Chapter 2

Precipitates in creep resistant austenitic stainless steels

The main grades of austenitic stainless steels have been presented in the previous chapter. With excellent corrosion and mechanical properties at high temperatures, they are choice materials for powerplant tubes which have to operate at temperatures above 950K, or for aeroengines.

The important role of precipitation in the achievement of good creep properties has been understood for long and extensively studied. Although some phases are now well documented, there are still contradictions and missing thermodynamic data, in particular, there is only a limited amount of information about phases like Z-phase or Cr_3Ni_2SiN which can be predominant precipitates in nitrogen-bearing steels.

This chapter is a review of common precipitates in austenitic stainless steels, in particular wrought heat-resistant steels of the AISI 300 family or 20/25 steels. Precipitates forming in age-hardening austenitic stainless steels are only briefly presented, having been previously reviewed by other authors, and can be considered out of the scope of this work.

2.1 Carbides and nitrides in austenitic stainless steels

2.1.a MX precipitates

The formation of MX precipitates in austenitic stainless steels occurs when strong carbide/nitride formers (Ti, Nb, V, Zr, Ta...) are added to the alloy.

These additions have two purposes:

- stabilising the alloy against intergranular corrosion. When stabilisation is the first aim, a stabilising heat-treatment is conducted at 840-900 °C for several hours before service. Most of the carbon is then 'tied-up' by precipitation of MC.

- Providing good creep resistance: when this is the first aim, a solution heat-treatment is given in order to dissolve as much MX as possible. Subsequent precipitation occurs during creep and increases strength. A typical solution treatment is 30-60 min at temperatures between 1100 and 1250 °C.

The second use is the one we will focus on.

Many studies have concentrated on MX precipitation, but also on the appropriate content necessary to obtain the best properties. The solubility of the MX precipitates and the stoichiometry are essential in determining the behaviour of the steel with regard to precipitation.

i   Structure and features of precipitation

MX carbonitrides have a NaCl fcc (face-centred cubic) structure, with lattice parameters as listed in table 2.1.

MX	a, Å	reference
NbN	4.39	JCPDS 38-1155
NbC	4.47	JCPDS 38-1364
TiN	4.24	JCPDS 38-1420
TiC	4.33	JCPDS 32-1383

Table 2.1: Lattice parameter of some MX precipitates (JCPDS: Joint Committee of Powder Diffraction Standard).

Often, measured lattice parameters have intermediate values, reflecting the existence of a solid solution between the different carbonitrides.

MX precipitates usually form on dislocations within the matrix, on stacking-faults (most often with TiC), on twin and grain boundaries. They have a characteristic cuboidal shape after sufficient ageing.

ii Solubility of MX carbides in austenite

Stabilisers such as Ti or Nb have long been known to reduce the solubility of carbon in austenite. Early studies of the problem consisted in the determination of two parameters: H, the heat of solution, and A, a constant as in:

$$\log[M][X] = A - \frac{H}{T}$$

where [M] is the weight percent of stabilising element in solution in the matrix, and similarly for [X]. The product [M][X] is often referred to as the solubility product. Strictly speaking, H is expressed in K.

The two following relationships can be found in many publications (e.g. [4, 6]):

$$\log[\text{Ti}][\text{C}] = 2.97 - \frac{6780}{T(\text{K})}$$
$$\log[\text{Nb}][\text{C}] = 4.55 - \frac{9350}{T(\text{K})}$$

They are essentially valid for a typical 18/12 steel, the concentrations are in weight percent. For a 20/25 steel, Kikuchi *et al.* [12] used for TiC H=10475, A=3.42 and for NbC, H=7900 and A=4.92, but it is not clear whether these values have been measured for 20/25. The solubility is, as shown in their work, an important factor in the achievement of good creep properties: they showed that adding M and X in excess of their solubility limits resulted in coarse MX in the matrix and induced faster coarsening of MX which later precipitated. However, until this limit is reached, the more M and X added the better because more MX particles will be formed.

It is therefore clear that knowing the solubility limits of MX carbides is important. However, modern high-temperature austenitic stainless steels often contain both carbon and nitrogen, and more than one strong carbide former (Ti+Nb, Nb+V...), and relationships as above are of limited use when it comes to estimate the solubility of multicomponent carbonitrides (e.g. (Ti,Nb)(C,N)).

Recently, some studies proposed different approaches to the problem of the solubility of multicomponent carbonitrides in austenite [13, 14, 15]. For example, Rios [13] proposed for Nb(C,N):

$$(\%\text{Nb}) \left[(\%\text{C}) / K_C^{1.15} + (\%\text{N}) / K_N^{1.15} \right]^{0.87} = 1$$

where

$$\log \ K_C = \Delta G^\circ_{NbC_{0.87}}/RT$$
$$\log \ K_N = \Delta G^\circ_{NbN_{0.87}}/RT$$

where $\Delta G^\circ_{NbC_{0.87}}$ is the Gibbs energy of formation of $NbC_{0.87}$ with infinite dissolution in the austenite as the reference state. However, one must notice that all these studies deal with MX in austenite for micro-alloyed steels. It seems clear, from the literature, that the presence of Ni and Cr introduces a further difficulty in austenitic stainless steels, the main one being the formation of Z-phase.

There is a general agreement that Z-phase (CrNbN) forms in Nb stabilised austenitic stainless steels, with a sufficient amount of nitrogen. In fact, it seems that as soon as 0.06N wt% is present in a typical 347 steel, Z-phase can be expected [16].

Moreover, in Cr/Ni steels, MX precipitates have been reported to start growing largely under-stoichiometric [17, 18]. No approaches have been found that dealt with the solubility of multicomponent carbonitrides in austenitic stainless steels susceptible of Z-phase formation. Indeed, Z-Phase is even absent from the SGTE (Scientific Group Thermodata Europe) thermodynamic databases accessed by programs such as MT-DATA or Thermocalc.

iii   Formation and stoichiometry of MX precipitates

A number of studies have been devoted to the determination of the correct quantities of M and X to use in order to have the best mechanical properties. As stated above, one factor is the solubility of MX. This has been clearly outlined by the work of Kikuchi *et al.* [12].

The second factor is the proportion of each element that has to be added, in such a way as to maximise the amount of precipitation for a given product [M][X]. It is also important to know, if stoichiometry is not respected, which of the elements is in excess, as this may influence the precipitation sequence.

Wadsworth *et al.* [19] proposed a quantitative approach to stoichiometry and showed that the amount of precipitate that can form drops quite sharply when M and X are not added in proportions corresponding to the composition of the expected carbide (figure 2.1). Using the data of Keown and Pickering [20], they showed that best creep lives were obtained when the Nb/C ratio was matching the stoichiometry Nb_4C_3 (for 18/12 or 18/10).

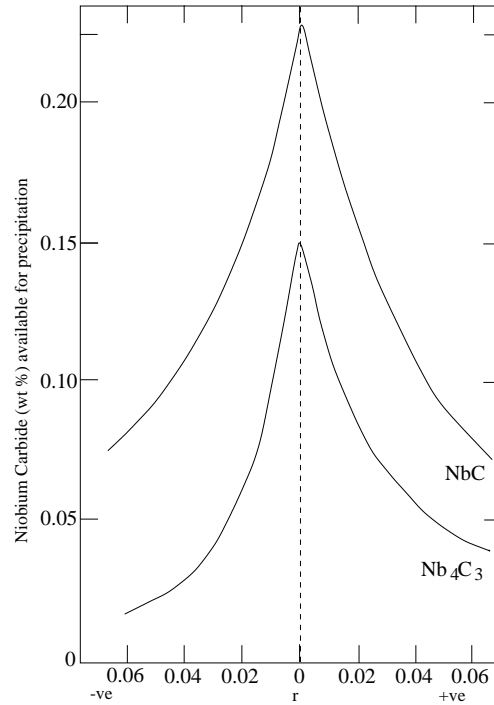Other studies have shown that best creep life in 20/25 alloys was obtained for a Nb/C

Figure 2.1: The amount of niobium carbide available for precipitation at 923 K (after solution treatment at 1373 K) as function of the degree of deviation from stoichiometry r, defined by $r = pB_T - qA_T$, where p and q are the mass fractions of A and B in the compound AB_n, and A_T and B_T the mass fraction of these elements in the alloy. After [19].

atomic ratio of 1/1 [12, 21]. The work done by Kikuchi *et al.* [12] does not highlight any serious contradiction since the first composition they tried around the atomic ratio 1:1 was 2:1, which means that any variation within this interval was not investigated. However, Adamson and Martin [21] have results for the weight ratios 8:1 and 10:1 (respectively atomic ratios 1:1 and 4:3), but find better creep properties for the 1:1 atomic ratio. A possible explanation is that NbC actually forms with the stoichiometry 1:1 in 20/25 steels.

