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Review of Z phase precipitation in 9–12 wt-%Cr steels

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REVIEW OF Z-PHASE PRECIPITATION IN 9-12WT%CR STEELS

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ABSTRACT

9-12wt%Cr steels for high temperature applications in fossil fired power plants rely upon precipitate strengthening from (V,Nb)N MX nitrides for long term creep strength. During prolonged exposure at service temperature another nitride precipitates: Cr(V,Nb)N Z-phase. The Z-phase slowly replaces MX, eventually causing a breakdown in creep strength. This paper reviews the Z-phase and its behaviour in 9-12wt%Cr steels including thermodynamic modelling, crystal structure, nucleation process and precipitation rate as a function of chemical composition. The influence of Z-phase precipitation upon long-term creep strength is assessed from several different 9-12wt%Cr steel grades and alloy design philosophies.

Keywords: Z-phase, MX, 9-12%Cr steels, precipitates, high temperature steels

1 Introduction

1.1 9-12wt%Cr steels
Because of their combination of high creep strength, oxidation resistance, good thermal fatigue properties and moderate cost, 9wt%Cr martensitic steels, such as 9Cr1Mo grade 91 (T/P91) or 9Cr2W grade 92 (T/P92), are used extensively for steam pipes, turbines and boilers in fossil fired steam power plants. Grade 92 has been in commercial use for over a decade and allows conversion of 49% of the fuel energy into electricity [1] and allows operating steam temperatures up to 600°C. In order to achieve a higher efficiency and the desirable reductions of CO_2 emissions, an increase in steam temperature is necessary, such as the widely quoted target value of 650°C [2]. Such an increase would require a doubling of the creep strength compared to grade 92, and an increase in Cr content for oxidation resistance would be a necessity. Attempts to develop such 11-12wt%Cr martensitic steels have not met with much success due to severe microstructural

instabilities caused by the high Cr content which have led to drastic drop in creep strength during long term service.

The long term creep strength of the 9-12wt%Cr martensitic steels relies primarily on precipitation strengthening by MX type nitrides with a chemical composition of (V,Nb)N. These MX precipitate as small and finely distributed particles in the microstructure during tempering and have a very low coarsening rate at the intended service temperature. However, they are not thermodynamically stable and will in time be replaced by a similar nitride known as the Z-phase, Cr(V,Nb)N, which is the cause of the microstructure instabilities [3]. The Z-phase will precipitate as large coarsely distributed particles that do not contribute to strengthening and consume the MX particles during their growth, causing a significant drop in creep strength. This replacement process is very slow and can even be on the scale of decades at service temperatures. With the only difference in chemical compositions between MX and Z-phase being Cr, an increase in the overall Cr content from 9wt% to 12wt% causes a critical acceleration of this process from decades to years. This causes a breakdown in creep strength within the lifetime of the power plants. The best known commercial example of such breakdowns is the 12Cr2W grade 122 (T/P122) [4] which was widely used for construction of power plants in Japan, but is now being completely replaced by 9wt%Cr steels such as grade 91 [5].

1.2 Z-phase background
The Z-phase has long been known to precipitate in austenitic steels in its Nb form, CrNbN, first reported in 1950 [6], although its crystal structure was first properly described in 1972 [7]. In contrast to the Z-phases usually seen in 9-12wt%Cr martensitic steels, the CrNbN precipitates very rapidly in low carbon austenitic steels as small and finely distributed rodlike particles, and is credited with beneficial strengthening effects, being thermally stable with a very low coarsening rate [8]. In 1981 these CrNbN Z-phases were identified in ferritic steels [9], however they formed as large granular particles in contrast to the austenitic steels. Z-phase investigations in 1971 of ternary systems at high temperature showed the presence of both CrNbN and CrTaN Z-phase type precipitates [10], but failed to identify any V variant of the nitrides, possibly due to the high temperatures used.
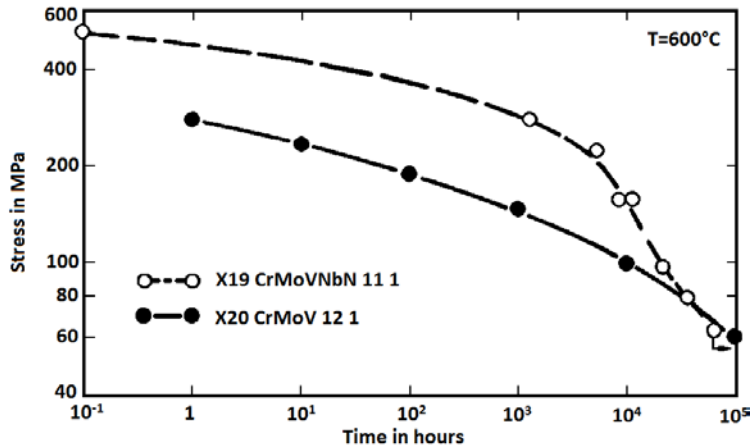
Figure 1: *Comparison of two high Cr steels at 600°C. X19 was the first martensitic steel where Z-phase was found, chemical compositions were not given. Reconstructed from [12].*

V-containing Z-phase was first found in austenitic steels in 1985 with the composition Cr(V,Nb)N [11], and in 1986 the Cr(V,Nb)N precipitates were also observed in a 11wt%Cr martensitic steel, X19 [12]. Although the X19 steel showed the same drop in creep strength as more recent high Cr martensitic steels, see Fig. 1, no connection was drawn between the appearance of Z-phase and the breakdown of X19. The detrimental effects of the Cr(V,Nb)N Z-phase in 9-12wt%Cr martensitic steels was first properly described in 1996 [3], where it was stated that the Z-phase was the thermodynamically stable nitride in 11-12wt%Cr martensitic steels. Furthermore it was concluded that precipitation of Cr(V,Nb)N Z-phase would dissolve the beneficial (V,Nb)N MX, and thus cause a breakdown in long term creep strength. Ni was hypothesised to have an accelerating effect on Z-phase precipitation.

This paper gives an overview of the more recent research on the Z-phase and offers a perspective of the current status of 9-12wt%Cr steels. At the start of the century, development of 11-12wt%Cr steels for operations at 650°C steam temperatures had taken place for some time. Long term creep tests were showing breakdowns for all of these steels, including commercially available alloys such as grade 122. The causes of the breakdowns were still debated as the results from [3] were not widely acknowledged. As a general realisation of the importance of Z-phase precipitation set in during the following years, observations of Z-phase precipitation in 9-12wt%Cr steels were made by many separate research groups [13-16]. While the most continuous research has been presented in papers from Danielsen or Sawada, many groups have been involved in more recent

characterising of Z-phase precipitation [17-24] as well as atomistic scale modelling [25-28].

