ON THE ROLE OF Z-PHASE IN HEAT RESISTANT STEELS
Vlastimil VODÁREK, František FILUŠ
VSB - Technical University of Ostrava, Ostrava, Czech Republic, vlastimil.vodarek@vsb.cz

Abstract
Dislocation creep in steels is controlled by evolution of dislocation substructure. However, changes in dislocation arrangement are strongly affected by dislocation interactions with precipitates. That is why both thermodynamic and dimensional stability of individual minor phases play a crucial role in the field of dislocation creep. The role of precipitates in the achievements of good creep properties has been extensively studied for a long time. Although many minor phases are now well documented, there are still contradictions and missing thermodynamic data about some minor phases. A limited amount of information is available about phases such as a Z–phase. Behaviour of this phase in austenitic and martensitic heat resistant steels is very different. Thermodynamic stability of the Z-phase is very high in both steels, however its solvus temperature and dimensional stability are much higher in austenitic steels. This paper deals with the basic Z-phase characteristics in both austenitic and (9-12)%Cr martensitic heat resistant steels.

Keywords: stability of Z-phase, creep resistance, austenitic steels, (9-12)%Cr martensitic steels.

1. INTRODUCTION
Creep properties of steels in the field of dislocation creep are controlled by the evolution of dislocation substructure, the formation and growth of subgrains [1]. Changes of dislocation structure are strongly affected by the formation, dissolution and coarsening of minor phases. The objectives are to develop steels exhibiting a balance of creep strength with adequate creep rupture and room temperature ductilities. Generally, the matrix solid solution and a high number density of the stable intragranular precipitates provide resistance to dislocation creep. The presence of grain boundary precipitates and the nature of precipitates determine grain boundary diffusion and sliding contributions to the creep rate [1].

One of the most successful methods of improving the long-term creep resistance of steels is based on increasing the extent of precipitation strengthening during creep exposure. This can be achieved by alloying of these steels with small amounts of strongly carbide or nitride forming elements, such as niobium or titanium. The role of precipitates in the achievements of good creep properties has been extensively studied for a long time [2]. Although many minor phases are now well documented there are still contradictions and missing thermodynamic data about some minor phases. A limited amount of information is available about phases such as a Z-phase which is a nitride with an ideal composition of NbCrN [3]. Its formation is not very clear, and even less clear is its relative stability when compared with other nitrides/carbonitrides [2]. This phase is regarded as a positive minor phase in austenitic heat resistant steels, however its precipitation in martensitic (9-12)%Cr steels can be accompanied by a significant decline in creep strength.

2. BEHAVIOUR OF Z-PHASE

2.1 Austenitic Heat Resistant Steels
Z-phase was firstly detected in 1950’s in austenitic steels containing niobium and nitrogen [2]. It has since been frequently credited with beneficial strengthening effects in heat resistant austenitic steels. However, Z-phase is seldom reported, even in alloys liable to form it on aging. This could be a result of its composition
and its general features of formation, which are not very different from those of MX precipitates. It forms very rapidly at grain boundaries, but also on dislocations within the matrix. The structure of Z-phase was fully determined by Jack and Jack [3]. It has a tetragonal cell of dimensions \( a = 0.3037\text{nm}, \ c = 0.7391\text{nm} \). Trial and error methods showed that Z-phase is a complex nitride with ideal cell contents \( \text{Nb}_2\text{Cr}_2\text{N}_2 \) and an atomic arrangement shown in Fig. 1. The metal atom arrangement is characterized by double layers of similar atoms alternating along the c axis of the unit cell to give an AABBAABB... sequence. Nitrogen atoms occupy octahedral interstices. It is considered that in specimens from steels of different composition and thermal history there will be differences in atomic ordering among the structural sites, and that there may well be substitution for niobium and chromium by atoms of other transition metals [3]. In this case the differences in unit cell dimensions and reflected intensities are not unexpected.

The solvus temperature of the NbCrN phase in austenitic stainless steels was reported to be between 1300 and 1350°C, depending on the steel composition [2]. Fig. 2 shows intragranular precipitation of Z-phase in the AISI 316LN+0.3%Nb steel after the following solution annealing: 1300°C/0.5h./water +1100°C/1.5h./water.

