Decomposition of Austenite in Austenitic Stainless Steels

A. F. PADILHA and P. R. RIOS¹⁾

Universidade de São Paulo, Departamento de Engenharia Metalúrgica e de Materiais, Av. Prof. Mello Moraes, 2463, São Paulo, 05508-900 Brazil. E-mail: padilha@usp.br 1) Universidade Federal Fluminense, Escola de Engenharia Industrial Metalúrgica de Volta Redonda, Av. dos Trabalhadores, 420, Volta Redonda, RJ, 27255-125 Brazil.

(Received on November 19, 2001; accepted in final form on January 18, 2002)

Austenitic stainless steels are probably the most important class of corrosion resistant metallic materials. In order to attain their good corrosion properties they rely essentially on two factors: a high chromium content that is responsible for the protective oxide film layer and a high nickel content that is responsible for the steel to remain austenitic. Thus the base composition is normally a Fe–Cr–Ni alloy. In practice the situation is much more complex with several other elements being present, such as, Mo, Mn, C, N among others. In such a complex situation one almost never has a single austenite phase but other phases invariably form. Those phases are, with few exceptions, undesirable and they can be detrimental to the corrosion and mechanical properties. It is therefore of considerable importance to study the formation of such phases. In this work the decomposition of austenite in austenitic stainless steels is reviewed in detail. First the binary equilibrium diagrams relevant to the system Fe–Cr–Ni are briefly presented as well as other diagrams, such as the Schaeffler diagram, that traditionally have been used to predict the phases present in these steels as a function of composition. Secondly the precipitation of carbides and intermetallic phases is presented in detail including nucleation sites and orientation relationships and the influence of several factors such as composition, previous deformation and solution annealing temperature. Next, the occurrence of other constituents such as nitrides, sulfides and borides is discussed. TTT diagrams are also briefly presented. Finally the formation of martensite in these steels is discussed.

KEY WORDS: austenitic stainless steel; precipitation behaviour; carbides; intermetallic compounds; TTT diagram; strain induced martensite.

1. Introduction

Austenitic stainless steels were invented in Essen, Germany, in the beginning of the 20th century.¹⁾ Their continuing development has resulted in complex steel compositions with substantial amounts of alloying elements. These alloying elements are of course introduced in the steel for one or more reasons but the final aim is mainly to obtain better mechanical properties and/or higher corrosion resistance. As usual the benefits of such additions invariably come attached to unavoidable disadvantages of which the most important is the potential microstructural instability of the material. Already during solidification or afterwards during thermomechanical processing and high temperature service a significant number of alloy phases or compounds can form. Even close to room temperature one might still have an unstable microstructure as the formation of strain induced martensite may occur. In the majority of the cases the formation of such phases is undesirable so that careful processing is needed to avoid or to minimize them.

Stainless steel plays an important role in the modern world, even if its tonnage represents only about 2% of the whole steel products. Austenitic stainless steels represent more than 2/3 of the total stainless steel world production. **Table 1** shows the standard compositions of common austenitic stainless steels classified according to the American Iron and Steel Institute (AISI). Other non-standard austenitic stainless steels will be mentioned later. More than half of the austenitic stainless steels used are types AISI 304 and 316 and their low carbon compositions: AISI 304L and 316L. Types AISI 321 and 347, titanium

and niobium stabilized, respectively, are also often employed. These four types, due to their foremost practical importance will receive special attention in this review.

Table 1 shows the main alloying elements and their corresponding composition ranges. In addition to iron, the main components are Cr to improve corrosion resistance and Ni to stabilize austenite. Chromium contents range from 15 to 26 wt% and nickel contents from 5 to 37 wt%. The 200 series have a lower Ni content than the 300 series. These steels have a high Mn content up to 15.5 wt% and also a high N content that partly replaces Ni as austenite stabilizers. In some steels one can find 2 to 4 wt% of molybdenum. Mo is primarily introduced to improve the resistance against pitting corrosion but it is also efficient in promoting solid solution hardening. More recently developed steels, known as superaustenitic stainless steels, can contain up to 6 wt% Mo. The term superaustenitic relates to austenitic stainless steels containing high amounts of chromium, nickel, molybdenum and nitrogen, resulting in an iron content close to or less than 50 wt%. One of the most well known superaustenitic stainless steels is the UNS S32654 (also known as 654 SMO[®]): Fe–0.02C–3Mn–24Cr–7.3Mo–22Ni–0.5Cu–0.5N (wt%). In most of the steels shown in Table 1 the maximum silicon content is 1 wt%. However, higher Si contents between 1 and 3 wt% can improve oxidation or scaling resistance. Even higher Si contents up to 5 wt% are used in certain cases to improve the corrosion resistance in nitric acid. Other alloying elements such as copper, boron or sulfur are sometimes added to the austenitic stainless steels and will be mentioned during the course of this review.

Table 1. Compositions (in weight %) of standard austenitic stainless steels (after Ref. 2)).

Type	UNS No.	Composition, % ^(a)							
		C	Mn	Si	Cr	Ni	P	S	Other
201	S20100	0.15	5.5-7.5	1.00	16.0-18.0	3.5-5.5	0.06	0.03	0.25 N
202	S20200	0.15	7.5-10.0	1.00	17.0-19.0	4.0-6.0	0.06	0.03	0.25 N
205	S20500	0.12-0.25	14.0-15.5	1.00	16.5-18.0	1.0-1.75	0.06	0.03	0.32-0.40 N
301	S30100	0.15	2.0	1.00	16.0-18.0	6.0-8.0	0.045	0.03	...
302	S30200	0.15	2.0	1.00	17.0-19.0	8.0-10.0	0.045	0.03	...
302B	S30215	0.15	2.0	2.0-3.0	17.0-19.0	8.0-10.0	0.045	0.03	...
303	S30300	0.15	2.0	1.00	17.0-19.0	8.0-10.0	0.20	0.15 min	0.6 Mo(b)
303Se	S30323	0.15	2.0	1.00	17.0-19.0	8.0-10.0	0.20	0.06	0.15 min Se
304	S30400	0.08	2.0	1.00	18.0-10.0	8.0-10.5	0.045	0.03	...
304H	S30409	0.04-0.10	2.0	1.00	18.0-20.0	8.0-10.5	0.045	0.03	...
304L	S30403	0.03	2.0	1.00	18.0-20.0	8.0-12.0	0.045	0.03	...
304LN	S30453	0.03	2.0	1.00	18.0-20.0	8.0-12.0	0.045	0.03	0.10-0.16 N
302Cu	S30430	0.08	2.0	1.00	17.0-19.0	8.0-10.0	0.045	0.03	3.0-4.0 Cu
304N	S30451	0.08	2.0	1.00	18.0-20.0	8.0-10.5	0.045	0.03	0.10-0.16 N
305	S30500	0.12	2.0	1.00	17.0-19.0	10.5-13.0	0.045	0.03	...
308	S30800	0.08	2.0	1.00	19.0-21.0	10.0-12.0	0.045	0.03	...
309	S30900	0.20	2.0	1.00	22.0-24.0	12.0-15.0	0.045	0.03	...
309S	S30908	0.08	2.0	1.00	22.0-24.0	12.0-15.0	0.045	0.03	...
310	S31000	0.25	2.0	1.50	24.0-26.0	19.0-22.0	0.045	0.03	...
310S	S31008	0.08	2.0	1.50	24.0-26.0	19.0-22.0	0.045	0.03	...
314	S31400	0.25	2.0	1.5-3.0	23.0-26.0	19.0-22.0	0.045	0.03	...
316	S31600	0.08	2.0	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
316F	S31620	0.08	2.0	1.00	16.0-18.0	10.0-14.0	0.20	0.10 min	1.75-2.5 Mo
316H	S31609	0.04-0.10	2.0	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
316L	S31603	0.03	2.0	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
316LN	S31653	0.03	2.0	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo; 0.10-0.16 N
316N	S31651	0.08	2.0	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo; 0.10-0.16 N
317	S31700	0.08	2.0	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3.0-4.0 Mo
317L	S31703	0.03	2.0	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3.0-4.0 Mo
321	S32100	0.08	2.0	1.00	17.0-19.0	9.0-12.0	0.045	0.03	5 × %C min Ti
321H	S32109	0.04-0.10	2.0	1.00	17.0-19.0	9.0-12.0	0.045	0.03	5 × %C min Ti
330	N08330	0.08	2.0	0.75-1.5	17.0-20.0	34.0-37.0	0.04	0.03	...
347	S34700	0.08	2.0	1.00	17.0-19.0	9.0-13.0	0.045	0.03	10 × %C min Nb
347H	S34709	0.04-0.10	2.0	1.00	17.0-19.0	9.0-13.0	0.045	0.03	8 × %C min - 1.0 max Nb
348	S34800	0.08	2.0	1.00	17.0-19.0	9.0-13.0	0.045	0.03	0.2 Co; 10 × %C min Nb; 0.10 Ta
348H	S34809	0.04-0.10	2.0	1.00	17.0-19.0	9.0-13.0	0.045	0.03	0.2 Co; 10 × %C min - 1.0 max Nb; 0.10 Ta
384	S38400	0.08	2.0	1.00	15.0-17.0	17.0-19.0	0.045	0.03	...

(a) Single values are maximum values unless otherwise indicated. (b) Optional

2. Phase Diagrams

Phase diagrams are important to predict the phases present in the austenitic stainless steels. Nevertheless they have limitations due to the complexity of multicomponent thermodynamic calculations and also due to the transformation kinetics that may prevent the attainment of the equilibrium phases. Regarding the first limitation, the number of relevant components is often more than five and published diagrams are rarely found to contain more than four components. As to the second limitation, the diffusion of alloying elements in austenite can be very slow and the precipitation of certain intermetallic compounds can take thousands of hours.

2.1. Equilibrium Diagrams

In this section the most relevant features of the binary diagrams^{3,4)} Fe–Cr, Fe–Ni, Cr–Ni, Fe–Mo, Fe–Ti, Ni–Ti, Fe–Nb, Fe–Mn and Fe–Si are considered. Next the Fe–Cr–Ni and Fe–Cr–Mo ternary diagrams and the quaternary Fe–Cr–Ni–Mo diagram are discussed. The individual characteristics of each phase will be presented later in this review.

The two main features of the Fe–Cr diagram, shown in Fig. 1, which are relevant to austenitic stainless steels, are the ferrite stabilizing character of Cr and the presence of sigma (σ) phase.

The Fe–Ni diagram clearly shows the strong austenite stabilizing effect of Ni. The intermetallic compound Ni_3Fe is not normally observed in austenitic stainless steels. Also the CrNi_2 compound present in the Cr–Ni diagram does not form in austenitic stainless steels. The Fe–Mo diagram shows that Mo is a strong ferrite stabilizer and also that it forms four intermetallic compounds with iron. Of those the sigma (σ) phase and the Laves Fe_2Mo phase often occur in the austenitic stainless steels. The mu (μ) phase, Fe_7Mo_6 ,

Fig. 1. Binary iron–chromium equilibrium diagram (after Ref. 3)).

occurs much less frequently in stainless steels. In the Fe–Ti diagram one can also see the very strong ferrite stabilizer character of the Ti and also the presence of a Laves, Fe_2Ti , phase that can occur in austenitic stainless steels, particularly in those in which the relationship Ti : C is high, “over-stabilized steels”. The Ni–Ti diagram shows the presence of the Ni_3Ti that can be used to produce precipitation strengthening in higher Ni austenitic stainless steels.

