnitude slower than Nb in the ferrite matrix. Figure 7 shows the influence of the Co content in the steel on the diffusivity of Ta and Nb in the bcc matrix i.e. increasing the Co content of the matrix results in a slower diffusivity of Ta and Nb in the steel matrix.

#### Interfacial energy of Z-phase

Like NbN and TaN, Z-phase has a low misfit in the (100)$_Z$//(100)$_{bcc}$ plane which leads to disc or blade shaped precipitates with (100)$_{matrix}$ as the habit plane. This means that the total interfacial energy is dominated by this low misfit interface. Fors and Wahnström [16] have calculated the energy of this interface for all NaCl-type MX carbides and nitrides in bcc Fe using atomistic and elastic modeling, assuming a semi-coherent interface containing interfacial dislocations. They found that the sum of chemical and elastic energy falls on a single curve that depends only on the misfit. Assuming that the chemical part of the interfacial energy in not dramatically different between MX/Fe and Z-phase/steel matrix, we can use this curve to estimate the interfacial energy between Z-phase and matrix. For CrNbN two measurements of the
lattice parameters exist in the literature, \(a=0.3029\) (all lattice parameters in nm) and \(c=0.7360\) \[17\], as well as \(a=0.3037\) and \(c=0.7391\) \[18\]. With a mean \(a_Z=0.3033\) and assuming that the matrix lattice parameter is similar to that of bcc Fe, 0.2866, we arrive at a misfit \(2(a_Z-a_{Fe})/(a_Z+a_{Fe})\) of 5.7%. Likewise, the measured lattice parameters of Cr-TaN, \(a=0.3004\) and \(c=0.7334\) \[17\], give a misfit of 4.7%. From the curve in Ref. \[16\] we then obtain interface energies of 0.85 and 0.71 Jm\(^{-2}\) for Cr-NbN and Cr-TaN, respectively.

**Solubilities of Nb and Ta**

The solubilities of Nb and Ta in the steel matrix at 650°C is expected to be low; an equilibrium calculation for Z-Nb using TCFE8 gives a Nb solubility of 9.6 at.ppm (and a very low N solubility of only 97 at.ppb). Due to database limitations, no calculation can be made for Z-Ta. APT analysis was made of the matrix of the two steels after aging at 650°C for 10,000 h. A dataset of approximately 4 millions atoms from the matrix of each of the steels gave the following matrix contents: Z-Nb 20.5 at.ppm Nb, 89 ppm N, and 13.25 at.% Cr; Z-Ta 17.4 ppm Ta, 87 ppm N, and 13.05 at.% Cr. Thus, the measured solubility of Nb is of the same order of magnitude as the equilibrium value, but the measured N content is about three orders of magnitude larger than the calculated value. Also, the measured solubility in Z-Ta is similar to that of Nb measured in Z-Nb.

**Composition of Z-phase**

The composition of the two Z-phases measured by APT are 35.7 at.% Cr, 30.1% Nb, and 28.85% N for Cr-NbN \[6\], and 35.37% Cr, 25.5% Ta, 33.9% N for Cr-TaN \[12\].

**Calculated coarsening constant**

A calculation of the coarsening constant can be made using the equation by Ågren et al. \[15\]:

\[
K_p = \frac{8}{9} \sum_{i=1}^{\mathcal{C}} \gamma_m^B \left( \frac{a_B}{a_i} \right)^2 \left( x_i^B - x_i^B \right) / \left( x_i^B \frac{D_i}{RT} \right)
\]

Equation 3
where $\gamma$ is the interfacial energy, $V_m^\beta$ is the molar volume of the precipitate phase, $D_i$ is the diffusion coefficient of element $i$ in the matrix, $x_i^\beta$ is the mole fraction of element $i$ in the precipitate, and $x_i^{\alpha/\beta}$ is the mole fraction of element $i$ at the precipitate/matrix interface.

The result for Z-Nb is $K=1.11 \times 10^{-30} \text{ (m}^3\text{s}^{-1})$ and for Z-Ta $K=1.04 \times 10^{-31} \text{ (m}^3\text{s}^{-1})$. Thus the calculated coarsening constant for CrTaN is a factor of 10 smaller than that of CrNbN, and the main reason for this is the ten times lower diffusivity of Ta than Nb in the steel matrix. The measured solubility of Ta in the matrix is only 15% smaller than that of Nb, and the estimated interfacial energy in Z-Ta is only 18% smaller than that of Z-Nb. It is interesting to note that the calculation of the coarsening constant is completely dominated by the Nb or Ta term in the equation. Thus, the low solubility of N is overwhelmed by the large diffusivity of N. Not even replacing the measured N solubility by a thousand times smaller calculated value leads to any effect on the calculated coarsening constant.