2 Review

2.1 Z-phase in 9-12wt%Cr steels
In [29] an investigation was carried out on numerous 9-12wt%Cr steel grades at different exposure conditions, some of them shown in table 1, with focus on the Z-phase content and its effect on the MX population. The presence of Z-phase could be verified in all of the investigated alloys if exposed for high temperatures (600-650°C) for an extended period (usually 10.000h). This confirmed the observations of [3] that the Z-phase was the most thermodynamically stable nitride in these types of alloys. The Z-phase could generally be found as relatively large precipitates in contrast to the small and finely distributed MX. While the amount of observed Z-phase was dependent on temperature and exposure time, there was a very clear trend towards 11-12wt%Cr having significantly higher Z-phase content compared to the 9wt%Cr steels. The quantity of MX was observed to be much lower in samples containing large amounts of Z-phase. Available creep data showed breakdowns in creep strength for the high Cr steels after some thousands of hours of exposure at 650°C, such as can be seen for X19 in Fig. 1. This corresponded with the occurrence of large scale Z-phase precipitation and dissolution of MX as outlined in [3], explaining why breakdowns in creep strength occurred in 11-12wt%Cr steels. Although Z-phase was also observed in 9wt%Cr steels, the precipitation occurred slowly with only small amounts being observed, even at very long exposure times. Large amounts of MX precipitates where still present in these steels, thus the creep strength should not be affected.

Table 1: *Chemical composition in wt% for X20, grade 91, grade 92 and grade 122 investigated in [29].*

	C	N	Si	Mn	Cr	Mo	W	Ni	Nb	V	Cu	B
X20	0.19	0.025	0.23	0.49	11.5	0.91	…	0.66	…	0.31	0.05	…
P91	0.10	0.053	0.36	0.37	8.30	0.95	…	0.15	0.07	0.21	…	…
P92	0.11	0.049	0.17	0.43	9.27	0.48	1.7	0.25	0.067	0.20	…	0.0026
T122	0.09	0.061	0.25	0.60	12.20	0.35	1.97	0.32	0.06	0.25	0.43	0.0021

The Z-phase had only been observed as Cr(V,Nb)N or CrNbN in various steels but investigations of older Nb-free X20 11wt%Cr type steels revealed that the Z-phase could also precipitate as CrVN [29]. In spite of the high Cr content only very low Z-phase amounts were found in X20, indicating a very slow precipitation without the presence of Nb. This is reflected in the creep curves of X20 which show stable creep behaviour of these steels compared to the Nb containing X19, see Fig. 1. Investigations of experimental alloys containing Ta in

[30] also showed it was possible to precipitate CrTaN and Cr(V,Ta)N in 9-12wt%Cr steels, indicating that the Z-phase can form as CrMN particles where M is any combination of V, Nb and Ta.

2.2 Thermodynamics

Experiments in [29] had shown Cr(V,Nb)N to dissolve and reform (V,Nb)N if exposed to temperatures above 800°C in 11wt%Cr steels. This solution temperature is much lower than its CrNbN counterpart in austenitic steels (1200-1300°C). A thermodynamic model of the Z-phase was developed in [31] based upon such experimental results together with an extensive amount of data from literature results of both martensitic and austenitic steels. The model is now incorporated in commercial ThermoCalc databases from version TCFE6 and onwards.
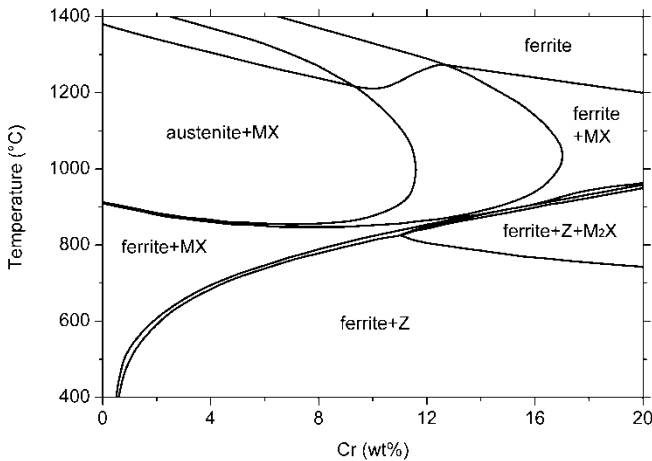

Figure 2: *Thermodynamic equilibrium of an iron alloy with a 0.06N 0.06Nb 0.21V composition (in wt%) and variation of Cr content. Reconstructed from [31].*

The model predicted the Z-phase to be the thermodynamically stable nitride in 9-12wt%Cr steels which would replace all MX in the relevant temperature range, see Fig. 2. Using driving force calculations, the difference of free energy for the system with and without Z-phase, the Z-phase precipitation speed could be estimated as a function of the chemical composition. These calculations verified the importance of Cr, which was found to be the most influential element. This is perhaps not surprising when considering the main difference between (V,Nb)N MX and Cr(V,Nb)N Z-phase is Cr. Elements that reduce the Cr content in the matrix will also influence the driving force, such as C forming chromium containing $M_{23}C_6$. Maybe more unexpectedly, Co is seen to increase the driving force of Z-phase as it reduces the Cr affinity of the matrix, which has also been

experimentally verified in [32-33]. Using Cr as a benchmark, an increase in the driving force equivalent of 1wt%Cr can be obtained by removing 0.1wt%C or adding around 4wt%Co. A high N content increases the driving force as MX can form as carbo-nitrides, thus being relatively stable at low N-contents, while Z-phase is believed to be a relatively pure nitride [11].

While the thermodynamic model is helpful in providing inputs for the prediction of precipitation kinetics, there are also discrepancies. For example the model does not indicate small amounts of Nb to have any significant effect on the precipitation speed, however experiments have proven otherwise [34]. Ni is also not predicted to have any effect although several sources show it accelerates Z-phase precipitation [3,35]. It is also important to note that the thermodynamic calculations use chemical composition and temperature as input. Factors such as diffusion, interfacial energy or microstructure have to be accounted for in kinetic models. Kinetic modelling of Z-phase has been attempted [36-37] but this is very complicated due to the nature of Z-phase (see *nucleation* and *interface* chapters) and cannot be covered by standard methods. Another complication is given in [38-39] which shows that for creep specimens, Z-phase would precipitate 2-4 times faster in the gauge length compared to the grip, something that would be very difficult to model. As the stresses in normal power plant conditions are relatively low compared to creep tests, it is very important to consider this kinetic phenomenon when investigating gauge lengths of creep specimens.
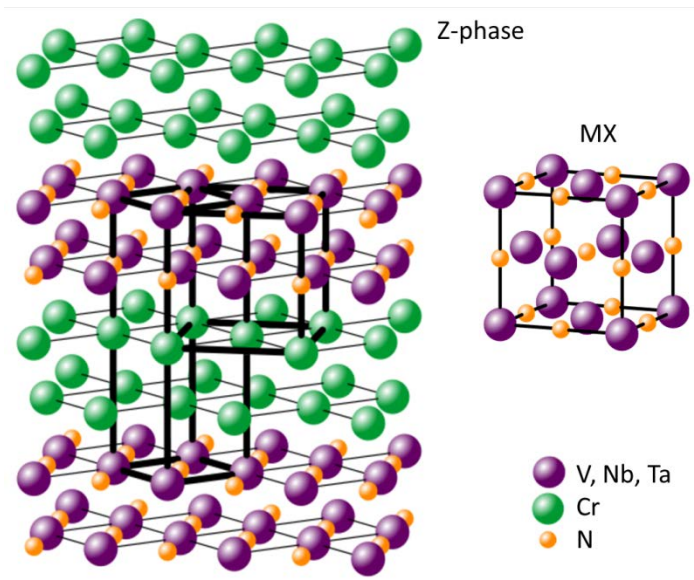

Figure 3: *The double layered tetragonal crystal structure of Z-phase compared to MX crystal structure. The Z-phase (tetragonal) and corresponding MX (cubic) unit cells are drawn in bold lines. Reconstructed from[47].*

2.3 Crystal structure

MX has a simple NaCl type crystal structure, where the lattice parameter depends on the chemical composition. NbN and TaN have lattice parameters of 0.439nm, significantly larger than the 0.413nm of VN. The most common MX in 9-12wt%Cr steels is (V,Nb)N with a lattice parameter around 0.420nm, depending on exact composition. The crystal structure of Z-phase is tetragonal [7] with the c lattice parameter being 0.739nm and a lattice parameter depending on the chemical composition, being 0.286nm for the V-rich Z-phases usually found in 9-12wt%Cr steels [3]. An overview of different Z-phase lattice parameters can be found in [30]. The Z-phase crystal structure can be described as a double layered structure with alternating layers of MX and Cr, see Fig. 3, thus there is a certain resemblance to the normal MX crystal structure.