It seems important to note that all these studies rely on relatively short term creep tests (as an average, less than 1000 h). No study has been found which confirms the importance of a stoichiometric addition on long term creep properties. Moreover, this explanation of the good creep properties of steels with stoichiometric additions of M and X assumes that MX precipitates form with their final stoichiometry, which has been proved wrong by different authors, as explained below.

The non-stoichiometry of MX precipitates in 18/12 austenitic stainless steels has been

confirmed by atom-probe analysis [17, 18]. It was noticed that MX was largely sub-stoichiometric for short ageing (typically 3 h at 750 °C), and contained a large amount of Cr substituting for M (Ti,Nb,V...). The following explanation was proposed: as MX has a lattice parameter larger than that of the austenite, a flow of vacancies is needed for the growth of MX and stress is generated. The substitution of M by Cr and the low carbon content both reduce the lattice parameter. Moreover, Cr is readily available while M has to diffuse over long distances. The formation of sub-stoichiometric, carbon-depleted MX precipitates is therefore kinetically advantageous. In more theoretical terms, this corresponds to two effects. Capillarity is likely to modify substantially the local equilibrium as the precipitates are very small. In fact, the composition changes reported in these references correlate with size changes. The second effect is the modification of local equilibrium to satisfy simultaneously the flux balance for different solutes. This could affect strongly the composition of MX, since the diffusivities of the elements involved are very different. It would similarly correlate with a size change unless the precipitates are only coarsening.

However, stoichiometric carbides still have a lower free energy and, during further ageing, they grow at the expense of sub-stoichiometric ones. This is because, according to Andrén *et al.* [17], the diffusivity of metallic elements within MX precipitates is so small that these precipitates can not change composition.

2.1.b   Z-Phase

Z-phase is a complex carbonitride which forms in Nb stabilised austenitic stainless steels containing a relatively high level of nitrogen. It has only recently been discovered, with its structure being fully determined by Jack and Jack in 1972 [22], and it appears from the most recent reviews (e.g. [4]) that the conditions of its formation are not very clear, and even less is its relative stability when compared to other carbonitrides.

i   Structure and composition

The structure of Z-Phase is commonly accepted to be the one described by Jack and Jack [22]: it has a tetragonal unit cell (space group P4/nmm), with a=3.037 Å and c=7.391 Å. The unit cell is obtained by ordering of Cr, Nb and N atoms, the formula being $Cr_2Nb_2N_2$ per unit cell. Vodárek [23] reports the following orientation relationship

for Z-phase in a type 316LN:

$$(001)_Z \parallel (001)_\gamma$$
$$[1\bar{1}0]_Z \parallel [100]_\gamma$$

In contrast to MX precipitates, it seems that Z-phase dissolves little (if at all) substitutional elements. Raghavan *et al.* [24] suggest that it can dissolve carbon and write CrNb(CN), without giving any evidence for this. The absence of a CrNbC phase suggests that if carbon can dissolve in Z-phase, it can only do so within small limits. Also, when Nb is in sufficient quantity, both Z-phase and NbC are found.

ii Occurrence

Z-phase is seldom reported, even in alloys liable to form it on ageing. This could be due to its composition and its general features of formation which are not very different from common MX precipitates.

It generally forms on grain-boundaries, very rapidly, but also on twin boundaries and within the matrix, where it is associated with dislocations [25]. When it forms, it is usually as a fine dispersion of particles [24, 25, 16], which makes it an interesting phase when good creep properties are sought. The morphology has been reported to be either cuboidal [25] or rod-like [17].

There is a good agreement that it forms at high temperatures: Raghavan *et al.* [24] report its formation during annealing (1 h at 1300 K) of a 18/12 containing 0.3Nb wt% and 0.09N wt%, with an orientation relationship indicating precipitation in the solid state. After ageing 8000 h at 866 K, it is still the predominant precipitate. Few $M_{23}C_6$ and σ-phase particles are present. These authors indicate that a 10 s heat-treatment at 1573 K is sufficient to dissolve all the Z-phase particles, which is not inconsistent with the work of Robinson *et al.* (quoted in [24]) which locates the solvus of Z-phase to be between 1573 K and 1623 K in a steel containing larger amounts of niobium and nitrogen.

Robinson and Jack [25] report the formation of Z-phase in a 20Cr/9Ni steel containing 0.38N wt% and 0.27Nb wt% between 700 and 1000 °C. At 1000 °C Z-phase is the first and only phase formed. It is found uniformly distributed after 30 min but coarsens rapidly. At 700 °C it starts to precipitate in the matrix after 16 h. At lower temperatures, Vodárek *et al.* [26] report a considerable dimensional stability of Z-phase in a type 316LN, with a mean size of 6 nm after 82 h at 650 °C and 12 nm after 37890 h at the same temperature.

Thorvaldsson and Dunlop [27], studying the effects of stabilising elements in austenitic stainless steels, used a 18/12 steel with 0.4V, 0.13Nb and 0.43N at%. After 5000 h at 750 °C, no Z-phase had formed, but a (Nb,V)(C,N) fcc carbonitride formed instead. Andrén *et al.* [17], with a steel of the same composition, in very similar conditions, found, on the contrary, that the MX precipitate had always a stoichiometry not far from $MX_{0.5}$, and contained sensibly as much chromium as Nb+V. However, the characteristic tetragonality was not observed and the authors suggested that they found a precursor state of the fully ordered Z-phase.

iii   Considerations on the stability of Z-phase

It seems quite reasonable to propose that Z-phase is the stable Nb containing phase in austenitic stainless steels with high nitrogen: Hughes [16] suggests that it can be expected in a typical 347 steel as soon as the weight percentage of N is greater than 0.06. Knowles [28] finds Z-phase in a 20/25 0.41Nb wt% steel with 0.028N wt%, which could indicate that chromium and/or nickel content play an important role in the solubility of this phase.

The problem arises, in many steels, to know whether NbC or Z-phase is the more stable. Very few studies have dealt with additions of Nb, C and N together in a way that could determine which phase is more stable: often Nb is in excess and both NbC and CrNbN form. Uno *et al.* [29] found that only Z-phase formed in a 18/12 Nb steel with carbon and nitrogen, the niobium content being lower than that required to combine either all C or all N. This would indicate that Z-phase is fast enough to form first when competition between NbC and CrNbN is likely to occur. On the other hand, Knowles [28] reported Nb(C,N) after 2 h at 850 °C in a 20/25 steel, transforming to Z-phase with further ageing. From the precipitation behaviour of NF709 [7], where Z-phase is reported after ageing times of 10^4 h at 750 °C, and C containing phases are $M_{23}C_6$ and M_6C one can infer that Z-phase is more stable than NbC and that the latter will dissolve for the former if Nb is in too small quantities. However, Raghavan *et al.* [24] deduce from a comparison between 347 (18/12 with 0.8Nb and 0.07C wt%) and 347AP (18/12 with 0.3Nb, 0.09N, 0.009C wt%) a greater stability of NbC, since Z is found to precipitate from the solid state but the NbC is found as residual particles. The conclusions of such a comparison have to be examined carefully as the compositions were different.

iv Conclusions on Z-phase

Generally, one can conclude that Z-phase precipitation is not fully understood. Points of agreement are its stability at high temperature and the features of its precipitation (fine dispersion). Proposed solvus temperatures differ between the various studies, but these differences are consistent with different compositions. It is difficult as yet to build a coherent view of the different kinetics observed. It is not clear whether Z-phase actually forms from MX precipitates as suggested by the results of Knowles [28] and Andrén *et al.* [17], or directly as suggested by Robinson *et al.* [25]. These observations could be reconciled if one could prove that the driving force for the formation of Z-phase in a 20Cr 10Ni (Robinson *et al.*) is significantly different than that in a 18/12. The importance of Z-phase in both ferritic and austenitic power plant steels, renders particularly necessary the assessment of the ternary system Cr, Nb, N to provide the thermodynamic parameters required for any prediction.