The orientation relationship between Z-phase and the austenitic matrix is defined by, Fig. 3:

\[
\begin{align*}
(001)_Z \parallel (001)_\gamma \\
[100]_Z \parallel [110]_\gamma
\end{align*}
\] (1)

Z-phase particles are short rods, a morphology which is defined by four equivalent prism facets with a common direction parallel to \( [001]_Z \) and by a pinakoid normal to this four-fold axis [4]. A preferential growth direction of rod-shaped precipitate particles is generally determined by the minimum directional mismatch. In the case under consideration, directional mismatch along parallel crystallographic directions which lie in the \( (001)_Z \parallel \{001\}_\gamma \) is isotropic, and equals 19.7%.
This large difference means that the growth of Z-phase particles along any direction that lies in the $(001)_Z$ is likely to be slow. The minimum mismatch between the inter-atomic spacing along parallel low-index directions of the Z-phase and austenite has been found in the case of $[001]_Z \parallel <001>\gamma$, where it is 3.0% [4]. The criterion of the minimum directional mismatch thus suggests that the preferential growth should be $[001]_Z$. Single trace analyses confirmed that the rod shaped particles are elongated in the $[001]_Z$ direction, but in some cases dimensions in this direction are almost comparable with those lying in the $(001)_Z$ [4]. This is thought to be attributable to the complicated double-layer structure of Z-phase.

Secondary Z-phase particles, which precipitate during ageing/creep exposure, are very dimensionally stable [6-8]. Fig. 4 shows a mixture of coarser primary and fine secondary Z-phase particles in the AISI 316LN +0.3%Nb steel after exposure at 650°C for 37 890h. The size of secondary Z-phase particles in Fig. 4 is only several tens of nanometres. Fig. 5 shows pinning of dislocations by secondary Z-phase particles. These particles nucleate directly from the solid solution. Studies on the effect of niobium additions to AISI 316LN steels revealed that the growing niobium content strongly reduced the minimum creep rate and prolonged the time to the onset of the tertiary stage of creep [5]. This can be attributed to intensive precipitation of fine secondary Z-phase particles on dislocations. However, the enhanced creep resistance of niobium-bearing steels in the primary and secondary stages has not been accompanied by the longer creep life that might have been expected [6]. It was found that niobium in these steels accelerated the formation and coarsening of η-Laves, $\text{M}_6\text{X}$ (Cr$_3$N$_2$Si type) and $\sigma$-phase [5-7]. The coarse particles at grain boundaries facilitated the intergranular failure mode, shortened the third stage of creep and contributed to relatively poor creep ductility of niobium bearing casts [7]. These results demonstrate that fine intragranular Z-phase particles can have a very positive effect on the secondary creep rate but the final effect of Z-phase particles on long-term creep properties will also depend on the formation and coarsening of other minor phases in the austenitic matrix [5].

Very few studies have dealt with additions of Nb, C and N together in a way that could determine relative stability of MX and Z-phase in austenitic steels. Niobium is often in excess and both NbX and NbCrN phases form [2,8,9].

**Fig. 4** Primary and fine secondary Z-phase particles in the AISI 316LN + 0.3%Nb steel after creep exposure 650°C/37 890h.

**Fig. 5** Fine secondary Z-phase particles on dislocations in the AISI 316LN + 0.1%Nb steel after creep exposure 650°C/58 936h.
2.1 Martensitic (9-12)%Cr Steels

Studies on 12CrMoVNbN steels, which had shown a dramatic drop in creep strength during long-term testing, revealed that precipitation of Z-phase occurred concurrently with breakdown in creep strength [10]. It was found that precipitation of Z-phase particles was accompanied by dissolution of fine $M_2X$ and $MX$ (VN) particles which are regarded to be beneficial to creep strength of (9-12)%Cr martensitic steels. The kinetics of precipitation of this minor phase was slow. Detailed electron microscopy studies revealed that particles of this phase had a tetragonal unit cell with dimensions of $a=0.286\text{nm}$ and $c=0.739\text{nm}$ [10]. These particles were rich in vanadium, chromium, niobium and nitrogen. Metallic composition of this phase approximately conforms to the ratio: 50at.%Cr and 50at.%($V$+$Nb$) [11]. It was proposed that partial substitution of niobium by vanadium in the original NbCrN phase was responsible for the reduction of the lattice parameter in the basal plane. This (Nb,V)CrN phase was referred to as modified Z-phase [10]. At early stages of Z-phase formation an FCC unit cell with the lattice parameter of $a=0.404\text{nm}$ can form and it is gradually transformed into the above tetragonal cell [12, 13]. The relationship between the FCC and tetragonal unit cells is shown in Fig. 6. It can be speculated that the FCC unit cell at early stages of the modified Z-phase formation is a consequence of deviations from double layer structure along the $c$ axis.