The Fe–Nb diagram shows the ferrite stabilizing character of the Nb and also the presence of a Laves phase, Fe_2Nb . The Fe_2Nb , similarly to the Fe_2Ti , can occur in austenitic stainless steels in which the relationship Nb : C is high, “over-stabilized steels”.

As to the Fe–Mn diagram the most relevant characteristic is the austenite stabilizing character of Mn.

Finally the Fe–Si diagram shows a strong ferrite stabiliz-

ing effect of Si but none of the five intermetallic compounds is found in commercial austenitic stainless steels.

The ternary Fe–Cr–Ni diagram is the basic diagram for austenitic stainless steels (**Fig. 2**). It shows the presence of only three solid phases: austenite, ferrite and sigma phase. For a high Cr/Ni ratio delta ferrite may occur during solidification and sigma phase may occur during aging at temperatures between 550 and 900°C. The compositional range of the sigma phase increases as the temperature is below 900°C as shown in **Fig. 2**.

The Fe–Cr–Mo diagram (**Fig. 3**) shows the presence of the chi (χ) phase. This phase is not found in the binary diagrams mentioned above and is frequently found during the aging of austenitic stainless steels containing Mo. **Figure 4** shows two isothermal sections of the 70wt%Fe–Cr–Ni–Mo quaternary system. One can see three intermetallic compounds that often form in austenitic stainless steels containing a few percent of Mo: sigma (σ), chi (χ) and Laves phase (η), Fe_2Mo .

The non-metallic elements: carbon, nitrogen, boron and sulfur are usually present in relatively small quantities but nevertheless their effect can be extremely important. This will be discussed below in relation to the solubility and stability of the precipitates that contain these elements.

2.2. Schaeffler, Delong and Other Nonequilibrium Diagrams

However useful equilibrium phase diagrams might be, they are rarely sufficient to predict the resulting microstructure after solidification. As a result “practical” methods were developed. The best known of those is the Schaeffler diagram. Schaeffler^{9–11)} divided the alloying elements in two groups: ferrite and austenite stabilizers. Schaeffler developed a formula by means of which the elements of each group could be expressed as an equivalent chromium content and as an equivalent nickel content. An example of such a diagram can be found in **Fig. 5**. The regions of the diagram represent the microstructure of each class of stainless steels. Schaeffler’s method therefore allows a rough evaluation of the microstructure as a function of the steel composition. However it does not take into consideration the influence of the cooling rate and aging heat treatments. These diagrams have also been used to estimate the microstructure of weld metal. The empirical formulas and the experiments present a considerable scatter with regard to the determination of the amount of delta ferrite in austenitic weld metals. In this particular circumstance DeLong¹³⁾ suggested a comparative method that has been adopted as a standard procedure by the International Welding Institute.

Other researchers adopted a similar methodology such as Hull¹⁴⁾ that analyzed 1 400 specimens in order to determine the effect of 13 alloying elements (Al, C, Cu, Co, Ni, Mn, Mo, N, Nb, Si, Ti, Ta, V and W) in addition to chromium and nickel in order to predict the resulting amount of delta ferrite in stainless steels. Espy¹⁵⁾ proposed an extended Schaeffler diagram based on his study of the effects of Cu, N, V and Al. Both Hull and Espy obtained expressions for the equivalent chromium and nickel in broad agreement with those of Schaeffler. An interesting historical discussion, especially about the diagrams that preceded the Schaeffler work, can be found in reference.¹⁶⁾

These diagrams although lacking the sound thermodynamical basis of the equilibrium diagrams are nevertheless technological charts of practical importance.

Austenitic stainless steels can solidify by several mechanisms or modes. The prediction of their solidification mode

Fig. 2. Three-dimensional view of the Fe–Cr–Ni equilibrium diagram (after Ref. 5)).

Fig. 3. 650°C isotherm of Fe–Cr–Mo equilibrium diagram (after Ref. 6)). (Fe,Cr)=solid solution, (Cr,Mo)=solid solution, $\text{Fe}_2\text{Mo}_6=\mu$ (μ) phase, σ =sigma phase, χ =chi phase.

and sequence can also be successfully done by using chromium and nickel equivalents ratios.¹⁷⁾

3. Carbide Precipitation

Wrought austenitic stainless steels usually contain up to 0.25 wt% of carbon (see Table 1) whereas some cast alloys may contain up to 0.75 wt%. Carbon solubility in austenite decreases rapidly as the temperature decreases. In addition, a high Ni content also decreases the carbon solubility (see **Fig. 6**). As a consequence precipitation of M_{23}C_6 carbide, where M represents Cr, Fe, Mo and Ni, is very common in this class of steels. The addition of “stabilizing elements” such as Ti, Nb and V decreases the carbon solubility even further invariably resulting in MC type carbides, where M represents Ti, Nb and/or V. The presence of molybdenum in certain alloys can cause the precipitation of η , a M_6C carbide, where M represents Fe, Mo and Cr. For usual carbon contents of wrought austenitic stainless steels precipitation of M_7C_3 carbide, where M represents Cr and Fe, does not take place, but for high carbon contents such as those re-

Fig. 4. Isothermal sections of the Fe-Cr-Ni-Mo system with constant iron content of 70 wt% at 1093 and 816°C (after Refs. 7 and 8)). α =ferrite, γ =austenite, σ =sigma phase, χ =chi phase, η =eta phase (Laves phase Fe_2Mo).

sulting from surface carburizing or in some high carbon cast alloys, M_7C_3 primary carbide can form from the melt. The carbide of the type M_3C ($\text{M}=\text{Fe}, \text{Mn}, \text{Cr}$) is not found in austenitic stainless steels.

In what follows precipitation of those four carbides in austenitic stainless steels is discussed in detail.

3.1. M_{23}C_6

M_{23}C_6 carbide was thought to be Cr_4C until 1933 when Westgren²⁰⁾ showed that Cr_{23}C_6 was the correct composition. It has an fcc structure (more details in Table 2) and Fe, Mo and Ni can substitute for Cr while B and N can partially substitute for C. Its lattice parameter is three times that of the austenite that produces a characteristic diffraction pattern when examined in the transmission electron microscope.²¹⁾ The lattice parameter increases with Mo and decreases with Fe content. The Ni content of the carbide is normally less than 5 wt% and its effect on the lattice parameter has not been reported. The thermal history appears to have a strong influence on the M_{23}C_6 composition. According to Goldschmidt²²⁾ Cr_{23}C_6 theoretically can dissolve up to 35 at% of the metallic elements. Philibert and coworkers²³⁾ have found up to 45 wt% of Fe in the carbide in a Fe-18wt%Cr-8wt%Ni steel after a short heat treatment at 750°C. After holding for 24 h at this same temperature the Fe content decreased to 24 wt%. Similar behavior was found by Da Casa and coworkers.²⁴⁾ In steels containing Mo, such as AISI 316 and 316L, the increase in lattice parameter with aging time can be explained by an increase in the Mo content of the carbide.²⁵⁾ The atoms of Mo and W

Fig. 5. Schaeffler constitution diagram for stainless steels (after Refs. 2) and 12)). The compositional ranges of the ferritic, martensitic, austenitic, and duplex alloys have been superimposed on this diagram.

Fig. 6. Influence of temperature and nickel content on the carbon solubility in Fe-18wt%Cr austenite (after Refs. 8), 18), 19)).

can occupy only certain positions in the carbide structure,²²⁾ the maximum fraction of which is 8.7 at%. The following chemical composition was found²⁵⁾ for the M_{23}C_6 in a AISI 316 steel: 63 wt% Cr; 18 wt% Fe; 14 wt% Mo and 5 wt% Ni, that corresponds approximately to $(\text{Cr}_{16}\text{Fe}_5\text{Mo}_2)\text{C}_6$. In that work²⁵⁾ the lattice parameter was found to vary between 1.0569 and 1.0676 nm. The presence of nitrogen in austenitic stainless steels inhibits the precipitation of M_{23}C_6 .²⁶⁾

The carbon solubility in equilibrium with the M_{23}C_6 carbide in a AISI 316 austenitic stainless steel was determined experimentally²⁷⁾ and is given below:

$$\log_{10} [\text{C (ppm)}] = 7.771 - (6272/T) \dots\dots\dots (1)$$

This relation yields values for the solubility of carbon of 0.16 wt% and 4 ppm at 1100 and 600°C, respectively. Therefore in non-stabilized austenitic stainless steels there is substantial precipitation during aging or during service at a high temperature.

The most favorable sites for the M_{23}C_6 carbide precipitation are grain boundaries, followed by incoherent twin boundaries, coherent twin boundaries and finally at the dislocations within the grains.²⁵⁾ Within the grains the precipitates exhibit the following orientation relationship with the austenitic matrix^{25,28)}:

$$\begin{aligned} \{001\}_{\gamma} // \{001\}_{\text{M}_{23}\text{C}_6} \\ \langle 100 \rangle_{\gamma} // \langle 100 \rangle_{\text{M}_{23}\text{C}_6} \end{aligned}$$

Figure 7 illustrates the precipitation of M_{23}C_6 on a grain

Table 2. Crystal structures and compositions of carbides which may appear in austenitic stainless steels.