2.1.c $M_{23}C_6$

i Structure and composition

$M_{23}C_6$ is a more general notation for $Cr_{23}C_6$, as often, Ni, Mo and Fe are found to substitute partially for chromium. It is the main carbide in non-stabilised C-containing austenitic stainless steels; nitrogen bearing steels form Cr_2N. It has a fcc structure (and space group Fm3m) of lattice parameter varying between 10.57 and 10.68 Å, which is about three times that of the austenite. It is often reported to grow with a cube to cube orientation relationship:

$$\{100\}_\gamma \parallel \{100\}_{M_{23}C_6}$$
$$\langle 010 \rangle_\gamma \parallel \langle 010 \rangle_{M_{23}C_6}$$

It is most of the time the main carbide found in austenitic stainless steels. Although it can be only metastable, it is always found in the early stage of precipitation because it nucleates very easily.

ii Morphologies and locations

$M_{23}C_6$ is most of the time reported to precipitate on the following nucleation sites, and in this order: grain boundaries, incoherent and coherent twin boundaries, intragranular sites. In Nb stabilised grades, it is sometimes reported to nucleate on undissolved (that

is, during the solution treatment) niobium carbonitrides. Generally, $M_{23}C_6$ only shows {111} and {110} interface planes. This has been explained by Beckitt and Clarck [30], who showed these planes have the best atomic correspondence with the austenite.

Precipitation on grain boundaries The precipitation of $M_{23}C_6$ has been the focus of many investigations, motivated by its importance in terms of corrosion resistance. $M_{23}C_6$ on grain boundaries is often associated with intergranular corrosion. It is found after very short ageing times (30 min at 750 °C, [31]), even in stabilised steels. It causes the grain boundary to move, and therefore shows on one side, the new grain boundary, while the other has a serrated aspect composed by the {111} interfaces. These precipitates are usually large. When boron is added, the number density of $M_{23}C_6$ particles along the grain boundaries increases [32], with beneficial effect for the creep rupture strength, as the grain boundary sliding and surface cracking are reduced. Other effects of boron in $M_{23}C_6$ will be dealt with later.
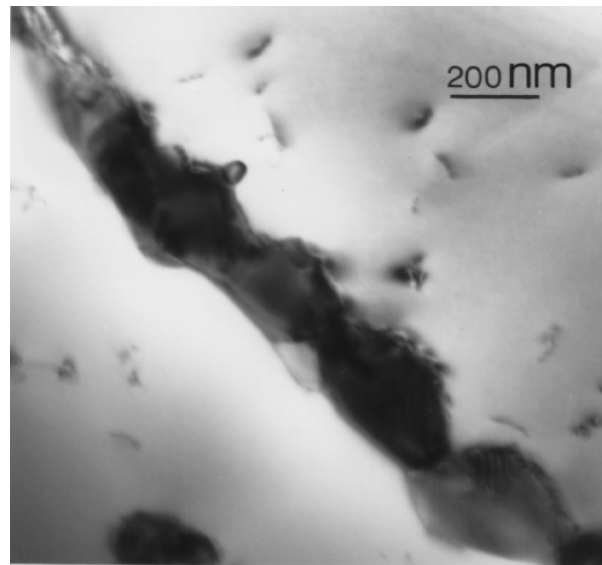

Figure 2.2: $M_{23}C_6$ on grain boundary.

Precipitation on incoherent and coherent twin boundaries On incoherent and coherent twin boundaries, $M_{23}C_6$ forms long plates parallel to the twin boundaries. The plates are, as for any form of $M_{23}C_6$ in austenitic stainless steels, bounded by {110} and {111} planes only. The large faces are {111} planes parallel to the twin boundaries.

Plates are initially growing from the incoherent twin boundary, but some are found later apparently detached from the boundary. Precipitation on the coherent boundary occurs more slowly than on incoherent ones. The mechanism of their formation has been subject
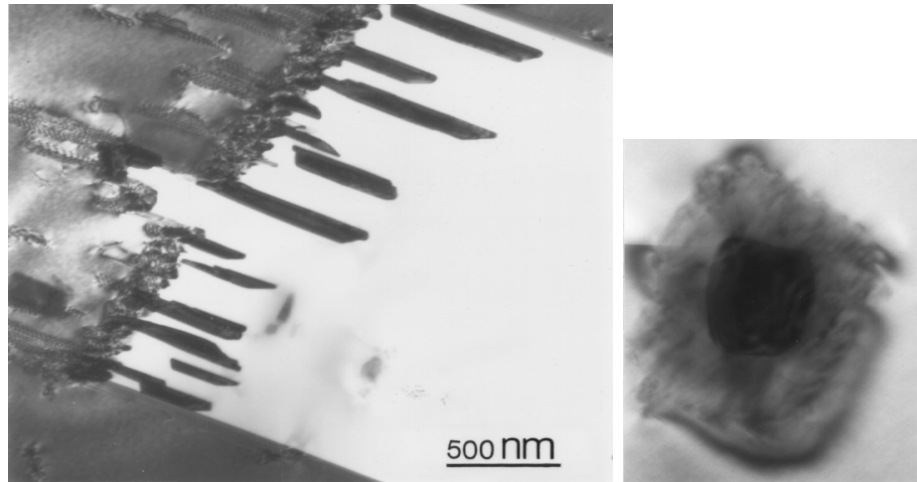

Figure 2.3: Plates of $M_{23}C_6$ growing from an incoherent twin boundary (left), and around a Nb(C,N) precipitate (right), work done for this project.

to controversy: Beckitt and Clarck [30] suggested that carbides growing on the incoherent twin boundary repel Shockley partial dislocations in the twin, and these cause nucleation of new plates in the twin. But detailed observations have lead Singhal and Martin [33] to conclude that stacking faults were first growing in the twin. $M_{23}C_6$ would then nucleate on the Shockley bounding dislocation and grow in the stacking fault, possibly helped by an enrichment of this stacking fault in chromium. Both fail to explain why these plates most of the time stand separated from the boundary and from each other (according to these mechanisms, they should be connected to the incoherent twin boundary by a stacking fault). Another mechanism has been proposed more recently by Sasmal [34]). Noticing that plates do not form away from the boundary or on coherent twin boundaries if the samples are directly put at ageing temperature after the solution treatment, Sasmal suggested that the formation of plates of $M_{23}C_6$ close but detached from the incoherent twin boundaries, and on coherent ones, was an effect of residual stress developed in these regions. One could here argue that stress only influences the formation: if it favours the formation of $M_{23}C_6$ plates parallel to the twin boundaries, there should still be a small percentage of plates growing in other equivalent directions.

Intragranular precipitation   In the austenite grains, $M_{23}C_6$ precipitates as cuboids or plates. The latter have the same characteristics as the plates growing from twin boundaries. The cuboids grow on dislocations until they form a continuous chain sharing their corner. These chains can form branches, forming secondary stringers of $M_{23}C_6$. Beckitt and Clarck [30] have proposed a satisfactory explanation for the formation of these secondary stringers: the growth of primary $M_{23}C_6$ generates dislocations on which further precipitation can occur. The direction of these secondary stringers is that expected by the mechanism, that is the direction of usual edge dislocations in austenite.

Another kind of intragranular precipitation has been reported by Sasmal [35]. Plates of $M_{23}C_6$ can form around undissolved Nb carbonitrides in Nb stabilised steels. In this case, the large faces are {110} and the edges are {111}. The reasons for this change are not clear, although a contribution of the strain around the undissolved particle is invoked.

iii   Role of other alloying elements

$M_{23}C_6$ is, initially, a chromium-iron carbide. However, its composition is susceptible to large variations. For example, in a typical 2.25Cr1Mo wt% steel, $M_{23}C_6$ has a composition of about 0.3Fe, 0.38Cr, 0.1Mo, 0.22C mole fraction (calculated with MT-DATA), while in a typical 304 it is closer to 0.04Fe, 0.65Cr, 0.11Mo, 0.22C. There is also evidence that, for a given steel composition, $M_{23}C_6$ composition undergoes large changes in the early stages of the precipitation. Lewis and Hattersley [31] quote a study by Philibert *et al.* in which the authors propose that M_7C_3 forms in the early stages of ageing in a 18/8 steel, as the Fe/Cr ratio is more consistent with the known composition of this phase. Similarly, Marshall [5] quotes a study in which the authors show that up to 40 wt% Fe can be found in $M_{23}C_6$ in the early stages of precipitation, and that the Mo content also increases with time. It is proposed here that these composition changes can be explained by the growth mechanism involved. In a multicomponent alloy, the interface has to move at a rate which is consistent with the flux of each element, in order to maintain local equilibrium. Therefore, the interfacial compositions are not in general given by a tie-line passing through the bulk composition, but by an alternative tie-line which permits the flux-balance (details are out of the scope of this review, see for example [36] or [37]).