Measuring the crystal structure of Cr(V,Nb)N and CrVN particles using electron diffraction in [40] has yielded surprising results, as both cubic and tetragonal diffraction patterns could be obtained from the same particles. The cubic crystal structure was measured to have a lattice parameter around 0.404nm, being slightly lower than the VN lattice parameter but corresponding to the lattice in Z-phase if it was cubic, see Fig. 3 (0.404nm = $\sqrt{2}$ x 0.286nm). In [41] X-ray diffraction measurements confirmed the presence of the cubic Z-phase crystal structure in steels containing Cr(V,Nb)N precipitates. The dual cubic/tetragonal crystal structure is believed to be connected with the transformation process of MX into Z-phase, with the cubic crystal structure being a metastable step towards forming the stable tetragonal crystal structure (see *nucleation* chapter). Experimental results from CrNbN and CrTaN have shown them to be more strictly tetragonal than CrVN, which could be because of their high nucleation speed compared to V-rich Z-phase.
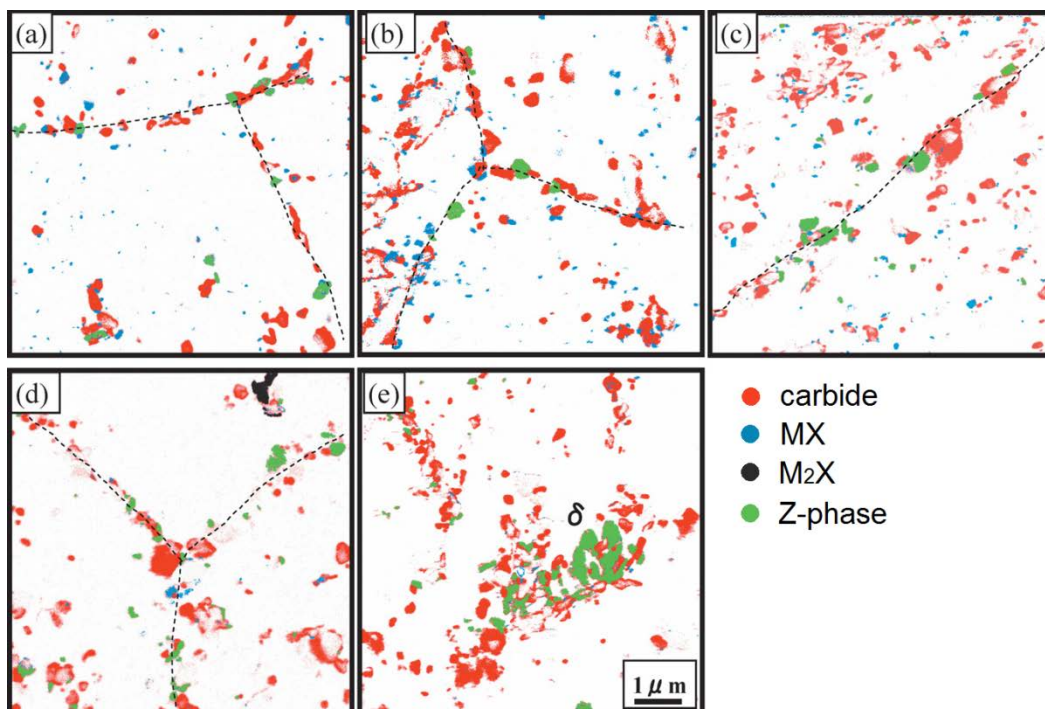
Figure 4: *Energy filtered TEM on carbon extraction replicas from different steel grades. Prior boundaries predicted by the distribution of precipitates are shown in dashed lines. e) is from a delta ferrite area. Reconstructed from [38].*

2.4 Identification

The Z-phase has roughly a chemical composition of ⅓Cr, ⅓(V+Nb) and ⅓N, the V/Nb ratio usually differs a lot from particle to particle. The similarities between V-rich MX, M_2X and Z-phase nitrides can present problems with identification. Since MX contains some amount of Cr and M_2X contains some amount of V, the chemical compositions can be very similar, $(V,Cr)N$ for MX, $(Cr,V)_2N$ for M_2X and CrVN for Z-phase. While energy filtered TEM is useful for investigating precipitate distribution [38], see Fig. 4, these similarities make mapping techniques difficult with more precise EDS measurements required to verify the results [5]. As indicated by Fig. 4 the Z-phase precipitate everywhere, but are preferentially located around prior austenite grain boundaries which accelerates recovery of the microstructure [38,41].

Difficulties in identifying Z-phase by crystal structure are also common. While the hexagonal crystal structure of M_2X is unrelated, the cubic crystal structure of Z-phase is almost identical to that of MX, lattice parameters being VN=0.413nm and CrVN=0.404nm [40]. An example of mistaken identity is shown in [4], where early Z-phase precipitation has been mistaken for Cr rich MX, leading to

the incorrect conclusion that the breakdown in creep strength of grade 122 happens before Z-phase precipitation takes place.
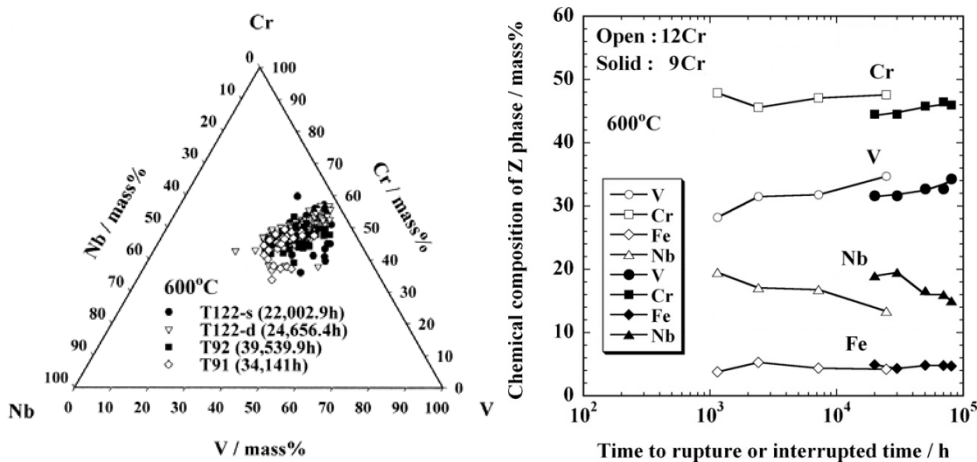
Figure 5: *Metallic composition of Z-phase a) in a ternary diagram and b) with change over time. Reconstructed from [38] and [42] respectively.*

Identifying the Cr content by EDS is the most reliable and easiest way to tell apart MX, M_2X and Z-phase. In general terms the Cr contents (metallic at%) are: M_2X Cr >70%, Z-phase Cr ≈50%, MX Cr <35%. Both for Z-phase and MX (but not M_2X) some of the V is usually replaced by Nb, however a large Nb content is in no way a prerequisite for a Z-phase composition. Typical metallic chemical compositions of Z-phase can be seen in Fig. 5a. It is observed that the average Nb content in Z-phase usually drops over time as more Z-phase precipitate [42], see Fig. 5b. This happens because Z-phase prefers Nb over V, and since 9-12%Cr steels usually have relatively low Nb contents it is quickly used up, making the Z-phase more V-rich when it has precipitated in greater quantity [29]. It is also worth noting that Z-phase contains a higher amount of Fe compared to MX and M_2X, around 5 at% of the metallic composition.