Carbide	Unit cell	Atoms per cell	Space group	Lattice parameters (nm)	Principal metallic elements	Occurrence
$M_{23}C_6$	fcc	116	Fm3m	$a = 1.057\text{--}1.068$	Cr, Fe, Mo, Ni	Nearly all stainless steels
MC	ord fcc	8	Fm3m	$a = 0.4131\text{--}0.4698$	Ti, Nb, V and/or Zr	AISI 321, AISI 347
M_6C	fcc	112	Fd3m	$a = 1.085\text{--}1.128$	Fe, Mo, Cr	AISI 316, AISI 316L
M_7C_3	pseudo hex.	40	Pnma	$a = 0.6928\text{--}0.6963$ $c = 0.4541\text{--}0.4511$	Cr, Fe	HH 40, HK 40, HP40

boundary of an titanium stabilized austenitic stainless steel after 1 000 h at 600°C.²⁹⁾

Those grain boundary nucleated carbides have a definite orientation relationship with only one austenitic grain and grow preferentially into the grain with which they do not have a definite orientation relationship.^{29,30)} The tendency of $M_{23}C_6$ to precipitate intergranularly depends strongly on the grain boundary structure.³¹⁾ Carbides tend to be detected at grain boundaries with higher Σ values or larger angles ($\Delta\theta$) from low- Σ coincidence site lattice misorientations.³¹⁾

High solution annealing temperatures can accelerate the start of the precipitation.²⁵⁾ Cold deformation, after solution annealing and before aging also accelerates precipitation and favors precipitation sites within the grains.²⁵⁾

The $M_{23}C_6$ carbide is normally the first phase to form in austenitic stainless steels. Depending on the carbon content, a significant amount of carbides can form after only a few minutes between 650 and 750°C. It is interesting however that in both stabilized and non-stabilized austenitic stainless steels there is at least a partial dissolution of $M_{23}C_6$ for long aging times. For example, Grot and Spruiell³²⁾ found the presence of $M_{23}C_6$ between 550 and 900°C for aging times up to 4 000 h in an AISI 321 Ti stabilized steel. In this same steel Leitnaker and Bentley³³⁾ could not find $M_{23}C_6$ after 17 years at 600°C. In the case of the stabilized steels the $M_{23}C_6$ dissolution takes place due to the precipitation of the more stable MC carbides. In non-stabilized steels the dissolution of $M_{23}C_6$ can also occur if there is significant precipitation of intermetallic phases such as σ phase, χ phase and Laves phase. The intermetallic phase precipitation can lower the Cr and Mo content of the matrix, increasing the carbon solubility leading to a partial dissolution of the $M_{23}C_6$ carbide.²⁵⁾

The $M_{23}C_6$ carbide is normally undesirable since its presence is associated with sensitization or intergranular corrosion and a decrease in ductility and toughness. On the other hand it has been shown that the presence of $M_{23}C_6$ carbides on the grain boundaries can make grain boundary sliding more difficult thus improving creep ductility.³⁴⁾

3.2. MC

The MC ($M = \text{Ti, Zr, Hf, V, Nb}$ and Ta) carbides are very stable and are invariably present in stabilized austenitic stainless steels such as AISI 321 (Ti stabilized), AISI 347 and 348 (Nb stabilized). The addition of elements that form MC carbides, normally called stabilizing elements, aims at hindering $M_{23}C_6$ precipitation and its associated undesirable consequences, particularly susceptibility to intergranular corrosion. However the addition of Ti, Zr or Hf results, unavoidably, in the formation of MN nitrides (see Sec. 5.1) and $M_4C_2S_2$ carbosulfides (see Sec. 5.3) that are even more stable than the MC carbide.^{29,31,32)} Laves phase, Fe_2M ($M = \text{Ti, Zr, Hf, V, Nb}$ and Ta), can also form (see Sec. 4.1.3). The precipitation of those phases will be discussed in subsequent sections.

The MC carbides have an fcc, NaCl type, structure.

Fig. 7. Grain-boundary $M_{23}C_6$ morphology in an austenitic stainless steel obtained by transmission electron microscopy (after A. F. Padilha, USP, Brazil).

Nitrogen can partially substitute for carbon in these carbides causing a decrease in the lattice parameter. They are sometimes referred to as carbonitrides, $M(C,N)$. The dissolution of Mo in TiC has been reported.²⁹⁾ However, there is little information available about the dissolution of metallic elements in MC carbides that form in the austenitic stainless steels. On the other hand specific studies on the phase diagrams of the carbides^{35,36)} report considerable miscibility among the MC carbides (TiC, ZrC, HfC, VC, NbC and TaC) and also that these carbides can dissolve some Cr, Mo and W. Andrén and coworkers³⁷⁾ report that for short aging times, typically 3 h at 750°C, the MC carbides are markedly sub-stoichiometric and can dissolve a considerable amount of Cr. Thorvaldsson and Dunlop³⁸⁾ found that a substantial amount of Cr is present in the MX ($X = C$ and/or N) precipitates but this amount decreases with increased aging time. The carbon solubility is smaller in the stabilized steels than on the non stabilized steels. This is shown by Eq. (2) determined³⁹⁾ for a steel with composition Fe–18wt%Cr–12wt%Ni–Nb and Eq. (3) determined⁴⁰⁾ for the titanium stabilized AISI 321 steel:

$$\log_{10} [Nb][C] = 4.55 - (9\,350/T) \dots\dots\dots (2)$$

$$\log_{10} [Ti][C] = 4.46 - (8\,900/T) \dots\dots\dots (3)$$

[Nb], [Ti] and [C] in Eqs. (2) and (3) are matrix concentrations in weight percent.

The presence of MC in stabilized steels, even for very low carbon contents, is expected. They basically show^{29,32,33)} two types of distribution: (i) a coarse dispersion, 1–10 μm in size, of primary particles formed during solidification; and (ii) a fine dispersion, 5–500 nm in size, of secondary precipitates. In the stabilized steels, part of the primary carbides can be dissolved during the solution annealing heat treatment at temperatures ranging from 1 050 to 1 150°C, and they reprecipitate as fine secondary precipitates during the aging heat treatment or when these materials are subjected to high-temperature applications. The MC carbide precipitation is predominantly intragranular, on dislocations and stacking faults. However, MC precipitation at grain boundaries can also occur.²⁹⁾ Nucleation and growth of NbC particles at grain boundaries is favored at extrinsic grain boundary dislocations and at grain boundary topographical defects.^{41,42)} **Figure 8** illustrates the precipitation of (Ti, Mo)C on dislocations in a titanium stabilized austenitic stainless steel after 24 h at 900°C.²⁹⁾

Although the lattice parameter difference between the matrix and the MC carbides is higher than 10%, for instance for NbC the mismatch is close to 25%, a cube-on-

Fig. 8. MC carbides precipitation on dislocations in a titanium stabilized austenitic stainless steel observed by transmission electron microscopy (after A. F. Padilha, USP, Brazil).

cube orientation relationship is frequently found between the MC and parent austenite:

$$\{001\}_{\gamma} // \{001\}_{MC}$$

$$\langle 100 \rangle_{\gamma} // \langle 100 \rangle_{MC}$$

It is worthy of note that the addition of stabilizing elements does not wholly suppress precipitation of $M_{23}C_6$, even if one adds a large amount of stabilizing elements. $M_{23}C_6$ carbides have been found⁴³⁾ in stabilized steels in which the Ti/C ratio was as high as 34 when the stoichiometric ratio is only 5. The precipitation of $M_{23}C_6$ becomes comparatively easier in relation to that of MC carbides as the temperature is decreased. For example around 600°C, $M_{23}C_6$ precipitation occurs before the MC carbide precipitation.²⁹⁾ This type of carbide has a particularly large resistance to coarsening.^{33,44)}

Finally, it must be mentioned that there is experimental evidence^{38,45,46)} that the MC to $M_{23}C_6$ transformation can take place in certain austenitic alloys after long times. However, in order to clarify this more systematic studies are required on the effect of variables such as MC carbide type and M/C ratio of the steel, Cr/Ni ratio of the steel, temperature, applied creep stress and precipitation sites.

3.3. M_6C

The carbides of the type M_6C ($M=Fe, Cr, Mo, W, Nb$ and V), also known as η -carbide, are often found in austenitic stainless steels containing molybdenum, tungsten and niobium, especially molybdenum. The M_6C carbide invariably contains more than one metallic element, requiring the presence of at least three types of atoms and is usually represented by the formulae A_3B_3C or A_4B_2C . The number of carbon atoms per unit cell is variable and there is evidence of this being a carbon sub-stoichiometric carbide.⁴⁷⁾ This type of carbide has an fcc, diamond type, structure. Nitrogen additions are believed⁴⁸⁾ to favor M_6C precipitation to the detriment of $M_{23}C_6$, because the former is able to dissolve more nitrogen than the latter. Nitrogen atoms replace carbon atoms in the lattice, reduce the lattice parameter and stabilize this phase. As $M_{23}C_6$ absorbs molybdenum during aging and the molybdenum content in $M_{23}C_6$ exceeds a threshold, an *in situ* $M_{23}C_6 \rightarrow M_6C$ transformation is possible, as originally suggested by Goldschmidt⁴⁹⁾ and reinforced by Weiss and Stickler.²⁵⁾ Due to the size of their unit cells, M_6C and austenite might be expected to show a cube-on-cube orientation relationship.

Comparatively less attention has been given to M_6C carbide in the literature, because it is not found (or only found

in small quantities) in most stainless steels. With the advent of the “superaustenitic” stainless steels that contain high levels of molybdenum and nitrogen, it is likely that more investigations will be done on this type of carbide and its effect on properties.

3.4. M_7C_3

M_7C_3 carbide has a pseudo-hexagonal crystal structure. Although it occurs both in the Fe–Cr–C and Fe–Cr–Ni–C systems,⁵⁰⁾ it does not occur in wrought stainless steels of the 300 series possessing the usual carbon content. The M_7C_3 ($M=Cr, Fe$) carbides can only be found in austenitic stainless steels for very high carbon:chromium ratios,^{17,51)} for example, during carburizing. During surface carburization of type AISI 316 stainless steel,⁵²⁾ the near surface region of the steel comprised predominantly M_7C_3 where the local carbon content was about 4 wt%. The ratio to $M_{23}C_6$ to M_7C_3 phases increased as the carbon content decreased from the surface to the center. Carburizing studies of AISI 300 series steels are not common and most of them were carried out in the 1970's. These studies were related to fast breeder reactors where the carburizing medium was liquid sodium. M_7C_3 is one of the most common phases in centrifugally cast austenitic stainless steels for gas-reformer and pyrolysis-furnace tubes used in the petrochemical industry^{53,54)} (see **Fig. 9**). M_7C_3 carbides are also important in high-chromium white cast irons that are traditionally employed in applications where there is a need for high resistance to abrasive wear. One common heat resistant steel of this type is HK 40 (Fe–0.4wt%C–25wt%Cr–20wt%Ni) specified in the ASTM A297 standard. During solidification, a eutectic of M_7C_3 and austenite is formed.⁵³⁾ During creep or service⁵³⁾ in the range 750–1 000°C, M_7C_3 gradually transforms to the more stable $M_{23}C_6$. The high chromium white cast irons contain 11–30 wt% chromium and 1.8–3.6 wt% carbon, as well as additions of molybdenum, manganese, nickel, and copper. The as-cast microstructure of this type of white cast iron consists of a dispersion of eutectic M_7C_3 and eventually M_3C in an austenitic matrix.⁵⁵⁾ In this case, the as-cast microstructure can be significantly changed by austenite destabilization heat treatments, when precipitation of secondary carbides of types M_3C or M_7C_3 or even $M_{23}C_6$ takes place.^{55,56)}

4. Precipitation of Intermetallic Phases

The three intermetallic phases most frequently found in the austenitic stainless steels are sigma phase (σ), chi phase (χ) and Laves phase (η). Other intermetallic phases can also be occasionally found: G, R, mu (μ), gamma prime (γ'), gamma double prime (γ''), η -Ni₃Ti and δ -Ni₃Nb. Precipitation of intermetallic phases from austenite is normally associated with undesirable consequences like matrix impoverishment in alloying elements such as chromium, molybdenum, and niobium as well as loss of ductility, toughness and corrosion resistance. Exceptions are γ' -Ni₃(Al, Ti) in precipitation-hardening iron-based superalloys and the Laves phase, Fe₂Nb, in austenitic stainless steels, since their occurrence can result in precipitation hardening.