In the same way, on the interstitial lattice, B can substitute for C; however in very small quantities. Boron is of particular interest as it promotes the formation of intragranular $M_{23}(C, B)_6$. There is some controversy about the mechanism involved, but it is possible

that B increases the lattice parameter of $M_{23}C_6$, therefore reducing the mismatch with the austenite. The presence of B in $M_{23}C_6$ has been shown using atom probe field ion microscopy (APFIM, e.g. [38]). The same is not true for nitrogen. It has long been believed to have a small solubility in $M_{23}C_6$ (e.g. [39]). However, recent experimental results supported by *ab initio* calculations indicate zero solubility of nitrogen in $M_{23}C_6$, the structure of which is destabilised if a small amount of carbon is replaced by nitrogen [10].

Except in the fine intragranular form, $M_{23}C_6$ precipitation is not desirable for good creep properties. It is often associated with intergranular corrosion, as its formation along the grain boundaries causes a local depletion in chromium and possibly local loss of the stainless property (the steel is then said to be sensitised, *i.e.* susceptible to intergranular corrosion).

iv   Solubility and kinetics of precipitation

The solubility of carbon in austenite, with regard to $M_{23}C_6$, has been described by empirical relationships such as [40]:

$$\log \left[C\right]_{\text{ppm}} = 7.71 - \frac{6272}{T(\text{K})}$$

As can be seen in figure 2.4, this is valid for a typical 18/12 steel, but one should be careful as it is sensibly modified by the chromium and nickel content. Increasing the chromium content reduces the solubility of carbon in austenite. It also increases the kinetics of $M_{23}C_6$ precipitation, as does an increase in carbon content: from 0.02 to 0.08C wt%, the nose of the C-curve is shifted from 100 h to 0.1 h.

$M_{23}C_6$ first precipitates on grain boundaries, then, with increasing time, on incoherent twin boundaries, coherent twin boundaries and finally in the matrix on dislocations. In the matrix, it forms as evenly spaced angular blocks. At long ageing times, grain boundary carbides can form a completely interlocked structure.

The kinetics of precipitation are affected by Mo, which stabilises the carbide and accelerates its formation. On the other hand, nitrogen is well-known to retard both the formation and coarsening rates of $M_{23}C_6$, and an often proposed explanation is that nitrogen reduces the diffusivity of Cr and C in the austenite [6], [12]. However, Degalaix and Foct [41] found that if the carbon content was higher than 0.08 wt%, increasing the nitrogen content could have the opposite effect. More recent investigations indicate that
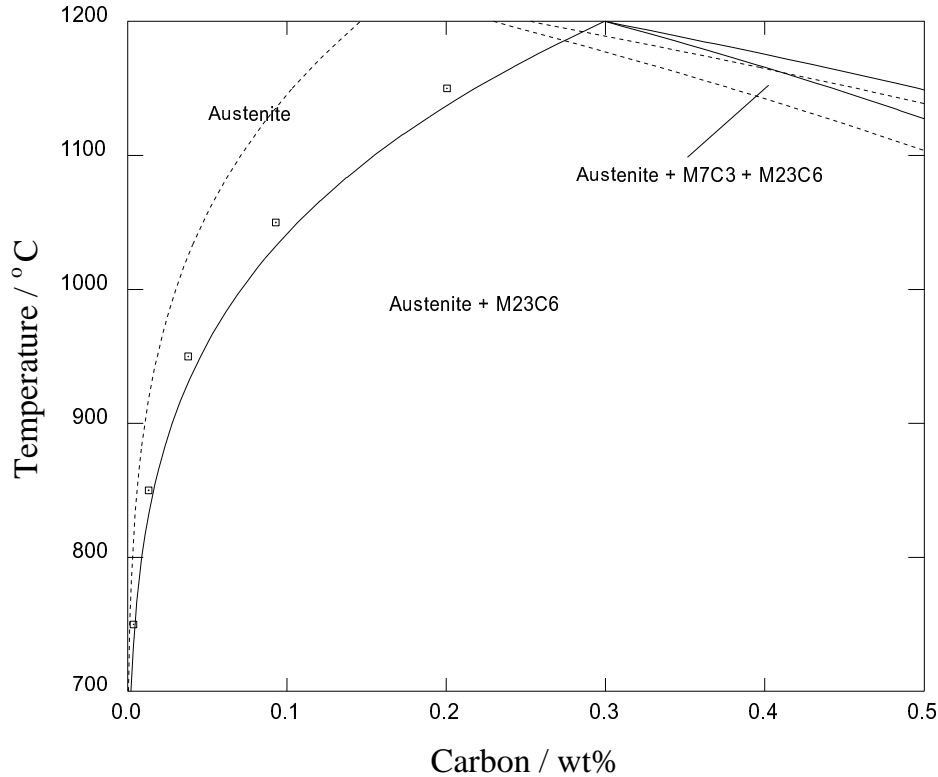
Figure 2.4: Solubility of C in austenite with regard to $M_{23}C_6$ precipitation. Calculated with MT-DATA (allowing for austenite, $M_{23}C_6$, M_7C_3 and liquid, with elements Fe, Cr, Ni, 0.3Si, 1.0Mn wt%). Solid lines for 18/12 and dashed lines for 20/25. The squares correspond to the empirical relationship from [40].

N actually enhances the diffusion of substitutional elements by increasing the formation of vacancies, but delays the nucleation of $M_{23}C_6$, the structure of which is destabilised when carbon is partially substituted by nitrogen [10].

v *Relative stability of* $\mathbf{M_{23}C_6}$

In a simple type 304 steel, $M_{23}C_6$ is often the only carbide found at any ageing time. Although sometimes M_6C is found [42], it is as a minor phase and no mention is made of an instability of $M_{23}C_6$ with regard to M_6C. When molybdenum is added (type 316), $M_{23}C_6$ can partially transform to M_6C (see further); it is however always reported that $M_{23}C_6$ remains the main carbide even after long ageing. In fact, $M_{23}C_6$ and M_6C also coexist in the X5CrNiMo1713 (17Cr, 13Cr, 5Mo wt%) studied by Thier *et al.* [43]. This is not the case when niobium is involved in the formation of M_6C, which seems then more

stable and becomes the dominant carbide at long ageing times [44].

In stabilised grades, the situation is much more complex: from the literature found, it is not possible to state clearly whether $M_{23}C_6$ is sometimes first formed or always follows MX precipitation, nor which phase is the more stable on long term ageing.

Thorvaldsson and Dunlop [27, 45, 46], studying the effect of different stabilising elements and their combinations, found that $M_{23}C_6$ was more stable than TiC, but less than NbC. This is consistent with Grot and Spruiell [47], who found formation of $M_{23}C_6$ in a type 321 after long term ageing, and with Kikuchi *et al.* [12] for a 20/25. These authors concluded that TiC retards the precipitation of $M_{23}C_6$ but does not suppress it.

On the other hand, Bentley and Leitnaker [48], studying a type 321 steel having been in service for 17 years at 600 °C did not find any $M_{23}C_6$ and concluded that TiC was more stable. Lai [49] observed no $M_{23}C_6$ in a type 321 used up to rupture (16000-29000 h at 600 °C).

Obviously, considerations of the relative stabilities of the two phases only make sense if the titanium content is enough to combine all carbon present, as in the opposite case, $M_{23}C_6$ forms with the excess carbon. The studies in which $M_{23}C_6$ formation appears as an anomaly deal with steels in which Ti content is higher or equal than that required for full stabilisation.

The agreement is better for NbC, which is more stable than $M_{23}C_6$. However, $M_{23}C_6$ can form as a transient phase.