2.5 Precipitation rate
In [34,41,43] the precipitation rate of Z-phase in several model alloys was investigated, especially how it would be affected with changes in chemical compositions. A 12CrVNbN alloy was designed for fast Z-phase precipitation while still retaining the N/V/Nb ratio of commercial grades, see table 2. This alloy was solely intended for studying the nitride evolution, thus C, W and Mo were not included to avoid any non-nitride particles, such as carbides or Laves phase, which could interfere with x-ray diffraction measurements. The 9CrVNbN alloy was similar to the 12CrVNbN but with a reduced Cr content for investigating the effect of Cr on precipitation speed, see table 2.

Table 2: *Composition of model alloys in wt%, balance Fe. From [34][41][47]*

	Cr	C	V	Nb	Ta	N	Ni	Mn	Si	W	Co	B
12CrVNbN	11.85	0.005	0.18	0.076	…	0.061	1.29	0.32	0.40	…	…	…
9CrVNbN	9.11	0.004	0.21	0.080	…	0.059	1.27	0.34	0.41	…	…	…
12CrVN	11.57	0.002	0.23	…	…	0.088	1.27	0.31	0.35	…	…	…
12CrTaN	11.79	0.005	…	…	0.39	0.033	0.50	0.48	0.30	2.90	7.30	0.004

Figure 6 shows XRD powder diffraction measurements of thermally aged 12CrVNbN and 9CrVNbN alloys at 650°C, showing the nitride evolution. After short term heat treatments the alloys contain only MX and M_2X nitrides. Two separate populations of MX nitrides are present: (V,Nb)N and (Nb,V)N. The lattice parameters of both precipitate types are dependent on the chemical composition, being in between that of pure VN and NbN. In the 12CrVNbN alloy the M_2X content is much higher which consumes some of the V, leaving the MX particles richer in Nb (higher lattice parameter). The MX particles are replaced relatively quickly by Z-phase in the 12CrVNbN specimens. A gradual shift takes place in the VN peak position towards a lower lattice parameter corresponding to the cubic Z-phase, which might be related to the Z-phase nucleation process. A Cr-enrichment of the MX was observed by EDS measurements at the same time interval [41]. In the 9CrVNbN alloy the Z-phase precipitation can be seen to appear at the end of the test durations, however the dissolution of MX has barely begun.
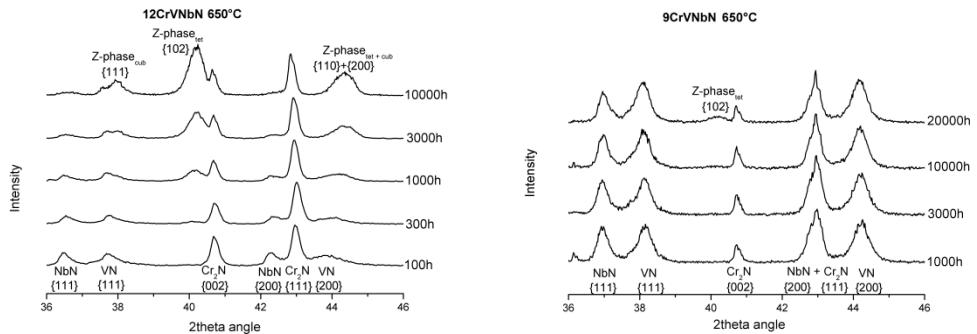
Figure 6: *XRD spectra of nitride evolution in 12CrVNbN and 9CrVNbN. Reconstructed from [43].*
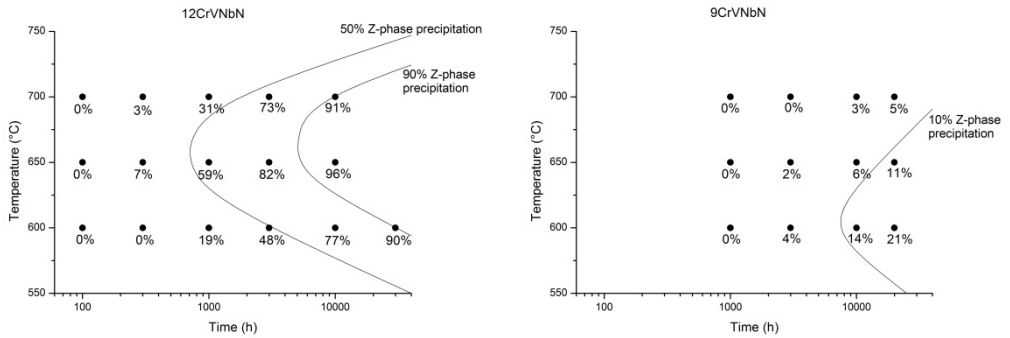
Figure 7: *Time-temperature-transformation curves showing the amount of MX transformed into Z-phase estimated from Rietveld data for 12CrVNbN and 9CrVNbN. Reconstructed from [43].*

The tests in Fig. 6 were carried out at 600, 650 and 700°C and a Rietveld refinement was made in order quantify the relative amount of each nitrides type, showing how much of the MX had been replaced by Z-phase. When plotting these data into a time-temperature-transformation (TTT) curve, accurate information could be obtained on the Z-phase precipitation speed, see Fig. 7. By comparing the 12CrVNbN and 9CrVNbN alloys, it can be seen that the Z-phase precipitates considerably faster in the 12wt%Cr alloy at all temperatures. Presence/no presence TEM measurements of Z-phase in commercial steels in [44] indicate both 9wt%Cr and 12wt%Cr steels have peak Z-phase precipitation speed at 650°C. However Fig. 7 shows the Z-phase to have peak precipitation at 650°C only for the 12CrVNbN alloy, while for the 9CrVNbN alloy it peaks at 600°C. This corresponds well with thermodynamic modelling which predicts Z-phase to be stable up to higher temperatures at higher Cr contents, see Fig. 2, thus an increase in Cr is expected to raise the TTT curve to higher temperatures. As no data were available from temperatures lower than 600°C, the 9CrVNbN TTT curve in Fig. 7 is based on an estimate that the precipitation will be slower at 550°C. The results indicate that the Z-phase content in 9wt%Cr steels could be underestimated if accelerated tests at 650°C are used instead of 600°C. It should be noted that these model alloys do not contain C, thus they have a higher Cr content in the matrix compared to commercial alloys. The matrix Cr contents would correspond to that of a 10wt%Cr and a 13wt%Cr commercial alloy containing 0.1wt%C. In addition the Ni contents of the model alloys are very high.