Intermetallic phases that occur in austenitic stainless steels (see **Table 3**) can be classified in two groups: i) topologically close packed phases, like σ , χ , Laves (η), G, R and Mu (μ) and ii) geometrically close packed phases, like γ' , γ'' , η -Ni₃Ti and δ -Ni₃Nb. The topologically close packed phases (TCP phases) are characterized by close-

packed layers of atoms separated from one another by relatively large interatomic distances.⁵⁷⁾ The layers of close-packed atoms are displaced from one another by sandwiched large atoms, developing a characteristic topology.⁵⁷⁾ In contrast, the geometrically close packed phases (GCP phases), are close packed in all directions. GCP phases have been observed to form mainly in nickel base alloys whereas the TCP phases have been observed mainly in the iron base alloys.⁵⁸⁾ In what follows, the precipitation of those phases in the austenitic stainless steels is discussed in detail.

4.1. Topologically Close Packed Phases (TCP Phases)

4.1.1. Sigma Phase (σ)

Sigma phase is probably the most studied and undesirable intermetallic phase of those mentioned above. Already in 1907, even before the discovery of the stainless steels, Treitschke and Tamman,⁵⁹⁾ studying the Fe–Cr system, conjectured that there was a compound in the 30–50 wt% Cr range. In 1927, Bain and Griffiths⁶⁰⁾ found in the Fe–Cr–Ni system a hard and brittle phase that they called “B constituent” where “B” stands for brittle. In 1936, Jett and Foote⁶¹⁾ called it sigma phase and in 1951, Bergmann and Shoemaker⁶²⁾ studied it in detail and obtained the crystallographic structure of the sigma phase in the Fe–Cr system.

Sigma-phase appears in several binary, tertiary, and quaternary systems such as Fe–Cr, Fe–Mo, Fe–V, Fe–Mn,

Fe–Cr–Ni, Fe–Cr–Mo, Fe–Cr–Mn and Fe–Cr–Ni–Mo. The σ -phase occurs for an electron/atom ratio between 5.6 and 7 and for an atomic radius ratio, in binary systems, between 0.96 and 1.16. Sigma phase precipitation in austenitic stainless steels occurs between 550 and 900°C. A typical σ -phase chemical composition, found²⁵⁾ in AISI 316 or 316L austenitic stainless steels, is the following (in wt%): 55% Fe; 29% Cr; 11% Mo and 5% Ni. The composition of sigma phase in austenitic stainless steels can be approximately written as: $(\text{Fe,Ni})_3(\text{Cr,Mo})_2$. Alloying elements such as chromium, manganese, molybdenum, tungsten, vanadium, silicon, titanium, niobium, and tantalum favor σ -phase formation, whereas nickel, cobalt, aluminum, carbon and nitrogen hinder its precipitation. A method has been developed by Dean and Plumbridge⁶³⁾ to estimate the sigma-forming tendency of a certain austenitic stainless steel based on its chemical composition. It precipitates mainly on grain boundaries, especially on triple junctions, and on incoherent twin boundaries and intragranular inclusions.²⁵⁾ Its morphology is usually equiaxed. **Figure 10** illustrates the precipitation of sigma phase on the grain boundaries of an AISI 316 steel after 28 100 h at 700°C. As described before, sigma phase precipitation depleted the adjacent matrix in chromium and molybdenum and thereby caused dissolution of carbides in this region.

Several orientation relationships between σ phase and austenite have been reported. Lewis⁶⁴⁾ and Weiss and Stickler²⁵⁾ found:

$$(111)_\gamma // (001)_\sigma$$

$$[0\bar{1}1]_\gamma // [140]_\sigma$$

whereas Beckitt⁶⁵⁾ found:

$$(111)_\gamma // (001)_\sigma$$

$$[\bar{1}10]_\gamma // [\bar{1}10]_\sigma$$

and Duhaj *et al.*⁶⁶⁾ found a mixture of several orientation relationships.

Sigma phase precipitation has a very slow kinetics and precipitate formation can take hundreds and sometimes thousands of hours. There are at least three reasons for the slow kinetics: (i) carbon and nitrogen are insoluble in σ -

Fig. 9. As cast microstructure showing M_7C_3 carbide network in an HP (Fe–0.43wt%C–26wt%Cr–32.6wt%Ni) austenitic stainless steel obtained by light microscopy (courtesy of Luiz Henrique de Almeida, UFRJ, Brazil).

Table 3. Crystal structures and compositions of intermetallic phases which may appear in austenitic stainless steels.

Phase	Unit cell	Atoms per cell	Space group	Lattice parameters (nm)	Composition	Occurrence
Sigma (σ)	bct	30	$P4_2/mnm$	$a = 0.87\text{--}0.92$ $c = 0.4554\text{--}0.48$	$(\text{Fe,Ni})_x(\text{Cr,Mo})_y$	AISI 304; AISI 304L; AISI 316; AISI 316L; AISI 321; AISI 347
Chi (χ)	bcc	58	$I43m$	$a = 0.881\text{--}0.895$	$(\text{Fe,Ni})_{36}\text{Cr}_{12}\text{Mo}_{10}$	AISI 316; AISI 316L; AISI 321
Laves (η)	hex.	12	$P6_3/mmc$	$a = 0.473\text{--}0.483$ $c = 0.772\text{--}0.786$	Fe_2Mo ; Fe_2Nb ; Fe_2Ta ; Fe_2Ti ; Fe_2W	AISI 316; AISI 316L; AISI 321; AISI 347
G	fcc	116	$Fd3m$	$a = 1.115\text{--}1.120$	$\text{Ni}_{16}\text{Nb}_6\text{Si}_7$; $\text{Ni}_{16}\text{Ti}_6\text{Si}_7$; $(\text{Ni,Fe,Cr})_{16}(\text{Nb,Ti})_6\text{Si}_7$	AISI 308; AISI 310S; AISI 329; Fe-20Cr-25Ni-Nb
R	hex.	53 (159)	$R3$	$a = 1.090$; $c = 1.934$	$\text{Fe}_{22}\text{Mo}_{18}\text{Cr}_{13}$; $(\text{Fe,Ni})_{10}\text{Cr}_5\text{Mo}_3\text{Si}_2$	Duplex Fe-22Cr-8Ni-3Mo; Superaustenitic UNS S32654; Maraging Fe-12Cr-9Ni-4Mo
Mu (μ)	rhombohedral	13	$R3m$	$a = 0.4762$; $c = 2.5015$	$(\text{Fe,Co})_7(\text{Mo,W})_6$; $(\text{Cr,Fe})_7(\text{Mo})_2(\text{Cr,Fe,Mo})_4$	Fe-17Cr-14Ni-6W; Fe-15Cr-40Ni-4W-2Mo-Al-Ti
γ'	fcc	4	$Pm3m$	$a = 0.3565\text{--}0.3601$	$(\text{Ni,Co,Fe,Cr})_3(\text{Al,Ti})$	Incoloy 800 and alloy A-286
γ''	bct	8	$P4_2/mnm$; $I4/mmm$	$a = 0.3624$; $c = 0.7406$	Ni_3Nb	Inconel 718
η	hex.	8	$P6_3/mmc$	$a = 0.5109$; $c = 0.8299$	Ni_3Ti	Overaged Incoloy 800 and alloy A-286
δ	orthorhombic	8	$Pmmn$	$a = 0.5116$; $b = 0.4259$; $c = 0.4565$	Ni_3Nb	Overaged Inconel 718

Fig. 10. Sigma phase on grain boundaries of an AISI 316 steel after 28 100 h at 700°C; sample was etched in V2A-Beize; scanning electron microscopy (courtesy of Michael Pohl, Ruhr-Universität Bochum, Germany).

phase; as a consequence, σ -phase normally appears only after carbide and nitride precipitation has already taken place and the matrix is impoverished in carbon and nitrogen; (ii) its nucleation is difficult on account of its crystal structure being complex and very different from the parent austenite; and (iii) it is very rich in substitutional elements thus requiring protracted diffusion times.

Cold deformation accelerates the start of the precipitation of sigma phase particularly if there is recrystallization^{66,25)} during the annealing treatment. An increase in the solution annealing temperature delays the start of sigma phase precipitation unless delta ferrite is formed during a annealing.²⁵⁾ In this case the sigma phase precipitation is accelerated in a subsequent aging treatment.^{67,68)} The rate of σ -phase precipitation from ferrite is about 100 times more rapid than the rate of σ -phase precipitation directly from austenite.⁶⁹⁾

4.1.2. Chi Phase (χ)

Andrews⁷⁰⁾ was the first to identify a phase with a α -Mn type cubic structure, the χ -phase, in Cr-Ni-Mo steels. Afterwards, Kasper⁷¹⁾ synthesized the χ -phase with a composition $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ and studied its crystalline structure in detail. The χ -phase was also found in the Fe-Cr-Ni-Ti system by Hughes and Llewellyn⁷²⁾ with a composition $\text{Fe}_{35}\text{Ni}_3\text{Cr}_{13}\text{Ti}_7$. Okafor and Carlson⁷³⁾ showed that the chi phase exhibits a wide range of stoichiometry, extending from the ternary chi phase $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ to $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_3\text{Ti}_7$, accompanied by a regular increase in lattice parameter. In general the χ -phase occurs for an electron/atom ratio between 6.3 and 7.8. The precipitation range of the chi phase is somewhat more narrow than that of sigma phase (550 to 900°C) and depends on the Mo content of the steel.

Similarly to the M_6C carbide discussed in Sec. 3.3, χ -phase precipitation can only occur if molybdenum or/and titanium is present. Several investigators identified χ -phase in type AISI 316 stainless steel.^{25,66,67)} Its composition is similar to that of the σ -phase, but in contrast to σ -phase, carbon can dissolve in the χ -phase. Due to this property, the χ -phase was classified⁴⁹⁾ in the past as a carbide-type M_{18}C . The χ -phase is found to form mainly on the grain boundaries, incoherent twin boundaries, coherent twin boundaries, and on dislocations within the matrix. The χ -phase exhibits^{25,66)} several morphologies and the following orientation relationship with austenite in the case of intragranular precipitation:

$$\begin{aligned} (111)_\gamma // (110)_\chi \\ [01\bar{1}]_\gamma // [\bar{1}10]_\chi \\ [\bar{2}11]_\gamma // [001]_\chi \end{aligned}$$

Owing to its ability to dissolve carbon and also to its easier nucleation, χ phase precipitation, when it occurs, precedes σ -phase formation. Increased solution treatment temperatures do not seem to affect the nucleation of χ phase, but its nucleation is accelerated by cold work.²⁵⁾ The χ phase has been less studied than the σ phase, nonetheless its presence is also considered to be detrimental to the steel properties.