2.1.d M_6C

M_6C is also known as η-carbide, but will be referred to as M_6C to avoid confusion with η-phase (Laves phase). It generally refers to a phase of very variable composition. In most cases, it is formed only after long ageing times, and therefore is quite little documented. Moreover, its appearance and disappearance are strongly linked to that of other constituents and it is difficult to give it any absolute position in a TTP (Time Temperature Precipitation) diagram.

i   *Structure and composition*

M_6C is a diamond-type fcc carbide whose lattice parameter varies between 10.95 and 11.28 Å. Its space group is Fd3m, which distinguishes it from $M_{23}C_6$ and G-phase which both are fcc of similar lattice parameters, but have a Fm3m space group. The η-carbide

structure is described by Stadelmaier [50]. This structure encompasses a wide range of compositions and only the ones which are commonly found in creep- resistant austenitic stainless steels will be reviewed here.

M_6C composition can be molybdenum-rich $((FeCr)_{21}Mo_3C_6)$ or niobium-rich (Fe_3Nb_3C). The molybdenum rich Fe_3Mo_3C (a=11.11 Å) was reported in high Mo steels, but never in austenitic steels [51]. Instead, a fraction of molybdenum is replaced by iron or chromium, and the lattice parameter is reduced (a=10.95 Å) [51]. The composition reported by Brun *et al.* [52] in a 316 steel containing Ti shows substantial amounts of Ni also dissolving in M_6C (see table 2.2).

Element	Si	Mo	Ti	Cr	Mn	Fe	Ni
at%	4.5	6.5	0.8	30	0.5	26.7	31

Table 2.2: Composition of M_6C as measured by Brun *et al.* in a 316 steel containing titanium.

Silicon has been reported to dissolve in this phase to form M_5SiC, but such a phase is very seldom found. Other elements which can be included in the general notation M are Ni, Ti, Co. In NF-709 (a 20/25 Nb stabilised, with 0.17N wt%), long-term ageing allows formation of Cr_3Ni_2SiC; such a composition has been reported by Williams *et al.* in a study of irradiated type 316 [53] and by Titchmarsh *et al.* in a similar steel [54], at rather low temperatures (466 °C) but not above 670 °C. Its formation in such steels is linked with the segregation effects caused by irradiation, in particular the Si segregation to point defect sinks. This particular composition has a lattice parameter of 10.62 Å (JCPDS 17-330), which makes it extremely similar to $M_{23}C_6$ from a structural point of view. Although always referred to as Cr_3Ni_2SiC, its actual composition includes substantial amounts of Mo and Fe (see table 2.3), the concentrations of which increase with temperature [53]. Williams [53] therefore proposed the more general formula $(Cr, Mo)_3(Ni, Fe)_2SiC$.

Temperature	Cr	Mo	Si	Ni	Fe
500 °C	35	11	20	24	10
600 °C	32	15	20	24	10

Table 2.3: Some compositions (at%) of Cr_3Ni_2SiC in irradiated 316, from [53].

Jargelius-Peterson [55] found a nitrogen rich similar phase (Cr_3Ni_2SiN) after furnace ageing of a 20Cr25Ni5Mo0.2N steel. It is reported after 5 h and 3000 h at 850 °C,

therefore being probably an equilibrium phase. In agreement with the observation that the Mo content increases with temperature, the composition found here includes as much as 25 wt% Mo (this is also due to the larger Mo content of the alloy).

ii   Occurrence and stability

Mo rich compositions

In a type 316 steel, the composition of M_6C is close to $(FeCr)_{21}Mo_3C_6$. Weiss and Stickler [51] proposed that it is formed as follows:

$$M_{23}C_6 \longrightarrow (FeCr)_{21}Mo_3C_6 \longrightarrow M_6C$$
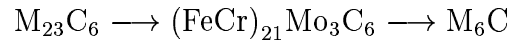
It is not reported by Minami *et al.* [44] after 10000 h at 750 °C (instead, χ-phase is found), neither by Lai and Meshkat [56] after 10000 h at 600 and 650 °C, nor by Barcik [57] for the same time, up to 900 °C. However, it was found by Stoter [58] in a specimen of 316 having been in service at 650 °C for 28000 and 60000 h, in very small amounts and always associated with $M_{23}C_6$.

Nitrogen seems to have a large influence on M_6C formation: Thier *et al.* [43] did not find this carbide after 1000 h in a type 316 with 0.037N wt%, but found it after only 1 h ageing at 900 °C when the nitrogen content was 0.069 wt%. Gavriljuk and Berns [10] suggest that the calculations performed by Jargelius-Petterson [59] raise controversy, as she shows that an increase of nitrogen in a 20Cr, 25Ni, 4.5Mo wt% steel reduces the driving force for M_6C. However, one must notice that M_6C is quite poorly described in the SGTE databases, as it only contains information about the Mo-rich carbide, that is to say it describes only one of the possible compositions of the η-structure. In this regard, it is possible to say that the η-structure is in both cases stabilised but with different compositions. In particular, Jargelius-Petterson [59] reports that M_5SiN is always present and favoured by high nitrogen contents. It seems therefore that nitrogen generally stabilises the η-structure, but the composition of this phase varies with the alloy.
In type 321 (Ti-stabilised), none of the studies found reports M_6C.

Nb-rich compositions

In type 347, on the contrary, the presence of Nb seems to promote the formation of a niobium rich M_6C. Care should be taken as Powell *et al.* [60] have given sensible arguments showing that G-phase and M_6C had often been mistaken. However, if the structures are very similar, the composition should differentiate clearly Fe_3Nb_3C or Cr_3Ni_2SiC (as

in NF709) from $Ni_{16}Nb_6Si_7$. The experimental methods must be linked with the results of the different studies. In general, Nb-rich M_6C seems to form only on long-term ageing. Kikuchi *et al.* [12] do not report it after 1000 h at 700 °C in a 20/25. In a 18/8 steel, it is reported between 600 and 800 °C by Minami *et al.* [44] at very long time ($\sim$50000 h) for 600 °C but faster ($\sim$2000 h) for 800 °C. They proposed a sequence illustrated in figure 2.5. This mechanism implies excess of Nb is present. If Nb is less than that required for
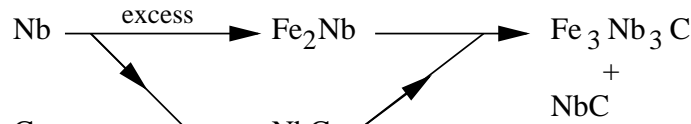

Figure 2.5: Precipitation sequence leading to M_6C when Nb is in excess, as proposed by Minami *et al.* in [61]

combination of all carbon, no such phase is observed (steel Tempaloy A1 in [44], similar to a 304 with 0.13Nb, 0.06Ti, 0.07C wt%)

In 20/25 alloys, as written above, M_6C and G-phase have probably been often mistaken (e.g. [62]) in early studies where identification relied on X-ray or electron diffraction only. It is difficult to conclude which phase forms preferentially: Ramaswamy *et al.* [63] report M_6C in a 20/25 with low Si content (0.03 wt%), but other studies report G-phase (Si content 0.4-0.7 wt%).

When nitrogen is present (in 347 or in 20/25) in sufficient quantities, Z-phase forms and it is difficult to have an idea of its stability with regard to M_6C.

Cr_3Ni_2SiX and G-Phase

G-phase, which is considered further, is an alternative Si-rich phase to Cr_3Ni_2SiC. As mentioned above, the composition Cr_3Ni_2SiC is very seldom reported in the literature. Titchmarsh and Williams have reported its formation in irradiated steels of composition close to that of 316 with addition of 1.8wt% Nb. They noted [54] and provided evidence [64] that G-phase formed preferentially only when carbon was not available.

In 20/25-Nb-C steels though, Powell *et al.* [60, 65], and Ecob *et al.* [66] have found G-phase and observed that NbC partially transforms to G-phase with time. It seems reasonable to propose that in 20/25, G-phase is stabilised with regard to Cr_3Ni_2SiC, probably because of the larger Ni content.