Z-phase precipitation in modified martensitic (9-12)%Cr steels generally represents a significant degradation mechanism [10,11]. This degradation mechanism was gradually confirmed in many (9-12)%Cr martensitic steels exhibiting so called sigmoidal behaviour. This type of behaviour is demonstrated in Fig. 7 on the TAF650 steel (11Cr-3W-3Co-VNbN) [12]. The higher testing temperature the shorter time to the inflexion point on creep curves. Metallographic investigations on this steel showed that precipitation of modified Z-phase was responsible for dissolution of fine MX particles and that the combined effect of Laves phase and Z-phase precipitation was responsible for the creep breakdown. Coarse Z-phase particles do not contribute to precipitation strengthening. The niobium and chromium contents in (9-12)%Cr steels have a strong influence on the precipitation of the modified Z-phase [11,12]. The (11-12)%Cr steels exhibit a much higher rate of Z-phase precipitation than 9%Cr steels. In modern 9%Cr steels, e.g. P91, no breakdown on creep curves has been observed yet. Precipitation of Z-phase was identified in such steels but the volume fraction of Z-phase was very small and beneficial MX particles were not completely dissolved [11].
As far as nucleation of the modified Z-phase is concerned an important role of MX particles was reported. In the case of secondary MX (VN) particles their direct (in situ) transformation to the Z-phase structure was proposed and experimentally proved \cite{15}. Nucleation of Z-phase particles was also observed on the primary MX (NbX) particles, Fig. 9. As the Z-phase nucleates it will grow at the expense of the MX particles. Dissolution of carbon rich NbX particles leads to additional precipitation of $M_{23}C_6$ carbides, which often form aggregates close to Z-phase particles. A gradual dissolution of NbX particles in the neighbourhood of the prior austenite grain boundaries was regarded responsible for the observations of accelerated dislocation recovery in these areas of P91 steel \cite{16}. The orientation relationship between Z-phase and the martensitic matrix was studied on samples corresponding to early stages of the Z-phase formation \cite{17}. Based on the analysis of the composed SADP's the orientation relationship was determined as:

\[
\begin{align*}
(001)_Z & \parallel (001)_\alpha \\
[010]_Z & \parallel [010]_\alpha
\end{align*}
\]

(2)

No orientation relationship was identified between primary NbX and Z-phase particles. The preferential growth of Z-phase particles in the plate-like form takes place on cube planes of the ferritic matrix due to a very small directional misfit in the \{001\}_\alpha and \{001\}_Z planes. This justifies a fast growth of modified Z-phase particles, Figs. 8 and 9.

The solution temperature of (Nb,V)CrN particles is significantly lower (T=800-830°C) than that of the NbCrN phase \cite{11}. Dissolution of (Nb,V)CrN particles in 9-12%Cr martensitic steels during annealing at temperatures above 800°C is accompanied by the formation of MX phase with the FCC unit cell of the dimension about a=0.420nm \cite{11}.

3. CONCLUSIONS

- Precipitation of fine Z-phase (NbCrN) particles in austenitic steels during creep reduces the secondary creep rate. However, the enhanced creep resistance of niobium and nitrogen bearing steels in the primary and secondary stages may not be accompanied by the longer creep life that might have been expected. It depends on the effect of niobium on the formation and coarsening of other minor phases.

- In martensitic (9-12)%Cr steels the modified Z-phase ((Nb,V)CrN) precipitates as large particles at the expense of beneficial fine MX particles. Coarse Z-phase particles do not contribute to precipitation strengthening. Thus the creep strength can be considerably lowered, depending on chemical composition of steels.
Basic characteristics of the Z-phase in austenitic and (9-12)%Cr martensitic heat resistant steels are summarised in Table 1.

Table 1 Selected Z-phase characteristics in heat resistant steels

<table>
<thead>
<tr>
<th>Steels</th>
<th>Thermodynamic Stability</th>
<th>Dimensional Stability</th>
<th>Kinetics of Precipitation</th>
<th>Solvus Temp. /°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic</td>
<td>high</td>
<td>very high</td>
<td>fast</td>
<td>1300 - 1350</td>
</tr>
<tr>
<td>Martensitic</td>
<td>high</td>
<td>low</td>
<td>slow</td>
<td>800 - 830</td>
</tr>
</tbody>
</table>

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