Comparing the measured and calculated coarsening constants, the measured constants are 25% higher (Z-Nb) and a factor of 2.7 higher (Z-Ta) than the calculated ones. Considering the uncertainties in both calculated and measured data, the agreement for Z-Nb must be regarded as good. The larger difference for Z-Ta suggests that the measured coarsening constant does not represent pure coarsening, but that there is still some growth at 3000 h. Extrapolating the measured radius to 100,000 h using the experimental coarsening constant gives a precipitate radius of 47 nm, i.e. twice the size at 10,000 h. Using instead the calculated coarsening constant we obtain 36 nm, i.e. an increase with only 50%.

### 3.5 The effect of Co

The addition of Co into Z-phase strengthened steels is favorable. Firstly, Co reduces the affinity of Cr to the steel matrix and hence accelerates the phase transformation from MX to Z-phase [4]. Secondly, considering the very limited amount of C in the trial steels, the addition of Co as an austenite stabilizer avoids the formation of detrimental $\delta$-ferrite [19]. Thirdly, the addition of Co, see Figure 7, decreases the diffusivity of Ta and Nb in the steel matrix, which is a very important parameter.
controlling the coarsening behavior of Z-phase precipitates. The addition of Co increases the Curie temperature of the steel. Because diffusion depends on ferromagnetic state of the metals, the addition of Co is believed to slow down the diffusion of atoms [20].

Dudova et al. [21] reported a beneficial effect of Co in a 3wt.% Co modified P92-type steel on the coarsening behavior of $\text{M}_{23}\text{C}_6$ precipitates during creep. The size of the $\text{M}_{23}\text{C}_6$ precipitates in the 3wt.% Co modified P92 after creep testing was smaller than that of in the P92 steel.

### 3.6 Effect of strain on Z-phase coarsening

To study the effect of strain on the coarsening behavior of Ta-based Z-phase precipitates, specimens from the grip and gauge of a Z-Ta steel crept for 6311 h at 650°C were prepared for TEM investigations. The heat treatment for this crept specimen differs from the aged specimens of Z-Ta steel. The measured ESR of Z-phase precipitates in the grip and gauge of the crept specimen were 15.9±0.7 and 19.3±0.6 nm respectively. Figure 8 shows STEM-BF micrographs of such precipitates in the Z-Ta steel.

Z-phase precipitates are 18% larger in the gauge portion, which is exposed to stress, compared to the grip portion, which is stress-free. There are possibly two reasons for such a phenomenon. Firstly, it might be due to the “solute drag effect” where substitutional atoms are carried by migrating dislocations [7], which increases the diffusivity of such elements for example Ta in the matrix. Secondly, as is shown in Figure 8, the interaction between dislocations and precipitates in the crept specimen leads to a higher effect of pipe diffusion to the precipitates [22]. Sawada et al. [23] reported that the number density of Z-phase precipitates were 2.5 times bigger in the gauge portion of the crept specimen compared to the grip portion in a 9% Cr steel crept at 600°C, which shows the influence of creep deformation on the Z-phase formation. It was assumed that the strain promoted the Cr diffusion enhancing the transformation from MX to Z-phase, and thus in the crept specimen more Z-phase was formed.

### 4. Conclusions
The coarsening constant at 650°C of two types of Z-phase, CrNbN and CrTaN, were investigated in two trial Z-phase strengthened steels both experimentally using TEM (based on the Ostwald ripening equation) during ageing for up to 10,000 h, and theoretically based on the coarsening model by Ågren et al.