The 12CrVN alloy investigated in [34] is similar to the 12CrVNbN alloy but has the Nb content replaced with V (based on at%), see table 1. The alloy was intended otherwise to be identical with 12CrVNbN, but unfortunately the N

content became too high in the 12CrVN alloy, resulting in extensive M_2X precipitation and lower MX population as some V enters M_2X. For the 12CrVN alloy there was almost no precipitation of Z-phase, very few could be identified using TEM in samples exposed at 650°C/30.000h, far from enough to be visible in XRD spectra. The lower MX content needs to be taken into account, especially since [45] reports precipitating M_2X instead of MX delays Z-phase precipitation, which does make sense considering the nucleation mechanism (see *nucleation* chapter). It would seem that Nb acts as a catalyst for the precipitation of Z-phase, and removing Nb causes the Z-phase precipitation to almost completely stop, even for high Cr steel grades. This was also the conclusion with investigations of Nb-free X20 commercial alloys in [29] which do not have the drop in strength seen in corresponding 11-12wt%Cr alloys with Nb, see Fig. 1. As the thermodynamic model does not show large changes in driving force with the addition of small amounts of Nb, the difference might be an effect of the increase in MX lattice parameter and interface energy when adding Nb [34].

2.6 Nucleation
Z-phase precipitation in 9-12wt%Cr steels was observed in [29] to be a slow process with continuous nucleation. From a thermodynamic point of view a normal nucleation in the matrix is difficult to explain as the Z-phase nucleates after the critical elements have left the matrix and formed MX particles. Experimental observations have been made of particles which contained both areas with MX and Z-phase composition inside them [29]. Closer investigations in [46] revealed actual gradients in the chemical composition inside the MX/Z-phase, see Fig. 8a, identifying them as hybrid particles. The areas with Z-phase composition are usually formed at edges of the MX particles, but this is not nucleation of Z-phase taking place on MX particles, but rather a gradual transformation of MX into Z-phase is taking place by Cr diffusion. As Cr diffuses from the matrix into MX particles, they are transformed both chemically and crystallographically into Z-phase. The Cr needed for this transformation can easily be supplied by the matrix, dissolving carbides or other Cr-rich precipitates is not necessary. While smaller MX particles could be seen to transform completely, for larger particles local areas were observed to transform into Z-phase first, usually in parallel at opposite sides of the particles, see Fig. 8b, indicating a preferred orientation relationship with the matrix. These Z-phase areas would then consume the rest of the particle by normal matrix diffusion, described in [41], as such matrix diffusion is considered to be faster than the slow transformation process. The transformation of MX to Z-phase is slow, but when first a few particles have transformed into Z-phase they will grow quickly by consuming other MX particles that have not transformed, eventually replacing the fine population of MX with a coarse population of Z-phase.
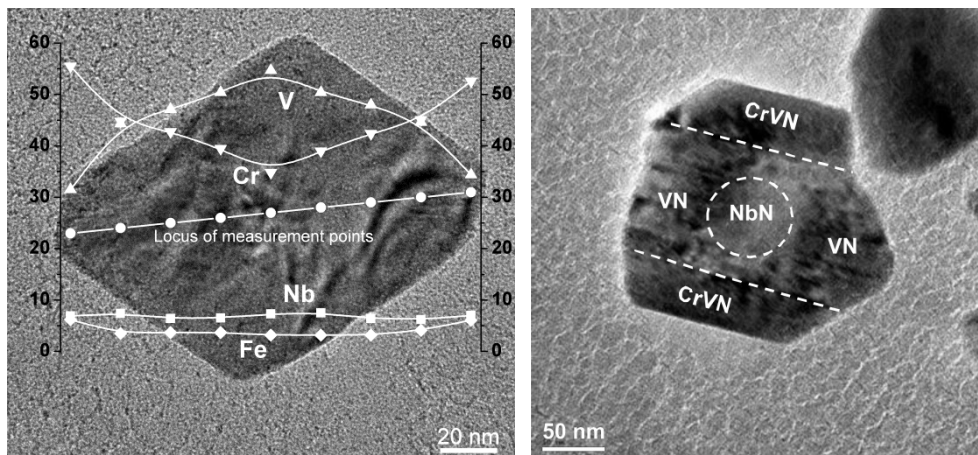
Figure 8: *a) EDS measurements (metallic elements only) of a particle with MX core and Z-phase rim. b) A large MX undergoing a transformation into Z-phase, major elements are noted. Reconstructed from [41].*

Further investigations of this transformation were done in [47] with atomic resolution TEM, using Ta versions of the MX/Z-phase nitrides as such systems were much easier to study: The transformation is much faster and a far better contrast could be obtained as Ta atoms are 3.5 times heavier than Cr atoms. A 12CrTaN alloy, see table 2, was investigated using HAADF where Cr atoms appear very dark in comparison to the bright Ta atoms, N atoms are not visible. In Fig. 9a the MX part of the precipitate can be recognised as a monotonous TaN crystal structure with uniform brightness, while the Z-phase structure can be recognised as alternating bright double layers (TaN) and dark double layers (Cr). As Cr diffuses into MX from the matrix, the dark double layers can be seen growing into the precipitates until a complete transformation has taken place resulting in a regular double layered structure, as seen in Fig. 9b.
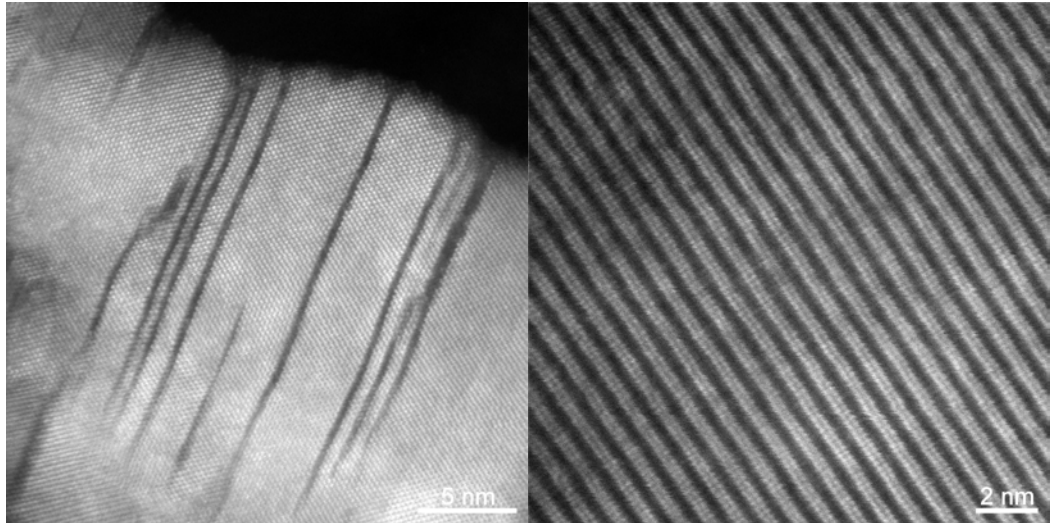
Figure 9: *A) Dark layers of Cr diffusing into a TaN particle. B) A fully transformed Z-phase crystal structure with alternating layers of TaN and Cr. Reconstructed from [47].*