4.1.3. Laves Phases (η)

There are three kinds of Laves phases, all with stoichiometry A_2B : C14 (MgZn_2 type); C15 (Cu_2Mg type) and C36 (MgNi_2 type). The Laves phases that occur more often in the austenitic stainless steels have a hexagonal close-packed structure of MgZn_2 type. The most common are Fe_2Mo , Fe_2Nb and Fe_2Ti , or a combination of all three, for

example, $\text{Fe}_2(\text{Mo}, \text{Nb}, \text{Ti})$. Zirconium also forms Laves phase with iron, with a fcc crystal structure of Cu_2Mg type. Vanadium on the other hand does not. Those phases were initially studied in the thirties by F. Laves and should exhibit an ideal ratio of atomic radii r_B/r_A equal to 1.225. Nonetheless ratios within the range of 1.10 to 1.46 can be found. It is certain that electronic factors in addition to geometric factors also have an influence in the formation of the Laves phases. In the Fe-Mo system the atomic radius ratio is close to 1.10 and in spite of that Fe_2Mo occurs. Whereas in the Ni-Nb system in which the atomic radius ratio is 1.18, closer to the ideal value, Ni_2Nb has not been observed. The Laves phases occur for electron/atom ratios between 6.33 and 8.0. The Laves phase is generally stable below²⁵⁾ 815°C, but this strongly depends on the Mo, Nb and Ti contents.

The Laves phase of Fe_2Mo type was found^{25,74)} in AISI 316 stainless steels with molybdenum contents between 2 and 3 wt% for long annealing times. For Ti stabilized steels it is possible⁷⁵⁾ to avoid precipitation of Fe_2Ti and Ni_3Ti for Ti contents in solid solution up to 0.5 wt%. This amount corresponds to an excess in relation to the stoichiometric amount of Ti needed to combine with all available carbon, forming TiC . In this regard, the niobium content is particularly critical. An excess of only 0.07 wt% niobium in relation to the stoichiometric content leads to precipitation of Fe_2Nb for long annealing times.⁷⁶⁾

The Fe_2Nb Laves phase precipitation⁷⁷⁻⁸⁰⁾ can cause significant precipitation hardening and exhibits the following orientation relationship with the austenitic matrix:

$$\begin{aligned} \{111\}_\gamma // \{0001\}_{\text{Fe}_2\text{Nb}} \\ [\bar{1}10]_\gamma // [10\bar{1}0]_{\text{Fe}_2\text{Nb}} \end{aligned}$$

During aging of austenitic stainless steels with an excess of niobium Fe_2Nb precipitation follows the sequence^{77,80)}: first it appears at grain boundaries, next at incoherent twin boundaries coherent twin boundaries and finally within the grain. The grain boundary precipitates can coarsen, forming roughly rounded shapes. In contrast, the almost continuous precipitate films on coherent twin boundaries show considerable resistance to coarsening.⁸⁰⁾

4.1.4. Other TCP Phases: G, R and Mu (μ)

The G, R and mu (μ) phases occur much less frequently and in smaller quantities in stainless steels than the σ , χ and Laves phases.

The G phase is a silicide of $\text{Ni}_{16}\text{Ti}_6\text{Si}_7$, $\text{Ni}_{16}\text{Nb}_6\text{Si}_7$ or $(\text{Ni}, \text{Fe}, \text{Cr})_{16}(\text{Nb}, \text{Ti})_6\text{Si}_6$ type. It has a complex fcc crystalline structure. Both in austenitic stainless steels^{81,82)} containing δ ferrite, such as low carbon AISI 310 and also AISI 308, or in duplex stainless steels,⁸³⁾ such as AISI 329, the G phase precipitates in ferrite between 250 and 500°C. The orientation relationship between G phase and ferrite most commonly found is⁸³⁾:

$$\begin{aligned} (001)_G // (001)_\alpha \\ (110)_G // (110)_\alpha \\ (111)_G // (111)_\alpha \end{aligned}$$

In a low carbon fully austenitic matrix,⁸⁴⁾ as in Fe-20%Cr-25%Ni-Nb, the G phase precipitates at grain boundaries and within the grains during aging at higher temperatures than in ferrite: 500 and 850°C. The G phase composition was determined by EDX analysis in this steel after annealing for 50 hr at 650°C. The result was (in wt%): 51 Ni; 29 Nb; 14 Si; 4.5 Fe and 1.5 Cr. The transformation

of NbC in G phase was also studied in high carbon modified-HP austenitic steels.⁸⁵⁾ Neutron irradiation can induce G phase precipitation in austenitic stainless steels.⁸⁶⁾

The R phase basically contains Mo–Fe–Cr and has a complex hexagonal crystalline structure. It has Mo, Fe and Si contents comparable to that of the Fe₂Mo Laves phase, but higher Cr contents. The R phase was found both in a Fe–22wt%Cr–8wt%Ni–3wt%Mo duplex stainless steel⁸⁷⁾ and in a Fe–3wt%Mn–24wt%Cr–22wt%Ni–7.3wt%Mo–0.5wt%N superaustenitic steel.⁸⁸⁾ In the duplex steels the G phase was found⁸⁷⁾ after aging between 550 and 600°C for 24 h, with the following orientation relationships:

$$\{30\bar{3}0\}_R // \{110\}_\alpha$$

$$\langle 0001 \rangle_R // \langle \bar{1}11 \rangle_\alpha$$

In the superaustenitic steel the R phase was found⁸⁸⁾ in the heat affected zone of welds, in regions that reached temperatures above 800°C. The R phase has been found⁸⁹⁾ in a Fe–12wt%Cr–9wt%Ni–4wt%Mo maraging stainless steel after isothermal tempering at 550°C for 100 h.

The μ (μ) phase is found in the ternary Fe–Cr–Mo⁹⁰⁾ and Fe–Cr–W⁹¹⁾ equilibrium diagrams. However the Mo and/or W contents of most austenitic stainless steels are not high enough to cause the formation of the μ phase. The μ phase formulae in Fe–Mo and Fe–W systems are Fe₇Mo₆ and Fe₇W₆, respectively. In ternary systems the μ phase is better represented by^{90,91)}: (Cr,Fe)₇(Mo,W)₂(Cr,Fe,Mo,W)₄. Matsuo and coworkers⁹²⁾ studied the Fe–0.01wt%C–0.4wt%Si–1.5wt%Mn–17wt%Cr–14wt%Ni alloy with W contents up to 12 wt%. Above 5 wt% W they found intergranular precipitation of μ phase that decreased the creep resistance of the material. Small amounts of grain boundary μ phase in the low carbon Fe–15Cr–40Ni–4W–2Mo–2.5Ti–2Al type alloy caused loss of impact toughness at ambient temperature.⁹³⁾ The ϵ phase initially precipitated preferentially at grain boundaries, but after long times the μ phase was seen to precipitate both at grain boundaries and within the grains.⁹³⁾

4.2. Geometrically Close Packed Phases (GCP Phases)

As mentioned before, the GCP phases mainly occur in nickel based alloys and their appearance in iron base alloys, especially in stainless steels, only takes place in some particular cases.

The phases that can form a coherent or semicoherent uniform particle dispersion with its consequent precipitation hardening effect in superalloys are the ordered fcc γ' -Ni₃(Al,Ti) and the ordered body-centered tetragonal γ'' -Ni₃Nb. The η -Ni₃Ti and δ -Ni₃Nb phases usually form due to overaging and are not as effective as γ' and γ'' for precipitation hardening and are often associated with a decrease in toughness. The most important class of iron-base superalloys comprises those alloys that are strengthened by precipitation of γ' in fcc matrixes, such as Incoloy 800, Incoloy 801, Incoloy 802 and alloy A-286. The 800 series Incolloys 800 are alloys with basic composition: Fe–21wt%Cr–32wt%Ni plus Ti and Al additions. These alloys are susceptible to γ' and η -Ni₃Ti precipitation.⁹⁴⁾ The A-286 superalloy has a basic composition: Fe–15Cr–26Ni–1.25Mo and also contains Ti and Al additions. Likewise, the 800 series alloys are also susceptible to γ' and η -Ni₃Ti precipitation. Whitcroft and Martin⁹⁵⁾ studied a series of four aluminum free austenitic steels containing 2 wt% Ti and 25 wt% Ni, with chromium contents ranging from 4% to 17% and found γ' -Ni₃Ti in every alloy after aging at 750°C. The iron-containing alloy Inconel 718 (contains

Table 4. Crystal structures and compositions of nitrides, borides and sulfides which may appear in austenitic stainless steels.

Phase	Unit cell	Atoms per cell	Space group	Lattice parameters (nm)	Composition	Occurrence
MN	ord fcc	8	Fm3m	a = 0.4097–0.4577	ZrN; TiN; NbN; VN	AISI 321
M ₂ N	hexagonal	9	P31m	a = 0.478–0.480; c = 0.444–0.447	(Cr,Fe) ₂ N	AISI 304+N AISI 316+N
Z-phase	tetragonal	6	P4/nmm	a = 0.3037; c = 0.7391	CrNNb	AISI 347+N
M ₂ B	orthorhombic	48	Fddd	a = 1.4585; b = 0.7331; c = 0.4223	Cr _{1.04} Fe _{0.96} B	AISI 304+B
M ₃ B ₂	tetragonal	10	P4/mbm	a = 0.5807; c = 0.3142	FeMo ₂ B ₂	AISI 316+B
M ₄ C ₂ S ₂	hexagonal	8	P6 ₃ /mmc	a = 0.320–0.339; c = 1.118–1.210	Ti ₄ C ₂ S ₂ Zr ₄ C ₂ S ₂	AISI 321

only about 18.5% iron) is considered a nickel-base superalloy and is hardened by γ'' -Ni₃Nb.⁹⁶⁾ In this alloy the appearance of δ -Ni₃Nb is a result of overaging.

5. Other Phases: Nitrides, Borides and Sulfides

Austenitic stainless steels normally have residual contents of N, B and S. In some cases these elements are added to obtain certain special properties. The low solubility of those elements in Fe–Cr–Ni austenite is the main cause for nitrides, borides and sulfides often being observed (see Table 4).

5.1. Nitrides

Nitrides that form in austenitic stainless steels can be grouped in two classes: (i) primary nitrides of type MN (M=Zr, Ti, Nb and V) formed in stabilized steels containing residual amounts of nitrogen (<0.1 wt%); and (ii) secondary nitrides of the type M₂N (M=Cr, Fe), which precipitate in stainless steels containing high levels of nitrogen (0.1 to 0.9 wt%). Nitrogen is added to stainless steels because it improves mechanical properties and corrosion resistance, and also because it is a strong austenite stabilizer.

The MN nitrides have the same crystalline structure as MC carbides, but they are even more stable and do not dissolve during solution annealing. These nitrides are usually sub-stoichiometric (MN_{1-x}) and often show significant solid solubility among themselves.⁹⁷⁾ They can dissolve small amounts of other metallic elements present in the matrix, such as Fe, Cr and Ni, but only very small amounts of carbon can be dissolved as carbon increases their unit cell and lattice parameter. Due to the high stability and consequent low solubility of these nitrides, almost all nitrogen forms nitrides, particularly in Ti stabilized steels. These nitrides²⁹⁾ have a faceted morphology and their size is typically 10–15 μ m.