However, in NF709 [7] (composition in table 1.1), Cr_3Ni_2SiC is reported. This is inconsistent with the studies quoted above which seem to indicate G-phase as a more stable phase. It is not clear however whether the presence of carbon or nitrogen was investigated or the composition Cr_3Ni_2SiC assumed. Investigations of the exact nature of this precipitate are required to determine whether it is a nitride or a carbide. A nitride would be expected as it would not be incoherent with the former observations that G-phase is more stable than Cr_3Ni_2SiC and that the η-structure is stabilised by nitrogen.

2.2 Intermetallic phases

2.2.a Sigma phase

σ-phase is a well-known intermetallic phase which forms in the Fe-Cr system, with a composition FeCr. In highly alloyed steels, its composition is variable. Its precipitation is associated with embrittlement. In creep resistant steels, it has a detrimental effect on creep properties when precipitated on grain boundaries, but little effect when it precipitates intragranularly.

i Structure and Composition

σ-phase has a tetragonal unit cell (space group $P4_2/mnm$) with a=8.80 Å and c=4.54 Å (FeCr). This unit cell contains 30 atoms. Reported orientation relationships are [6]:

$$(111)_\gamma \parallel (001)_\sigma$$
$$\left(0\bar{1}1\right)_\gamma \parallel (140)_\sigma$$
$$\text{or}$$
$$(111)_\gamma \parallel (001)_\sigma$$
$$\left(\bar{1}10\right)_\gamma \parallel \left(\bar{1}10\right)_\sigma$$

The composition varies quite widely and it is difficult to give a formula. For example, Jargelius-Petterson [59] reports the following range of composition for σ-phase in a 20/25 with Mo content varying between 4.5 and 6.0 wt%:

Element	Si	Cr	Mn	Fe	Ni	Mo
wt%	0-1	27-32	1-9	35-43	8-15	10-16

for a type 316 [39], a typical composition is (other elements not given):

Element	Fe	Cr	Mo
wt%	44	29.2	8.3

ii   Occurrence

An in-depth review of σ-phase precipitation in Cr-Ni austenitic steels has been done by Barcik [67]. σ-phase precipitates first on triple points then on grain faces. After long term ageing at high temperature, it also forms on incoherent twin boundaries and intragranular inclusions. The mechanism of nucleation is still a matter of controversy, particularly on the role of δ-ferrite and $M_{23}C_6$ in the nucleation process. Studies have reported its formation associated with the dissolution of $M_{23}C_6$, but also independently [6]. It is found in most of the grades of austenitic stainless steels: type 304, 316 (Mo), 321 (Ti stabilised) and 347 (Nb stabilised) (e.g. [44]). However, it forms after different times. The 25Cr-20Ni steels can exhibit as much as 20 wt% of σ-phase.
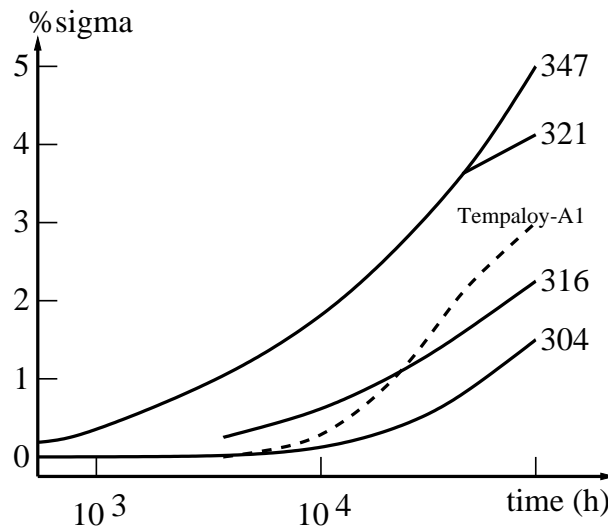

Figure 2.6: Precipitation of σ-phase in different grades of austenitic stainless steels. Tempaloy-A1 is an 18/10 with a Nb/C ratio of 1.86, whereas the 347 has a ratio of 17.40. The percentage is the area etched by KOH. After [44].

In stabilised grades, its formation is faster than in other grades: Minami *et al.* [44] report precipitation of σ-phase after 1000 h at 700 °C in 347 and 321 (347 precipitating σ-phase slightly faster than 321). In 304, 316 and Tempaloy-A1, σ-phase is found in significant quantities only after 10000 h (fig 2.6). It is worth noting that Tempaloy-A1 is Nb stabilised, but with a Nb/C ratio of 1.86, while this ratio is 17.40 in the 347. This

correlates well with the fact that σ-phase forms when the carbon content falls below a critical value and the chromium equivalent is higher than 18 wt%. In the 347 steel, almost all the carbon is rapidly precipitated as NbC, while the low Nb content of Tempaloy-A1 leaves some carbon in solution. The different trend for 321 could be linked to the instability of TiC with regard to $M_{23}C_6$. The precipitation of $M_{23}C_6$ lowers both the carbon and the chromium content. The results of Grot and Spruiell [47] show on the contrary no σ-phase forming up to 2000 h in a type 321. σ-phase is also found in 20/25 (fig 2.7). Different factors affect the formation of σ-phase. Elements like Cr, Nb, Ti or Mo are known to promote σ-phase formation. Silicon promotes and accelerates its formation. In general, the formation of σ-phase in austenite is about 100 times slower than in ferrite. Consequently, the presence of δ-ferrite accelerates σ-phase precipitation. [67]

A method has been developed by Woodyatt *et al.* [6] to estimate the σ-forming tendency of an alloy, based on the electron vacancy number $\overline{N}_v$:

$$\begin{aligned}
\overline{N}_v \quad &= \quad 0.66\text{Ni} + 1.71\text{Co} + 2.66\text{Fe} + 4.66(\text{Cr} + \text{Mo} + \text{W}) \\
&\quad + 5.66\text{V} + 6.66\text{Zr} + 10.66\text{Nb} \quad \text{at\%}
\end{aligned}$$

If $\overline{N}_v$ is higher than 2.52, the alloy should form σ-phase.

2.2.b   Laves phase

Laves phase is found in various grades of austenitic stainless steels. It is often a minor constituent. It precipitates intragranularly in the form of equiaxed particles, occasionally on grain boundaries [51]. Whether Laves phase has a detrimental effect or not on creep properties is still discussed. In niobium stabilised steels however, it is likely that Laves phase are detrimental because they allow formation of M_6C (see below).

   i   Structure and composition

Laves phase is a hexagonal phase of space group P6$_3$/*mmc*, with a=4.73 Å and c=7.72 Å. The main factor determining its formation being the relative atomic size of the constituent atoms, the ranges of composition are quite small. Jargelius-Petterson [59] measured the following composition for Laves phase in a 20/25 with 5Mo wt%:

After 10 min at 850 °C					
Element	Fe	Mo	Cr	Ni	Mn	Si
wt%	29 ± 2	36 ± 2	19 ± 2	13 ± 1	1.5 ± 0.8	1.8 ± 0.5
After 3000 h at 850 °C					
wt%	37 ± 1	35 ± 1	12 ± 1	14 ± 1	~ 0	0.7 ± 0.2

This shows that Laves phase probably does not form at its exact equilibrium composition. In stabilised grades, Fe_2Nb or Fe_2Ti (more seldom) can form.

Denham *et al.* [68] proposed for Fe_2Nb the following orientation relationships:

$$(0001)_{Fe_2Nb} \parallel (111)_{\gamma}$$
$$(10\bar{1}0)_{Fe_2Nb} \parallel (\bar{1}10)_{\gamma}$$

ii   Occurrence

In type 304, Laves phase is not found, due to the absence of Mo, Nb or Ti. In type 316, which contains typically 2-2.5Mo wt%, it is found after relatively long ageing times: Minami *et al.* [44] report its formation after a minimum of 1000 h, between 625 and 800 °C. The experimental results of Lai [69] are in agreement with the dissolution of Fe_2Mo above 800 °C. Coherently, White and Le May [70] do not report any Laves phase precipitation between 640 and 800 °C for ageing times up to 900 h. Weiss and Stickler [51] report a slightly higher maximum temperature for Laves precipitation in type 316 as they found it up to 815 °C. Its formation interacts in a competitive way with that of σ and χ phases. For example, the presence of δ-ferrite delays its formation because it enhances that of σ and χ phases.