2.7 Interface

In [48] investigations of the CrTaN and CrNbN type Z-phases in thinfoils revealed a few nm thick interface, best described as an amorphous shell enveloping the crystalline nitride, separating the nitrides from the crystalline ferrite, see Fig. 10. Darkfield investigations using selected area electron diffraction and fast fourier transformation of atomic resolution imaging confirmed the amorphous nature of the interface between nitride and matrix. Since the precipitate particles were completely embedded inside the steel matrix, this was not an influence of sample preparation. The chemical composition of the amorphous shells was very close to that of the crystalline nitride. When investigating carbon extraction replicas, the amorphous shells would crystallise during beam exposure in the TEM, indicating that it is purely an interface effect which is no longer stable once the matrix has been removed. In order for such an amorphous interface to form, the crystal-crystal interfacial energy must be higher than the combined matrix-amorphous and nitride-amorphous interface energies plus the required amorphisation energy. Similar 1-2nm thin amorphous interfaces are frequently observed at grain boundaries for sintered materials, and are usually known as Intergranular Glassy Films (IGF) which are considered to stabilise the interface. The formation of amorphous shells around precipitates would indicate an extraordinarily high interface energy. As the interfacial energy governs the coarsening rate (Ostwald ripening) this would indicate that CrTaN and CrNbN Z-phase would have higher coarsening rates compared to normal V-based MX in commercial steels.
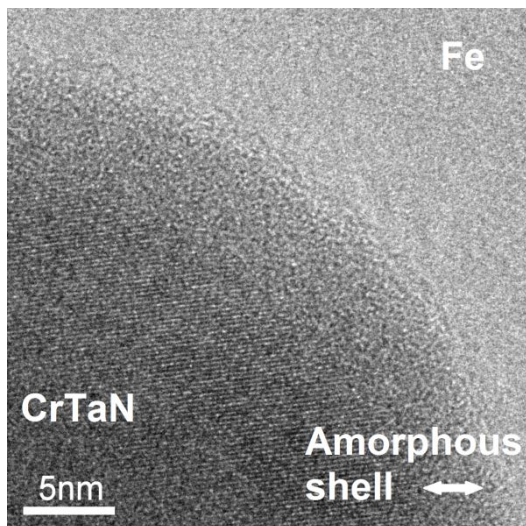
Figure 10: *The interface between steel matrix (not in focus) and CrTaN Z-phase (in focus). The crystalline planes of the Z-phase are visible, but stop a few nanometres before the interface. Reconstructed from [48].*

3 Perspective

3.1 Cr content

The investigations of Z-phase points towards all 9-12wt%Cr steels strengthened by normal V/Nb based MX nitrides will develop Z-phase to some degree. The experimental results have shown when Z-phase starts to appear in numbers a breakdown of the creep strength will take place because of the diminished MX content. The precipitation speed of the Z-phase largely depends on the chemical composition, and it is especially important to note that a high Cr content can significantly accelerate the precipitation process. Systematic studies of the long term creep strength as a function of Cr content can be found in the literature, which also show that breakdowns in creep strength are accelerated with higher Cr contents. An example from [49] is shown in Fig. 11, where six identical steel compositions except variations in Cr content, see table 3, are creep tested. The high Cr steels suffer breakdown in creep strength before the lower Cr steels; for the 11.5Cr alloy breakdown occurs after roughly 3000h, 10.5Cr after 10.000h, 9.5Cr after 30.000h and 8.5Cr has not suffered any breakdown within the test duration of 60.000h. It is highly likely that this behaviour is caused by Z-phase precipitation. While these steels contain a high content of B and a low content of N, the MX nitride particles still seem to play a crucial role for their precipitation strengthening. It should be noticed that these alloys contain 3wt%Co so the Z-phase precipitation can thus be considered to be accelerated by almost 1wt%Cr

compared to commercial steels. For example the 8.5Cr alloy would correspond to a 9.5wt%Cr commercial steel.
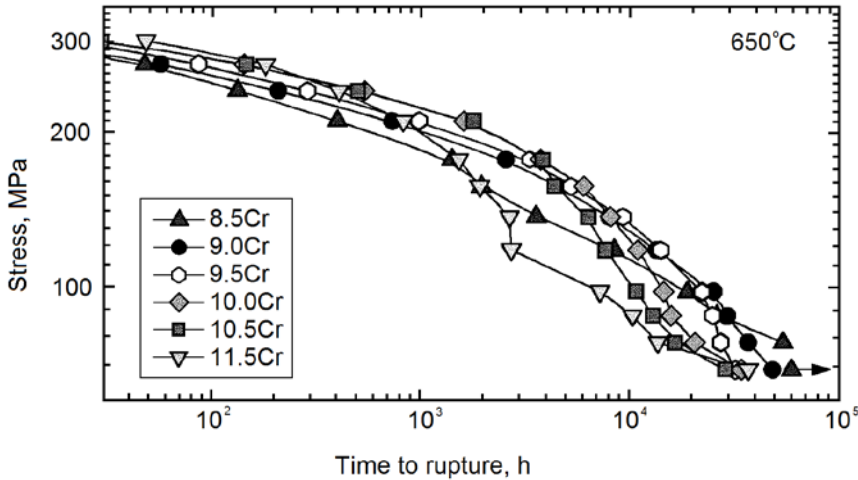
Figure 11: *Creep curves of several experimental steels where the Cr content is varied. Higher Cr content accelerates the breakdown which most likely is caused by Z-phase precipitation. Reconstructed from [49].*

Table 3: *The chemical composition of the steels shown in Fig. 11 given in wt%, balance Fe. [49]*

Steel	C	Si	Ni	Cr	Mo	V	Nb	W	Co	B	N
8.5Cr	0.10	0.03	0.20	8.56	0.11	0.15	0.07	3.45	2.99	0.009	0.020
9.0Cr	0.09	0.03	0.21	9.04	0.11	0.15	0.06	3.55	2.98	0.009	0.020
9.5Cr	0.10	0.03	0.21	9.51	0.11	0.15	0.06	3.58	2.99	0.009	0.020
10.0Cr	0.09	0.03	0.21	10.06	0.11	0.15	0.06	3.55	3.02	0.011	0.020
10.5Cr	0.10	0.03	0.20	10.50	0.10	0.15	0.06	3.54	3.00	0.010	0.021
11.5Cr	0.10	0.03	0.21	11.59	0.11	0.15	0.07	3.60	3.04	0.010	0.020

3.2 Experimental 9wt%Cr steels

While Z-phase precipitation is more extensive in steel with higher Cr contents, the problem also exists in certain 9wt%Cr steels. A novel attempt has been made to create a 9wt%Cr steel with a very high creep strength based on a very low C content, using extensive MX precipitation for strengthening instead of carbides [50]. This concept, called MARN, showed excellent creep performance for up to 10.000h at 650°C, see Fig. 12a, however no further creep data has been released for a decade. The low C content allows more Cr in the matrix that otherwise would have formed carbides, and combined with a 3wt%Co this could cause the steel to have a Z-phase precipitation rate almost equivalent to an 11wt%Cr commercial steel. Z-phase precipitation during creep exposures have been reported [51], this would inevitably lead to a drastic reduction in MX particles.