On the other hand, the maximum solubility of nitrogen^{98–100)} in Fe–Cr–Ni or Fe–Cr–Mn–Ni austenites is about 0.9 wt%. This solubility decreases considerably with temperature below 1000°C.^{98–100)} The (Cr,Fe)₂N nitrides can precipitate continuously or discontinuously.^{100,101)} Chromium nitride precipitation in austenitic stainless steels with commercial levels (<0.1 wt%) of nitrogen usually occurs in a continuous mode on grain boundaries, inside the grains and at dislocations. Discontinuous precipitation of chromium nitride is not a common observation in this class of steels. This kind of discontinuous precipitation was only observed in some austenitic stainless steels, especially in austenitic stainless steels with very high nitrogen content. Nitrogen depletion of the matrix due to precipitation of nitrides can make austenite unstable and it can make possible the formation of ferrite and sigma phase at aging tempera-

tures.¹⁰⁰⁾ Finally, nitrogen in solid solution delays the precipitation of phases which do not dissolve or dissolve very little nitrogen, such as $M_{23}C_6$, σ , χ and Laves phase.^{26,102)}

The Z phase is a nitride that forms in stainless steels containing niobium and more than 0.4 wt% nitrogen.¹⁰³⁾ The Z phase was detected first by Hughes and Andrews¹⁰⁴⁾ in Fe–18Cr–Ni–Nb steels after creep testing in the range 750 to 850°C. Its occurrence was first reported by Hugues and Andrews in 1957 in the discussion to Hagel and Beattie¹⁰⁵⁾ paper. After some initial controversy, its crystalline structure was determined by Jack and Jack¹⁰⁶⁾ to be tetragonal (space group P4/nmm). In addition to Cr, N and Nb the Z phase can also contain Mo.¹⁰³⁾ In niobium stabilized stainless steels, whenever the Z phase forms so does NbC, which is probably more stable than the Z phase.¹⁰⁷⁾ The Z phase precipitation can take place within a wide temperature range from 600 to 1200°C. It forms on grain boundaries and within grains with different morphologies. The orientation relationship between austenite and Z phase found is¹⁰³⁾:

$$\begin{aligned} (001)_\gamma // (001)_Z \\ [100]_\gamma // [\bar{1}10]_Z \end{aligned}$$

5.2. Borides

The positive influence of small additions, 10–80 ppm, of boron on the creep behavior and hot workability of austenitic stainless steels is well established. Nonetheless, if boron content is too high it may cause the formation of a low-melting point (1150–1225°C) eutectic, which may cause hot shortness during hot working and welding. Boron forms an eutectic: $L \rightarrow \gamma + (Cr, Fe)_2B$ with the Fe–Cr–Ni austenitic alloys. The eutectic temperature is not much higher than 1200°C for 2 wt% B. The maximum solubility of boron in austenite for a Fe–16wt%Cr–13wt%Ni steel is about 200 ppm at the eutectic temperature and decreases to about 20 ppm below 900°C.¹⁰⁸⁾ These results were confirmed by Goldschmidt^{109,110)} in Fe–20wt%Cr–25wt%Ni and Fe–18wt%Cr–15wt%Ni steels.

When held between 650 and 1050°C, stainless steels containing more than about 30 ppm of boron are susceptible to the precipitation of two types of orthorhombic borides: $(Cr, Fe)_2B$ and $(Cr, Fe, Mo)_3B_2$. The M_2B is found more frequently and the M_3B_2 occurs only in steels with higher molybdenum contents.¹¹¹⁾ The $(Cr, Fe)_2B$ phase precipitates chiefly on the grain boundaries.^{112,113)} When it precipitates within the grain it is often found to form at the incoherent phase boundaries of primary carbides. The beneficial effects of boron are normally associated with boron in solid solution. The volume fraction of borides is very small and has no significant effect on mechanical properties. Notwithstanding in nuclear applications the amount and the distribution of boron are important. The reason for this is that the B-10 isotope can react with neutrons producing helium, which causes high-temperature embrittlement.¹¹²⁾

5.3. Sulfides

Kaneko and coworkers¹¹⁴⁾ determined the following sequence of thermodynamic stability for the sulfide forming elements in steels: $Zr > Ti > Mn > Nb > V > Cr > Al > Mo > W > Fe > Ni > Co > Si$. Da Casa and Nileschwar¹¹⁵⁾ confirmed the large affinity between Ti and sulfur. They found titanium sulfides in an AISI 321 steel with S contents as low as 20 ppm (in wt%). The high frequency with which Ti sulfides are found and identified in Ti stabilized^{29,32,33,115,116)} austenitic stainless steels seem to confirm this. These sul-

fides form during solidification. They are fractured and re-distributed during mechanical work. For this reason they appear²⁹⁾ in groups of aligned particles roughly 2 to 5 μm in size.

Although it is now known that the crystalline structure of Ti sulfide is hexagonal, there was initially some doubt about its structure, composition and representation. Gemmil and coworkers¹¹⁷⁾ found Ti sulfide for the first time in Ti stabilized austenitic stainless steels and called it Y phase. These authors¹¹⁷⁾ suggested that the Y phase would be a structural modification of TiN and indexed it as a hexagonal structure. Later, Brown and coworkers¹¹⁸⁾ in a similar alloy extracted a phase that when chemically analyzed, contained sulfur. This phase had diffraction peaks that agreed well with those found by Gemmil¹¹⁷⁾ for the Y phase. They called it τ phase and suggested the formula Ti_2S . After this, Frick and Rhode¹¹⁹⁾ and Kudielka and Rhode¹²⁰⁾ showed that the hexagonal structure of Ti_2S and Zr_2S could become more compact and more stable by the dissolution of carbon. These authors suggested that the formulae $Ti_4C_2S_2$ and $Zr_4C_2S_2$ better represented the composition of these sulfides or carbosulfides.

6. Time–Temperature–Precipitation Diagrams

The time–temperature–transformation/precipitation (TTT/TTP) diagrams together with the continuous-cooling-transformation/precipitation (CCT/CCP) diagrams have been used for over seventy years to represent the kinetics of phase transformations in steels to guide heat-treating.¹²¹⁾ In the case of austenitic stainless steels, the final heat-treatment before use is often solution annealing, particularly in the non-stabilized austenitic stainless steels. So, for these steels, the TTT/TTP diagrams are mainly used to represent the sequence of precipitation and the competition among different phases. The available diagrams for these steels are normally isothermal TTT diagrams and only show the curves corresponding to the start of the precipitation. As the austenite in these steels is far more stable than the austenite in low carbon steels, the martensite start (M_s) and finish (M_f) lines are located at low temperatures are not usually show in these diagrams.

The microstructure of the austenitic stainless steels at room temperature following rapid cooling from the solution annealing temperature consists primarily of a low stacking fault energy polycrystalline matrix^{122–124)} and the wrought materials present high frequency of annealing twins.¹²⁵⁾ The solution annealing heat-treatment is carried out around 1050°C, because higher solution temperatures may cause abnormal grain growth, particularly in the stabilized steels.¹²⁶⁾ However, even after rapid cooling austenite is rarely the only phase present. The most common phases present after the solution annealing heat treatment are Ti(N, C), TiC, Nb(C, N), $Ti_4C_2S_2$ and oxide inclusions containing variable contents of silicon, chromium, niobium, titanium and aluminum. The total volume fraction of these phases after the solution annealing is usually less than 0.5 vol%. After precipitation the total volume fraction of non-austenitic phases is usually less than 10 vol%.^{25,29,32)}

Carbide and nitride (in the high N steels) precipitation precedes the precipitation of intermetallic phases. The precipitation of $M_{23}C_6$ on the grain boundaries almost always takes place first. A comparison between the curve for the start of $M_{23}C_6$ with that for the MC in the stabilized steels reveals that the MC start curve is located at higher temperatures and longer times.^{29,127)} The upper part of both curves

Fig. 11. Time-temperature-precipitation diagram of the DIN W. Nr. 1.4970 austenitic stainless steel solution annealed for 30 min at 1130°C and water quenched prior to aging (after A. F. Padilha, USP, Brazil). The stability regions of the various precipitated phases are represented by C-curves.

cross at about 850°C. For this reason in stabilized steels it is usual practice to carry out a precipitation heat-treatment after solution annealing, a stabilization heat treatment. This treatment is carried out between 850 and 900°C to induce the precipitation of MC carbides and reduce the risk of occurrence of intergranular corrosion due to the precipitation of $M_{23}C_6$ (see Fig. 11).

The M_6C precipitation depends on the presence of Mo and Nb in the steels and only takes place for long times and in small amounts. Figure 11 shows²⁹⁾ the TTT diagram of a Fe-15wt%Cr-15wt%Ni-1.2wt%Mo Ti stabilized austenitic steel containing 45 ppm (in wt%) of boron. Notice that in this alloy the precipitation of intermetallic phases and of M_6C did not occur.^{29,128)} The primary phase TiN, (Ti, Mo)C and $Ti_4C_2S_2$, that remained after the solution annealing are not shown in the diagram. The mentioned low boron content was enough to cause a boride precipitation.

The precipitation of intermetallic phases takes place after precipitation of carbides and nitrides due to the following factors: (i) the intermetallic phase, sigma and Laves in particular, do not dissolve carbon and nitrogen; (ii) the diffusivities of the substitutional elements that form these phases are low; (iii) the orientation relationship of these phases with austenite are not favorable for their nucleation, especially for sigma phase. These same arguments can explain why the chi phase precipitation can precede sigma phase precipitation, as mentioned in Sec. 4.1.2. It is believed that chi phase may dissolve carbon and moreover shows more favorable orientation relationships with the austenite than sigma. The chi phase precipitation depends also on the presence of Mo and/or Ti in the steel, and Laves phase precipitation depends on the presence of Mo, Nb and/or Ti. The sigma phase is the only intermetallic phase among the three mentioned above that occurs in the binary Fe-Cr system. In the steels containing Mo and/or Ti, precipitation of Laves phase occurs below 850°C. The presence of Nb significantly increases the highest temperature in which sigma and Laves phase can form, increasing it to about 950°C.¹²⁹⁾ According to Lai,⁷⁴⁾ below 700°C the precipitation of sigma phase in an AISI 316 steel takes place after Laves (η) phase precipitation is finished. The Laves phase nucleates predominantly on dislocations while the sigma phase nucleates mainly on grain boundaries.⁷⁰⁾ Figure 12 shows²⁵⁾ the TTT diagram of an AISI 316 steel. It is interesting to point out that, in this case, the steel contained only 2.05 wt% Mo and

Fig. 12. Time-temperature-precipitation diagram of the AISI 316 austenitic stainless steel solution annealed for 1.5 h at 1260°C and water quenched prior to aging (after Ref. 25)). The stability regions of the various precipitated phases are represented by C-curves. σ =sigma phase, χ =chi phase, η =eta phase (Laves phase).