In titanium stabilised grades, the formation of Fe_2Ti is never reported in compositions similar to that of a 321 steel. Minami *et al.* do not report it for ageing times up to 50000 h between 600 and 750 °C, in a type 321. However, it is found by Beattie and Hagel [71] in a A286 type alloy, containing 16Cr, 26Ni and 1.8Ti wt%, after 1000 h at 815 °C. This is directly related to the large amount of Ti used in such steels compared to a typical 321.

In niobium stabilised steels, Fe_2Nb is frequently reported after long ageing times, but as a transient phase which disappears for Fe_3Nb_3C. It is reported to form in a type 347 with 0.87Nb and 0.05C wt%, after 1000 h between 650 and 800 °C, and disappear after 5000-10000 h [44]. However, its formation is dependent on the availability of niobium. In the same study, the steel Tempaloy-A1 (18/10 with 0.13Nb for 0.07C wt%) does not

precipitate Laves phase after ageing treatments up to 25000 h. Instead, only NbC is found (figure 2.5). The same results are reported by Raghavan *et al.* [24], who found NbC and Laves phase in a type 347 with 0.8Nb and 0.07C wt% (8000 h at ~600 °C), but only Z-phase in a modified 347 with 0.3Nb and 0.09N wt%. It is therefore probable that both NbC and Z-phase are more stable than Fe_2Nb.

2.2.c χ phase

χ phase is most of the time a minor intermetallic phase. It is mainly found in type 316 above 750 °C

i *Structure and composition*

χ phase is a bcc (body-centred cubic) phase of space group $I\overline{1}\overline{4}3m$. The unit cell contains 58 atoms and has a lattice parameter varying between 8.807 and 8.878 Å.

A typical composition is $Fe_{36}Cr_{12}Mo_{10}$ but the phase has a high tolerance for metal interchanges. The structure has large holes which allow presence of carbon, sometimes making this phase better described as a $M_{18}C$ carbide. It nucleates on grain boundaries, incoherent twin boundaries but also intragranularly on dislocations.

ii *Occurrence*

Although it is sometimes (but seldom) present in very small quantities in 321 [47], χ phase is only a significant phase in type 316, when the ageing temperature is high enough. For example, it is reported by Minami *et al.* for times up to 25000 h and temperatures between 700 and 850 °C, and by Lai *et al.*, as being the main phase with σ-phase between 715-850 °C for times up to 5000 h, but not by Stoter [58] after 28000 and 60000 h at 650 °C.

2.2.d G-phase

G-phase is a silicide forming in austenitic stainless steels stabilised with Ti or Nb. It has been first reported by Beattie and Versnyder in 1956, in a A286 type steel, that is, a precipitation-hardening 26Ni-15Cr with variable (0 to 2.3wt %) Ti and Al contents. It has long been believed to form only under irradiation in steels of the 300 series and in 20/25 steels. However, Powell *et al.* showed, in 1985 [60] that it formed under normal ageing in 20/25 Nb stabilised alloys, in the temperature range 500-850 °C, and suggested that it had been identified as M_6C in earlier studies of the same steel.

i   Structure and composition

G-phase has a general formula $A_{16}D_6C_7$ where A and D are transition elements, and C a group IV element [66]. A is usually nickel, D niobium [60, 65, 66] or titanium [49]. Ecob *et al.* [66] mentioned the possibility of substitution, in small quantities, of D (*ie* Nb or Ti) by Fe or Cr, and Powell *et al.* [60] measured the following composition:

Element	Ni	Nb	Si	Fe	Cr
wt%	51	29	14	4.5	1.5

Table 2.4: Composition of G-phase measured in [60]

Lai found a titanium-containing G-phase in a type 321 steel, and gives a composition sensibly richer in nickel (table 2.5). Note that none of these compositions clearly shows

Element	Ni	Ti	Si	Fe	Cr
wt%	63.3	20.9	12.2	3.47	0.13

Table 2.5: Composition of G-phase measured in [49]

substitution of D when trying to match the stoichiometric formula.

G-phase has a fcc structure with a lattice parameter of 11.2 Å, this corresponds to a content of 116 atoms per unit cell. The space group for this structure is Fm3m. It is remarkable that the lattice parameter seems to be the same for $Ni_{16}Nb_6Si_7$ [60, 65] and $Ni_{16}Ti_6Si_7$ [49, 71]. In a earlier study, Sumerling *et al.* [62], studying a 20/25 Nb stabilised steel, found a lattice parameter of 11.25 ± 0.05 Å for a phase they identified as M_6C.

As mentioned before, Powell *et al.* have suggested that G-phase was identified as M_6C in early works on 20/25 Nb steels, because of close compositions and structures. A detailed investigation of the structure is sufficient to solve the problem [66], but additional evidence has been sought by the use of EELS (Electron Energy Loss Spectroscopy) (as in [60]) or a wavelength-dispersive crystal spectrometer in SEM (as in [49]), both techniques making possible quantitative measurements of light elements (C,N). These studies have confirmed the absence of interstitial elements in G-phase.

ii   Occurrence of G-phase in austenitic stainless steels

The general features of G-phase formation are:

1. It forms very predominantly on grain-boundaries (from where its name).

2. It is now clear that it forms in 20/25 Nb stabilised steels and to an extent which depends on the Si content.

3. It has also been reported in a type 321 steel, but other results are contradictory.

Ti-rich G-phase

In one of the first studies on G-phase [71], the Ti-rich G-phase is reported in a A286 type steel. It is not clear in what conditions of temperature and time it forms, as it was often found to resist the solution-treatment. However, G-phase was not found in the alloy containing only 0.01Si wt%, but formed at higher contents, and the volume fraction increased with the Si content. Adding 2 wt% of Al suppressed the formation of G-phase. This work also included a steel in which the Ti content is more similar to that used in the 300 series, and no G-phase was found.

The only report found of Ti rich G-phase in type 321 has been quoted above [49]. Three out of seven type 321 steels show G-phase after 16000h and 50000h at 600 °C. The common factors between the three type 321 steels which are found to form Ti rich G-phase in this study are their small grain sizes and an excess of Ti with regard to the amount of carbon present. However, in similar conditions, other studies [44, 48]) do not report G-phase.

Nb-rich G-phase

In 20/25-Nb-C stabilised steels, it is now clear that G-phase can form [60, 65, 66] and, following the suggestion of Powell *et al.* [60], the works of Sumerling *et al.* [62] and Dewey *et al.* [72] may be regarded as other evidence for G-phase formation if one accepts that M_6C must be read as G-phase. In [62], in particular, the authors measured a lattice parameter of 11.25 ± 0.05 Å which is much closer to the G-phase parameter.

Powell *et al.* summarised their work in a TTP (Time Temperature Precipitation) diagram shown in figure 2.7. In their alloy (0.68Nb, 0.037C, 0.61Si wt%), G-phase forms between 500 and 850 °C, first on residual grain boundary particles of NbC, and only after very long ageing on NbC particles in the matrix. The authors propose that this is due to the easier diffusion of required elements in the grain boundaries.

Ecob *et al.* [66], comparing the occurrence of G-phase in similar 20/25-Nb stabilised steels, noticed that alloys apparently similar in composition exhibited different relative
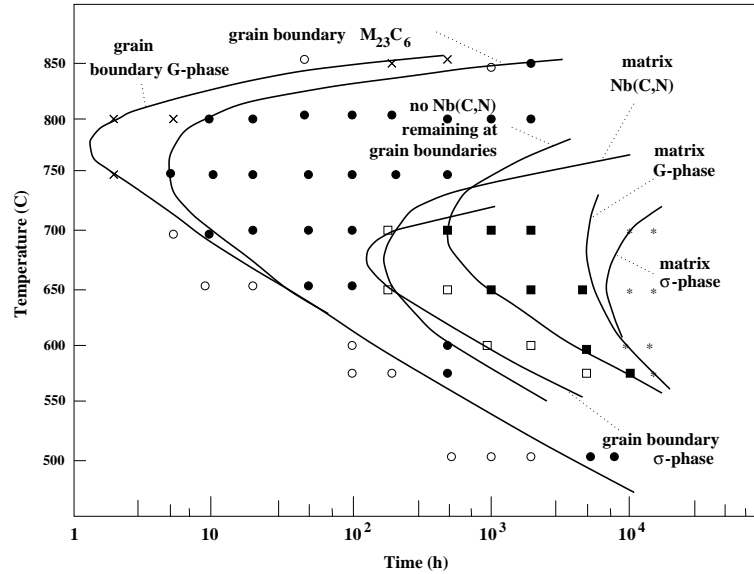
Figure 2.7: TTP diagram from Powell *et al.* [60].

stabilities of NbC with regard to G-phase. They found that an increase in the oxygen content led to a greater instability of NbC with regard to G-phase, and proposed that oxygen and silicon are involved in a co-segregation process, a greater amount of oxygen segregating around NbC leading to a greater segregation of Si in the same way. The silicon rich region is more favourable to G-phase formation.