By using relatively high B contents, around 0.01wt%, the creep strength of 9-12wt%Cr steels can be increased considerably, however a low N content would be required to avoid formation of large BN particles [52]. Balancing low N with high B contents has produced alloys with remarkably high creep strength, Fig. 12a shows the creep curve of an alloy with a 0.008wt%N/0.014wt%B balance called MARBN (also copied as NPM in Europe). When increasing the N content to 0.065wt% the B effect is lost, see Fig. 12b. Reducing the N content below 0.008wt% in MARBN will significantly lower the creep strength, giving an excellent indication of what happens when MX is removed from these steels. At very low N concentrations even tiny amounts of N can increase the creep strength considerably. The 0.0034N curve has about 10 times longer time to rupture compared to the 0.0015N curve at 100MPa, which illustrates the importance of the MX in these steels. Having a low N content, such as 0.008wt%, causes the MX to form as carbonitrides, (V,Nb)(N,C), which does reduce the driving force for Z-phase precipitation as the Z-phase forms as more pure nitrides [31]. Still the Z-phase is known to precipitate in steels with N contents close to 0.02wt% [19,29,33], indications of this are also seen in Fig. 11, thus it might be a poor choice to include 3wt%Co in MARBN.
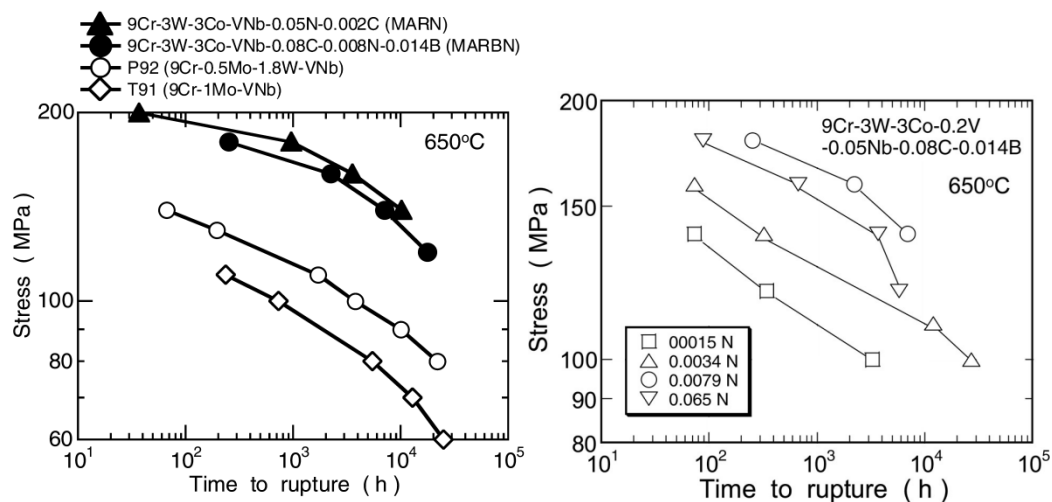
Figure 12: *a) Creep curves for MARN and MARBN compared to grade 92 and grade 91. b) Creep curves for MARBN with different N contents. Reconstructed from [52].*

3.3 Commercial 9wt%Cr steels

Normally 9wt%Cr commercial steels have very slow Z-phase precipitation, but they are not immune to it. In order to quantify the problem, very long creep exposures need to be carried out. A study in [35] on two different commercial grade 91 heats has shown extensive Z-phase precipitation after creep tests up to

80.000h at 600°C in one heat but not the other, see Fig. 13. The Z-phase was shown to noticeably replace MX particles from around 30.000h of exposure in the MGC heat, gradually reducing the MX density with time followed by what was considered premature failure. When investigating a very similar heat MgC, see table 4, at roughly the same exposure time, much less precipitation of Z-phase could be observed and the MX density remained stable. This was also reflected in the creep curves, where MgC demonstrated superior long term creep strength over MGC although their short term strengths where the same. It was concluded that the higher Ni content was the cause for increased Z-phase precipitation, a similar conclusion that was reached in the first extensive study of Z-phase precipitation in 9-12wt%Cr steels [3]. It is not known how such a comparatively small amount of Ni can affect the Z-phase precipitation as neither MX nor Z-phase contain Ni and the thermodynamic modelling does not indicate any influence of Ni [31]. As [35] points out, an in-depth investigation of the acceleration mechanism of the Z-phase formation by Ni is needed.

Table 4: *The chemical composition of the steels shown in Fig. 13 given in wt%, balance Fe. [35]*

	C	Si	Mn	Ni	Cr	Mo	V	Nb	N
MGC	0.09	0.29	0.35	0.28	8.70	0.90	0.22	0.072	0.044
MgC	0.10	0.24	0.44	0.04	8.74	0.94	0.21	0.076	0.058
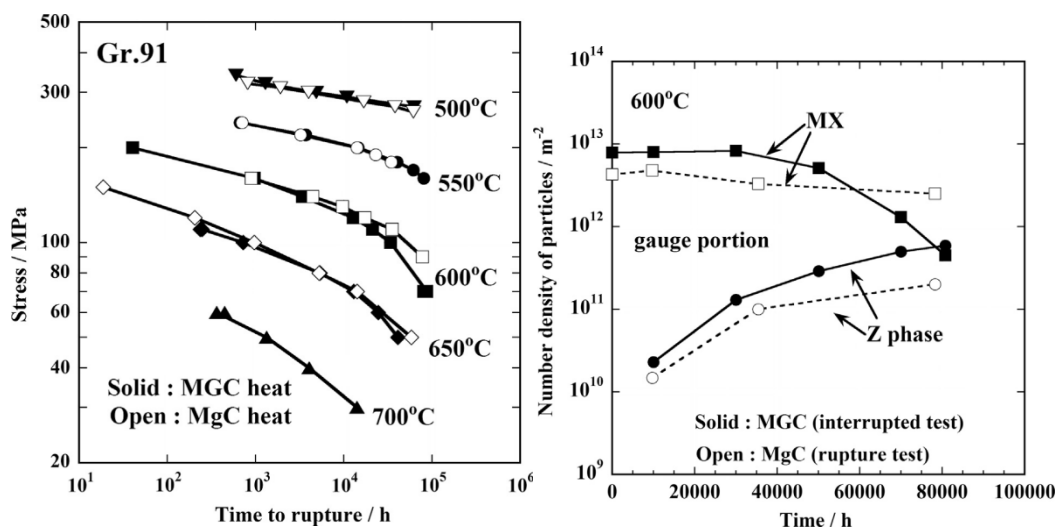
Figure 13: *Long term creep strength of two grade 91 heats with the Z-phase precipitation and MX dissolution showing a correlation between MX density and creep strength. Reconstructed from [35].*

3.4 Experimental 11-12wt%Cr steels
There are not many 11-12wt%Cr steels currently under development due to the obvious breakdowns in creep strength experienced by such steels. Most

development has continued as 9wt%Cr steels, with some high Cr steels simply having their Cr content reduced. However, for certain components of fossil fired power plants there is a need for high oxidation resistance but only moderate creep strength which has encouraged the development of steels with high Cr contents. In [53] an 11-12wt%Cr steel VM12-SHC is described, where the Z-phase precipitation is simply allowed to run its course with the steel being designed upon whatever strength is left thereafter. The creep strength is not high compared to grade 92, however its oxidation resistance is superior. In such a case the Z-phase precipitation rate is not important as once it has fully precipitated the strength will stabilise at much the same level. This is illustrated in Fig. 11, where after long time exposure the 9.5wt%-11.5wt%Cr steels end up at the same strength level as they all have developed Z-phase, while the 8.5wt%Cr steel is much stronger since it still contains MX.