Both experimental and theoretical coarsening constants show that Ta-based Z-phase coarsens much slower compared to the Nb-based Z-phase during isothermal ageing at 650°C. The experimental coarsening constant for Z-Nb was determined to $1.4 \times 10^{-30}$ (m$^3$s$^{-1}$) and for Z-Ta to $2.8 \times 10^{-31}$ (m$^3$s$^{-1}$), a factor of 5 smaller. The theoretical coarsening constant for Z-Nb is only slightly smaller than the experimental value, whereas the theoretical constant for Z-Ta is considerably smaller (a factor of 2.7) than the experimental value, suggesting that the experimental value represents a mixture of growth and coarsening. The measured solubility of Nb and Ta in the steel matrix (20.5 at. ppm Nb and 17.4 at. ppm Ta) are close to each other. The estimated interfacial energy based on the Z-phase and matrix misfit is also not very different from each other. Thus, the factor of 10 smaller diffusivity of Ta in the steel matrix compared to that of Nb is believed to be the main reason for the lower coarsening rate of the Ta-based Z-phase.

Comparison between the size of Z-phase precipitates in the gauge and grip portions of a crept specimen showed that Ta-based Z-phase coarsens faster in the gauge portion, which is strained, compared to the grip portion, which is stress-free and does not deform. After 6300 h at 650°C, precipitates in the gauge section (1% strain) were 18% larger than in the grip portion.

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References


*Figure 1.* Creep rupture strength for the Z-Nb and Z-Ta steels at 650°C. (Both steels were austenitized at 1150°C/1 h and tempered at 650°C/24 h. No data for 100 Mpa is available for Z-Ta.)
Figure 2. STEM-EDX elemental mapping of the Z-Nb (left side) and Z-Ta (right side) trial steel aged for 3000 h at 650°C. Typical EDX spectra from Laves-phase and Z-phase precipitates are also provided in both steels. Note that the difference in the Fe peak in the spectra for Laves-phase precipitates is attributed to the contribution from the steel matrix to the EDX measurements due to the difference in the size of the analyzed precipitates.
Figure 3. STEM/BF micrograph of Z-Ta steel aged for 10,000 h at 650°C showing the typical morphology of Z-phase precipitates in TEM images and b) a schematic drawing showing the morphology of Z-phase precipitates in three dimensions.
Figure 4. STEM/BF micrographs showing the evolution of Z-phase precipitates in the Z-Nb trial steel aged at 650°C for a) 1000 h, b) 3000 h, c) 10,000 h and the Z-Ta trial steel aged at 650°C for d) 1000 h, e) 3000 h, and f) 10,000 h.

Figure 5. Size distribution ($d_{\text{mean}}$ measured via PD method) of Z-phase precipitates after 1000, 3000, and 10,000 h ageing at 650°C.
Figure 6. The size evolution of Z-phase precipitates during ageing at 650°C measured via equivalent sphere radius (ESR) and the radius measured via “particle diameter” method. The lines are drawn to guide the eyes.

Figure 7. The influence of the Co content on the diffusivity of Nb and Ta at 650°C in the ferrite matrix. Calculations were made based on the compositions of Z-Nb and Z-Ta except for Co (and Fe) that was varied between 0 and 10 wt.%.
**Figure 8.** STEM/BF micrograph of the Z-Ta steel (1050/1h +700/7h) from a) the grip of a crept specimen (thermally aged) b) the gauge of the crept specimen (corresponding to the region with 1% reduction of area).

**Table 1.** Chemical composition of two investigated Z-phase strengthened steels, Fe in balance.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Co</th>
<th>B</th>
<th>N</th>
<th>Nb</th>
<th>Ta</th>
</tr>
</thead>
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<tr>
<td>Z-Nb</td>
<td>at%</td>
<td>0.02</td>
<td>0.50</td>
<td>0.60</td>
<td>12.64</td>
<td>1.47</td>
<td>0.87</td>
<td>5.2</td>
<td>0.02</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>wt%</td>
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<td>0.50</td>
<td>0.30</td>
<td>11.64</td>
<td>1.47</td>
<td>2.82</td>
<td>5.4</td>
<td>0.004</td>
<td>0.036</td>
<td>0.26</td>
</tr>
<tr>
<td>Z-Ta</td>
<td>at%</td>
<td>0.02</td>
<td>0.49</td>
<td>0.60</td>
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<td>0.50</td>
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<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>wt%</td>
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<td>0.48</td>
<td>0.30</td>
<td>11.79</td>
<td>0.50</td>
<td>2.90</td>
<td>7.3</td>
<td>0.004</td>
<td>0.033</td>
<td>-</td>
</tr>
</tbody>
</table>