In 20/25-Nb-N steels however, as it has been discussed in the section regarding M_6C, it seems that Cr_3Ni_2SiN forms preferentially to G-phase. No results could be found that support this hypothesis.

In common 18/12-Nb steels, G-phase seems to be found only under irradiation [54, 53]. Increasing the Si content to 6 wt% resulted in the formation during furnace ageing of Nb G-phase, although provided that carbon was not available to form Cr_3Ni_2SiC. However, no study has been found which reports niobium G-phase in ordinary 18/12 steels.

2.2.e Ni_3Ti and related precipitates

Precipitates such as Ni_3Ti, $Ni_3(Ti, Al)$, are only found in a particular class of austenitic stainless steels: the precipitation hardening ones. A typical steel in this category is A286, a 15Cr-25Ni-Al-Ti steel. They contain titanium and aluminium in quantities substantially larger than the 300 series and related compositions, to form γ' or other Ni, Ti, Al precipitates, as summarised in figure 2.8. However, there are very few studies in which
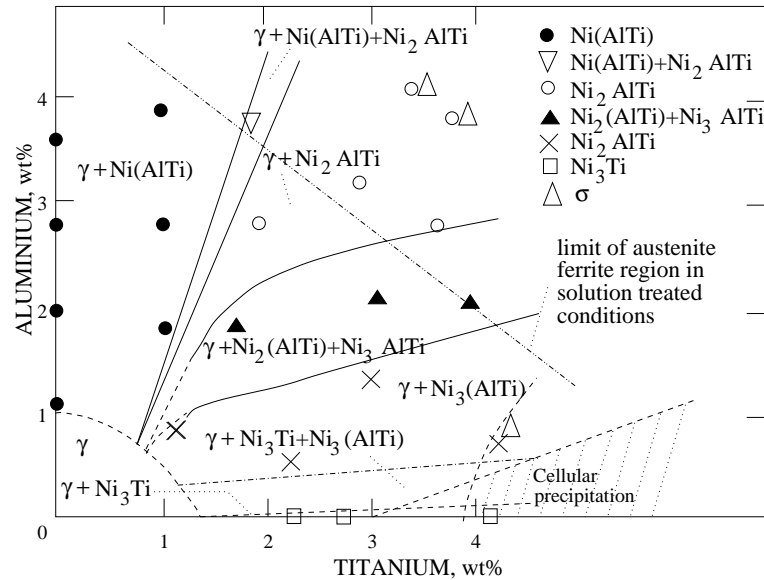
Figure 2.8: Effect of aluminium and titanium on the equilibrium phases present at 800 °C in 15Cr-25Ni austenitic steels, from [73].

the creep properties of these steels are given attention, and long term information is not available (e.g. [74]). For this reason and because the precipitation in these steels has been reviewed in [75], [73], it has been decided not to cover in depth these precipitates. These are [75]:

- γ' is a fcc Ni_3Al or $Ni_3(Ti, Al)$ intermetallic compound of lattice parameter 3.60 Å. It is also the transient structure of Ni_3Ti.

- η is hexagonal (a=5.09 Å c=8.32 Å) and is the equilibrium structure of Ni_3Ti.

- β is NiAl, formed at lower temperatures (up to 700 °C) and short ageing times (10-100h).

2.3 Other precipitates

Attention has been concentrated on precipitates most often reported and studied in creep resistant austenitic stainless steels. However, other phases are sometimes reported depending on the alloying elements.

2.3.a Cr_2N

It forms in non-stabilised austenitic stainless steels with high nitrogen (0.2 wt% at 900 °C with 20Ni wt%) [41]. It has a hcp (hexagonal close-packed) unit cell of lattice parameters a=4.78 Å and c=4.44 Å [6]. Although a major precipitate in high-nitrogen non-stabilised steels, it is not in either nitrogen-bearing non-stabilised creep-resistant austenitic stainless steels because of the lower N content used, or in stabilised nitrogen bearing grades, because Z-phase seems to form preferentially. A detailed review of Cr_2N can be found in [10].

2.3.b   Pi-nitride

It is reported by Jargelius-Petterson [55, 59] to form in a non-stabilised 20/25 steel with 0.21N wt%. The composition after 10 min at 850 °C is:

Element	Si	Mn	Cr	Ni	Mo	Fe
wt%	1.0 ± 0.2	1.1 ± 0.3	47 ± 1	20 ± 1	13 ± 1	19 ± 1

It has a cubic structure of lattice parameter a=6.3 Å [55].

2.3.c   Titanium carbosulphides

The titanium carbosulphide $Ti_4C_2S_2$ is reported by Lai [49] in different type 321 steels aged at ∼600 °C for times between 16000 and 53000 h, and by Minami *et al.* [44] in a similar steel; they clarify that this phase is already present in the solution-treated condition. It has a hcp structure of lattice parameter a=3.21 Å and c=11.12 Å.

2.3.d   Copper precipitates

Few data are available concerning the effect of copper in creep resistant austenitic stainless steels. Tohyama *et al.* [76] used 3 wt% copper in Tempaloy-A1, a steel similar to 347, with addition of a small amount of titanium. This results in precipitation of a copper-rich phase, independently of the precipitation of other precipitates. The creep rupture strength is significantly increased in comparison to the original composition.

2.3.e   Chromium phosphides

The chromium phospide Cr_3P has been reported by Rowcliffe *et al.* [77], in a 18/10 steel with 0.3 wt% P. It has a tetragonal unit cell with a=9.186 Å and c=4.558 Å.

2.4   Concluding Remarks

An attempt has been here made to review the characteristics of the main precipitates found in austenitic stainless steels. Whereas the early stages of precipitation are quite well understood in the usual grades of austenitic steels, this is far from the case for the new generations of nitrogen-bearing stabilised austenitic steels. There is a lack of knowledge about the phases which precipitate during long-term ageing, particularly with respect to thermodynamic data.

Z-phase, which plays an essential role in recent creep-resistant austenitic or ferritic stainless steels, is not present in the SGTE databases commonly used with thermodynamic calculation packages such as MT-DATA or ThermoCalc. The kinetics of its formation are also rather obscure.

In discussing the stability of M_6C, there is some confusion which arises from the fact that this phase is most often referred to as one particular composition of the η-structure rather than the η-structure itself. Similarly, thermodynamic data are only available for the Mo-rich pole of the η-structure. Other important compositions which are not present in the SGTE databases include Fe_3Nb_3C and Cr_3Ni_2SiX.

The formation of MX precipitates is well documented, but again, thermodynamic data are missing to model the solubility of Cr, which is likely to be important in the kinetics of precipitation. An assessment of the Cr-Nb-N system could help improving the description of NbX precipitates, and would also provide thermodynamic data for Z-phase.

Precipitate	Structure	Parameter (Å)	Composition
NbC	fcc	a=4.47	NbC
NbN	fcc	a=4.40	NbN
TiC	fcc	a=4.33	TiC
TiN	fcc	a=4.24	TiN
Z-phase	tetragonal	a=3.037 c=7.391	CrNbN
$M_{23}C_6$	fcc	a=10.57-10.68	$Cr_{16}Fe_5Mo_2C$ (e.g.)
M_6C	diamond cubic	a=10.62-11.28	$(FeCr)_{21}Mo_3C$; Fe_3Nb_3C; M_5SiC
Sigma	tetragonal	a=8.80 c=4.54	Fe,Ni,Cr,Mo
Laves phase	hexagonal	a=4.73 c=7.72	Fe_2Mo, Fe_2Nb
χ-phase	bcc	a=8.807-8.878	$Fe_{36}Cr_{12}Mo_{10}$
G-phase	fcc	a=11.2	$Ni_{16}Nb_6Si_7$, $Ni_{16}Ti_6Si_7$

Table 2.6: Crystal structure and composition of the main precipitates in austenitic stainless steels