3.5 Nb-free steels
Development of 12wt%Cr steels for operation at 650°C has been attempted for a long time but has largely been a failure. While it seems unlikely that an 11-12wt%Cr steel based on Nb/V MX nitrides can be designed without a drop in creep strength from Z-phase precipitation, there is a way of effectively stopping the Z-phase precipitation in these alloys: removing Nb. Even in 11-12wt%Cr steels pure CrVN Z-phase will be extremely slow to precipitate [34]. However such steels do not derive the same kind of strength from VN as commercial steels do from (V,Nb)N as the VN are not as finely distributed. An example is the X20 steels from Fig. 1 which are still in service. In [54] an attempt to design a Nb-free 11wt%Cr alloy with moderate creep strength and good oxidation resistance was made. Short term creep tests at 6000h showed the strength to be slightly below that of grade 92, with long term creep tests still running. It is however unlikely that removing Nb alone would produce steels with creep properties good enough for operations above 600°C unless used in specific components with relatively low strength requirements.

3.6 Z-phase strengthened steels
A different approach to create a 12wt%Cr steel was attempted in [55] based on the idea that Z-phase could be used as the strengthening nitride agent instead of MX. Inspiration was drawn from austenitic steels, where very small finely distributed CrNbN Z-phase are thermally stable with a low coarsening rate and provide considerable creep strength [8]. For normal V-containing steels the transformation rate of MX to Z-phase is relatively slow, giving the Z-phases that precipitate first plenty of time to consume nearby MX precipitates during growth, leading to a coarse distribution of large Z-phases. If a fast precipitation rate could be obtained, all of the fine MX precipitates would immediately transform into fine Z-phase precipitates, and thus the growth process could be avoided

altogether. Steels based upon Z-phase nitride strengthening could be combined with a high Cr contents for oxidation resistance, in fact a high Cr content would be necessary to obtain a fast transformation.
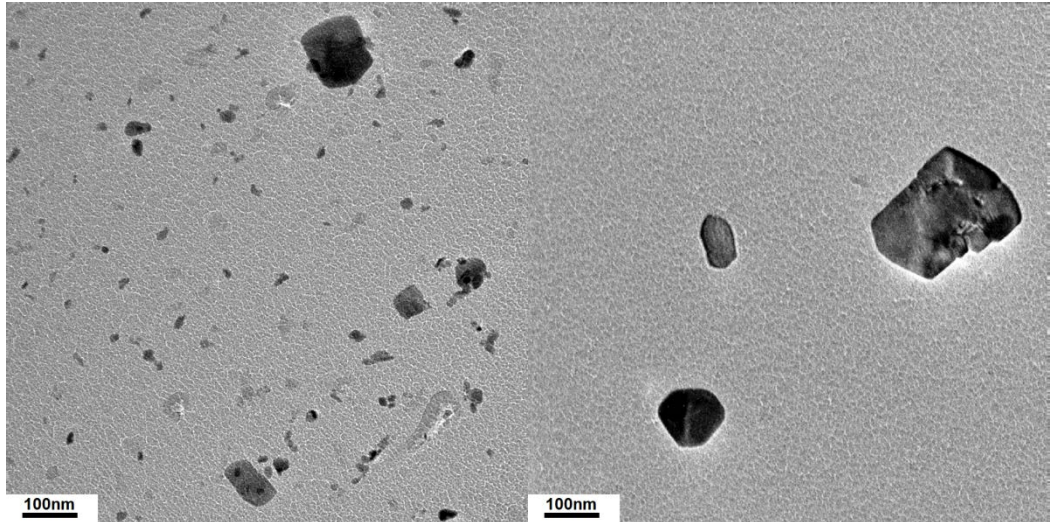
Figure 14: *CrTaN precipitates from the 12CrTaN alloy, exposed at 650°C for A) 1000h and B) 38000h, showing the relatively high coarsening rate compared to MX. Reconstructed from [56].*

In order to obtain a very fast transformation, V can be replaced by Nb or Ta as to promote CrNbN or CrTaN type Z-phases instead of the slowly precipitating CrVN. The C content must be kept very low, as C would stabilize the MX type Nb(N,C) or Ta(N,C) carbonitrides. The best results were obtained with the Ta-containing 12CrTaN alloy shown in table 1, which had a very fast Z-phase formation rate. The MX in this steel transform into Z-phase already during tempering and are present as small and finely distributed precipitates which provided an initial creep strength which is higher than that of commercial grades such as grade 92. Unfortunately the coarsening rate (Ostwald ripening) of both CrNbN and CrTaN type Z-phases were found to be much higher than (V,Nb)N type MX at temperatures of 600-650°C [56], see Fig. 14, probably due to the high interface energy indicated by the amorphous interface [48], see Fig. 10. Thus the long term creep strength of the Z-phase strengthened steels cannot compare to that of commercial steels at these temperatures.

3.7 Outlook
Designing 11-12wt%Cr with traditional (V,Nb)N MX precipitates has not been a success as the increase in Cr promotes C(V,Nb)N Z-phase precipitation. It is important to note that it is the Cr content that remains in the matrix that promotes Z-phase precipitation, not the overall composition. Adding or removing elements

that react with Cr need to be considered, for example 0.1%C will remove roughly 1%Cr from the matrix. Other elements also affect the Z-phase precipitation kinetics, adding Co or Ni has been shown to accelerate Z-phase, causing breakdown in creep strength even in 9%Cr steels. Such elements should be avoided in all steels if strengthening from traditional MX is sought. The Z-phase precipitation is all but stopped when removing Nb from MX, however this makes the MX a less effective strengthening component. If an optimum MX population is to be obtained it needs to be kinetically stable (very slow Z-phase transformation) and finely distributed in the microstructure. The small amount of Nb used in commercial steel, typically 0.06wt%, could perhaps be replaced by another element that can enter MX and ensure a fine distribution, but not be prone to Z-phase transformation as Nb and Ta are. It is clear that some sort of innovation in this class of steels is needed, perhaps by using other types of strengthening agents which could allow a higher Cr content to be used. However, there are no indications that a breakthrough in this field will take place in the near future.

4 Conclusion

It has been shown that Z-phase will eventually precipitate and replace the beneficial MX in all 9-12wt%Cr martensitic steels, thus causing a breakdown in long term creep strength. Thermodynamic modelling and quantitative experiments have shown Cr to be a crucial factor in increasing the precipitation rate. For 9wt%Cr steels the Z-phase precipitation is very slow and may not affect the creep strength within the lifetime of a power plant, while for the 11-12wt%Cr steels the Z-phase will precipitate faster and remove the crucial strengthening effect of the MX particles. Attempts to improve both oxidation resistance and creep strength for 9-12wt%Cr steels in the last couple of decades have largely failed. It seems unlikely that long term creep strength based on the traditional MX together with high oxidation resistance based on 11-12%wtCr can be obtained at the same time. There has been no substantial improvement in this class steels since grade 92, which was developed in the 1980´s, thus it has not been possible to produce martensitic steels for operations at 650°C.

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