M_6C was not found.²⁵⁾ In the same work, another AISI 316 L steel with 2.66 wt% Mo M_6C could also be found.

Only a very limited number of TTP diagrams are available. The main reason for this is probably the complexity of the precipitation reactions in these steels that require a large amount of work for the determination of such a diagram.

7. Martensite Formation

Austenite in stainless steels in general and the austenite in the 300 steels series in particular is not a stable phase. In the solution-treated condition, the M_s temperature is normally below room temperature. The M_d temperature, the temperature below which martensite will form under deformation, of the majority of those steels is above room temperature. Two kinds of martensite can occur in stainless steels: α' (bcc, ferromagnetic) and ϵ (hcp, non-ferromagnetic). Transformation of austenite to martensite can be also induced in austenitic stainless steels by cathodic charging of hydrogen.¹³⁰⁾ The lattice parameters are typically:

$$a_{\alpha'} = 0.2872 \text{ nm};$$

and

$$a_{\epsilon} = 0.2532 \text{ nm}; \quad c_{\epsilon} = 0.4114 \text{ nm}$$

Assuming¹³¹⁾ $a_{\gamma} = 0.3585 \text{ nm}$, one can calculate that the $\gamma \rightarrow \alpha'$ transformation causes a volume increase of 2.57%, while the $\gamma \rightarrow \epsilon$ transformation causes a volume decrease of 0.81%. The orientation relationship between the parent phase and martensite most often reported for stainless steels are:

$$(111)_{\gamma} // (011)_{\alpha'}$$

$$[\bar{1}\bar{1}0]_{\gamma} // [\bar{1}\bar{1}1]_{\alpha'}$$

and

$$(111)_{\gamma} // (0001)_{\epsilon}$$

$$[\bar{1}\bar{1}0]_{\gamma} // [\bar{1}210]_{\epsilon}$$

7.1. Transformation during Cooling

There are several empirical equations that relate the M_s temperature to the chemical composition. Eichelmann and Hull's¹³²⁾ is one of the most widely used:

$$M_s(^{\circ}\text{C}) = 1302 - 42(\%\text{Cr}) - 61(\%\text{Ni}) - 33(\%\text{Mn}) \\ - 28(\%\text{Si}) - 1667(\%[\text{C} + \text{N}]) \dots\dots\dots(4)$$

Equation (4) suggests that many steels in Table 1, when cooled to cryogenic temperatures, will form α' martensite. The ability to form α' martensite becomes greater during cooling after sensitization. M_{23}C_6 precipitation at the grain boundaries causes impoverishment of chromium, carbon and other alloying elements in the vicinity of the grain boundaries. This leads to a higher M_s temperature, making the material more susceptible to the formation of α' martensite close to the grain boundaries during cooling.¹³³⁾ For ε martensite no equations like Eq. (4) are reported. However it is reasonable to expect that the formation of ε martensite increases with a decrease in the stacking fault energy of austenite.^{134,135)}

7.2. Strain Induced Transformation

The most frequent case of martensite formation at room temperature in stainless steels is that of strain induced martensite.

The formation and the amount of α' and ε depend on the steel composition, on its stacking fault energy, and on the temperature, amount and rate of deformation. According to Kaieda and Oguchi,¹³⁶⁾ the amount of α' depends also on the stress state during deformation.

There are several empirical equations that relate the M_d temperature with the chemical composition. One of the most often employed is due to Angel¹³⁷⁾:

$$M_d(30/50)(^{\circ}\text{C}) = 413 - 13.7(\%\text{Cr}) - 9.5(\%\text{Ni}) \\ - 8.1(\%\text{Mn}) - 18.5(\%\text{Mo}) - 9.2(\%\text{Si}) \\ - 462(\%[\text{C} + \text{N}]) \dots\dots\dots(5)$$

Where $M_d(30/50)(^{\circ}\text{C})$ is the temperature at which 50 vol% α' is formed after a true tensile strain of 30%.

For the majority of austenitic stainless steels, the M_d temperature is above room temperature. For ε martensite such empirical equations are not available. The susceptibility of the austenite to form martensite and the amount of martensite formed increase with a decrease in the deformation temperature. The effect of deformation rate is difficult to study because, as the deformation rate is increased, the specimen temperature is also increased due to Joule heating.

The simultaneous formation of α' and ε makes the understanding of their formation mechanism difficult. Mangonon and Thomas,^{138,139)} working with an AISI 304 stainless steels, found that for a 20% deformation at -196°C , the amount of α' formed could reach values around 50 vol%. During deformation, the amount of ε increased until 5% of deformation and afterwards decreased. On the other hand, the amount of α' increased continuously with deformation. According to those authors,^{138,139)} α' martensite formed preferentially at the intersections between the ε plates with the twin boundaries and with grain boundaries. Those same authors further reported that ε martensite could also form during cooling to low temperatures in the absence of plastic deformation, whereas for α' formation deformation was necessary. Seetharaman and Krishnan,¹⁴⁰⁾ working with an AISI 316 steel, also found that during deformation at low temperatures the formation of ε martensite precedes the formation of α' . They also found that the amount of ε increases with the deformation, goes through a maximum and afterwards decreases, whereas the amount of α' continuously increases with deformation.

The results of Mongonon and Thomas^{138,139)} and of Seetharaman and Krishnan¹⁴⁰⁾ suggest the following transformation sequence: $\gamma \rightarrow \varepsilon \rightarrow \alpha'$; ε martensite is generated from austenite, and is then transformed into α' martensite; α' martensite can be also directly formed from austenite.

When stainless steels containing deformation induced martensite are annealed, the martensite may revert to austenite. This reversion usually occurs at temperatures lower and for shorter times than those required for the recrystallization of the deformed stainless steel.¹⁴¹⁾ The formability of the austenitic alloys is influenced greatly by martensitic transformation during straining.^{142,143)} Recently, Burstein and co-workers¹⁴⁴⁾ showed that strain induced martensite in AISI 304L can be removed by appropriate electrochemical treatment in aqueous solutions at much lower temperatures than conventional annealing heat treatments.

Acknowledgements

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and to FAPESP (contract 99/10796-8) for the financial support.

REFERENCES

- 1) B. Strauß and E. Maurer: *Kruppsche Monatsh.*, **1** (1920), 120.
- 2) ASM Speciality Handbook: Stainless Steels, ed. by J. R. Davis, ASM International, Materials Park, OH, (1994), 13.
- 3) V. G. Rivlin and G. V. Raynor: *Int. Met. Rev.*, **25** (1980), 21.
- 4) ASM Handbook, Vol. 3: Phase Diagrams, ed. by H. Baker, ASM International, Materials Park, OH, (1992).
- 5) H.-J. Eekstein: *Korrosionbeständige Stähle*, Deutscher Verlag für Grundstoffindustrie GmbH, Leipzig, (1990), 18.
- 6) Metals Handbook, 8th Ed.: Metallography, Structures and Phase Diagrams, Vol. 8, ASM International, Materials Park, OH, (1973), 421.
- 7) J. Bechtoldt and H. C. Vacher: *J. Res. Natl. Bur. Stand.*, **58** (1957), 7.
- 8) E. Folkhard: *Welding Metallurgy of Stainless Steels*, Springer-Verlag, Wien, (1984), 1.
- 9) A. L. Schaeffler: *Weld. J.*, **26** (1947), Res. Suppl., 603s.
- 10) A. L. Schaeffler: *Iron Age*, **162** (1948), 73.
- 11) A. L. Schaeffler: *Met. Prog.*, **56** (1949), 680,680B.
- 12) *Welding Handbook*, Vol. 4: Metals and Their Weldability, 6th Ed., American Welding Society, Miami, Florida, (1972).
- 13) W. T. DeLong: *Weld. J.*, **53** (1974), Res. Suppl., 273s.
- 14) F. C. Hull: *Weld. J.*, **52** (1973), Res. Suppl., 193s.
- 15) R. H. Espy: *Weld. J.*, **61** (1982), Res. Suppl., 149s.
- 16) M. Schirra: *Stahl Eisen*, **112** (1992), 117.
- 17) G. K. Allan: *Ironmaking Steelmaking*, **22** (1995), 465.
- 18) H. Tuma, M. Vyclický and K. Löbl: *Arch. Eisenhüttenwes.*, **41** (1970), 983.
- 19) H. Gerlach: *Drahtwelt*, **56** (1970), 25.
- 20) A. Westgren: *Nature*, **132** (1933), 480.
- 21) P. D. Southwick and R. W. K. Honeycombe: *Met. Sci.*, **16** (1982), 475.
- 22) H. J. Goldschmidt: *J. Iron Steel Inst.*, **160** (1948), 345.
- 23) J. Philibert, G. Henry, M. Robert and J. Plateau: *Mem. Sci. Rev. Metall.*, **58** (1961), 557.
- 24) C. Da Casa, V. B. Nileswhar and D. A. Melford: *J. Iron Steel Inst.*, **207** (1969), 1325.
- 25) B. Weiss and R. Stickler: *Metall. Trans. A*, **3** (1972), 851.
- 26) U. K. Mudali, P. Shankar, D. Sundaraman and R. K. Dayal: *Mater. Sci. Technol.*, **15** (1999), 1451.
- 27) M. Deighton: *J. Iron Steel Inst.*, **208** (1970), 1012.
- 28) J. E. Spruiell, J. Scott, C. S. Ary and R. L. Hardin: *Metall. Trans. A*, **4** (1973), 1533.
- 29) A. F. Padilha, G. Schanz and K. Anderko: *J. Nucl. Mater.*, **105** (1982), 77.
- 30) M. Lagerquist and R. Lagneborg: *Scand. J. Metall.*, **1** (1972), 81.
- 31) H. Kokawa, M. Shimada and Y. S. Sato: *JOM*, **52** (2000), No. 7, 34.
- 32) A. S. Grot and J. E. Spruiell: *Metall. Trans. A*, **6** (1975), 2023.
- 33) J. A. Leitnaker and Bentley: *Metall. Trans. A*, **8** (1977), 1605.
- 34) F. E. Asbury and G. Willoughby: *J. Iron Steel Inst.*, **204** (1966), 32.
- 35) L. E. Toth: *Transition Metal, Carbides and Nitrides*, Academic Press, New York, (1971).
- 36) H. Holleck: *Binäre und ternäre Carbide- und Nitridsysteme der Übergangsmetalle*, Gebrüder Bornträger, Berlin, (1984).
- 37) H. O. Aandén, A. Henjered and H. Norden: *J. Mater. Sci.*, **15** (1980), 2365.
- 38) T. Thorvaldsson and G. L. Dunlop: *Met. Sci.*, **16** (1982), 184.

- 39) S. R. Keown and F. B. Pickering: Proc. Conf. Creep Strength in Steel and High-Temperature Alloys, Sheffield, Metals Society, London, (1974), 134.
- 40) P. G. Stone, J. Orr and J. C. Guest: *J. British Nucl. Energy Soc.*, **14** (1975), 25.
- 41) A. R. Jones, P. R. Howell and B. Ralph: *J. Mater. Sci.*, **11** (1976), 1593.
- 42) A. R. Jones, P. R. Howell and B. Ralph: *J. Mater. Sci.*, **11** (1976), 1600.
- 43) L. K. Singhal and J. W. Martin: *J. Iron Steel Inst.*, **205** (1967), 947.
- 44) T. Thorwaldsson and G. L. Dunlop: Proc. 5th Int. Conf. on Strength of Metals and Alloys, Vol. 1, ed. by P. Hasen, V. Gerold and G. Kostorz, Pergamon Press, Aachen, (1979), 755.
- 45) T. Thorwaldsson and G. L. Dunlop: *Met. Sci.*, **14** (1980), 513.
- 46) P. R. Howell, J. O. Nilsson and G. L. Dunlop: *J. Mater. Sci.*, **13** (1978), 2022.
- 47) A. C. Franker and H. H. Stadelmaier: *Trans. Am. Inst. Mining Met. Eng. (AIME)*, **245** (1969), 847.
- 48) H. Thier, A. Bäuml and E. Schmidtman: *Arch. Eisenhüttenwes.*, **40** (1969), 333.
- 49) H. J. Goldschmidt: Interstitial Alloys, Butterworths, London, (1967).
- 50) C. Qiu: *Steel Res.*, **64** (1993), 618.
- 51) H. Tuma, P. Gröbner and K. Löbl: *Arch. Eisenhüttenwes.*, **40** (1969), 727.
- 52) J. R. Gwyther, M. R. Hobdell and A. J. Hooper: *Met. Technol.*, **1** (1974), 406.
- 53) H. W.-Tai and R. W. K. Honeycombe: *Mater. Sci. Technol.*, **1** (1985), 385.
- 54) G. D. Barbabala, L. H. de Almeida, T. L. da Silveira and I. Le May: *Mater. Charact.*, **26** (1991), 1.
- 55) C. P. Tabrett, I. R. Sare and M. R. Ghomashchi: *Int. Mater. Rev.*, **41** (1996), 59.
- 56) G. L. F. Powell and J. V. Bee: *J. Mater. Sci.*, **31** (1996), 707.
- 57) C. T. Sims: The Superalloys, ed. by C. T. Sims and W. C. Hagel, John Wiley & Sons, New York, (1972), 259.
- 58) H. J. Beattie, Jr. and W. C. Hagel: *Trans. Am. Inst. Mining Met. Eng.*, **233** (1965), 272.
- 59) W. Treitschke and G. Tammann: *Z. Anorg. Chem.*, **55** (1907), 402.
- 60) E. C. Bain and W. E. Griffiths: *Trans. Am. Inst. Mining Met. Eng.*, **75** (1927), 166.
- 61) E. R. Jett and F. Foote: *Metals and Alloys*, **7** (1936), 207.
- 62) G. Bergman and D. P. Shoemaker: *J. Chem. Phys.*, **19** (1951), 515.
- 63) M. S. Dean and W. J. Plumbridge: *Nucl. Energy*, **21** (1982), 119.
- 64) M. H. Lewis: *Acta Metall.*, **14** (1966), 1421.
- 65) F. R. Beckitt: *J. Iron Steel Inst.*, **207** (1969), 632.
- 66) P. Duhaj, J. Ivan and E. Makovický: *J. Iron Steel Inst.*, **206** (1968), 1245.
- 67) H. Wiegand and M. Doruk: *Arch. Eisenhüttenwes.*, **33** (1962), 559.
- 68) L. K. Singhal and J. W. Martin: *Acta Metall.*, **16** (1968), 1441.
- 69) J. Barcik: *Mater. Sci. Technol.*, **4** (1988), 5.
- 70) K. W. Andrews: *Nature*, **164** (1949), 1015.
- 71) J. S. Kasper: *Acta Metall.*, **2** (1954), 456.
- 72) H. Hughes and D. T. Llewellyn: *J. Iron Steel Inst.*, **192** (1959), 170.
- 73) I. C. I. Okafor and O. N. Carlson: *Metall. Trans. A*, **9** (1978), 1651.
- 74) J. K. L. Lai: *Mater. Sci. Eng.*, **58** (1983), 195.
- 75) B. Hattersley and W. Hume-Rothery: *J. Iron Steel Inst.*, **204** (1966), 683.
- 76) K. Bungardt, G. Lennartz and K. Wetzlar: *Arch. Eisenhüttenwes.*, **30** (1959), 429.
- 77) A. W. Denhan and J. M. Silcock: *J. Iron Steel Inst.*, **207** (1969), 585.
- 78) I. Kirman: *J. Iron Steel Inst.*, **207** (1969), 1612.
- 79) H.-J. Kestenbach and L. O. Bueno: *Mater. Sci. Eng.*, **66** (1984), L19.
- 80) A. F. Padilha, M. Pohl and L. V. Ramanathan: *Prakt. Metallogr.*, **31** (1994), 436.
- 81) A. V. Kington and F. W. Noble: *Mater. Sci. Technol.*, **11** (1995), 268.
- 82) J. M. Vitek, S. A. David, D. J. Alexander, J. R. Keiser and R. K. Nanstad: *Acta Metall. Mater.*, **39** (1991), 503.
- 83) A. Mateo, L. Llanes, M. Anglada, A. Redjaimia and G. Metauer: *J. Mater. Sci.*, **32** (1997), 4533.
- 84) D. J. Powell, R. Pilkington and D. A. Miller: *Acta Metall.*, **36** (1988), 713.
- 85) R. A. P. Ibañez, G. D. de Almeida Soares, L. H. de Almeida and I. Le May: *Mater. Charact.*, **30** (1993), 243.
- 86) T. M. Williams, J. M. Titchmarsh and D. R. Arkell: *J. Nucl. Mater.*, **107** (1982), 222.
- 87) J.-O. Nilsson and P. Liu: *Mater. Sci. Technol.*, **7** (1991), 853.
- 88) S. Heino, E. M. Knutson-Wedel and B. Karlsson: *Mater. Sci. Technol.*, **15** (1999), 101.
- 89) P. Liu, A. H. Stigenberg and J.-O. Nilsson: *Acta Metall. Mater.*, **43** (1995), 2881.
- 90) J.-O. Anderson and N. Lange: *Metall. Trans. A*, **19A** (1988), 1385.
- 91) P. Gustafson: *Metall. Trans. A*, **19A** (1988), 2531.
- 92) T. Matsuo, G. Gao, Y. Kondo and R. Tanaka: *Tetsu-to-Hagané*, **71** (1986), 869.
- 93) G. Chen, X. Xie, K. Ni, Z. Xu, M. Zhang and Y. Ju: Proc. Superalloys 80, ed. by J. K. Tien et al., ASM, Metals Park, OH, (1980), 323.
- 94) P. G. Stone, J. Orr and J. C. Guest: *J. British Nucl. Energy Soc.*, **15** (1975), 25.
- 95) C. S. Whitcroft and J. W. Martin: *Mater. Charact.*, **39** (1997), 91.
- 96) I. Kirman and D. H. Warrington: *J. Iron Steel Inst.*, **205** (1967), 1264.
- 97) P. Duwez and F. Odell: *J. Electrochem. Soc.*, **97** (1950), 299.
- 98) R. P. Reed: *JOM*, **41** (1989), 16.
- 99) W. M. Small: *Scr. Metall. Mater.*, **24** (1990), 1695.
- 100) I. F. Machado and A. F. Padilha: *Steel Res.*, **67** (1996), 285.
- 101) R. F. A. Jargelius-Pettersson: *Z. Metallkd.*, **89** (1998), 177.
- 102) H. Thier, A. Bäuml and E. Schmidtman: *Arch. Eisenhüttenwes.*, **40** (1969), 333.
- 103) V. Vodárek: *Scr. Metall. Mater.*, **25** (1991), 549.
- 104) H. Hughes: *J. Iron Steel Inst.*, **205** (1967), 775.
- 105) W. C. Hagel and H. J. Beattie, Jr.: *Trans. Am. Soc. Met.*, **49** (1957), 978.
- 106) D. H. Jack and K. H. Jack: *J. Iron Steel Inst.*, **210** (1970), 790.
- 107) R. Ayer, C. F. Klein and C. N. Marzinsky: *Metall. Trans. A*, **23A** (1992), 2455.
- 108) H. Brandis and E. Horn: *DEW-Technische Berichte (Germany)*, **9** (1969), 213.
- 109) H. J. Goldschmidt: *J. Iron Steel Inst.*, **209** (1971), 900.
- 110) H. J. Goldschmidt: *J. Iron Steel Inst.*, **209** (1971), 910.
- 111) J. R. Donati, D. Guttmann and G. Zacharie: *Rev. Métall., Cah. Inf. Tech.*, **71** (1974), 917.
- 112) A. F. Padilha and G. Schanz: *J. Nucl. Mater.*, **95** (1980), 229.
- 113) X. X. Yao: *Mater. Sci. Eng. A*, **A271** (1999), 353.
- 114) H. Kaneko, T. Nishizawa and K. Tamaki: *J. Jpn. Inst. Met.*, **27** (1963), 299.
- 115) C. Da Casa and V. B. Nileshwar: *J. Iron Steel Inst.*, **207** (1969), 1003.
- 116) Y. Mandiang and G. Cizeron: *Mater. Sci. Eng. A*, **A206** (1996), 233.
- 117) M. G. Gemmill, H. Hughes, J. D. Murray, F. B. Pickering and K. W. Andrews: *J. Iron Steel Inst.*, **184** (1956), 122.
- 118) J. F. Brown, W. D. Clark and A. Parker: *Metallurgia*, **56** (1957), 215.
- 119) C. Frick and H. Rhode: *Arch. Eisenhüttenwes.*, **31** (1960), 419.
- 120) H. Kudielka and H. Rhode: *Z. Kristallogr.*, **114** (1960), 447.
- 121) E. S. Davenport and E. C. Bain: *Trans. Am. Inst. Mining Met. Eng.*, **90** (1930), 117.
- 122) R. E. Schramm and R. P. Reed: *Metall. Trans. A*, **6A** (1975), 1345.
- 123) C. G. Rhodes and A. W. Thompson: *Metall. Trans. A*, **8A** (1977), 1901.
- 124) W. Reick, M. Pohl and A. F. Padilha: *Steel Res.*, **67** (1996), 253.
- 125) J. M. Silcock, R. W. Rookes and J. Barford: *J. Iron Steel Inst.*, **204** (1966), 623.
- 126) A. F. Padilha, J. C. Dutra and V. Randle: *Mater. Sci. Technol.*, **15** (1999), 1009.
- 127) S. M. Box and F. G. Wilson: *J. Iron Steel Inst.*, **210** (1972), 718.
- 128) W. Kesternich and D. Meertens: *Acta Metall.*, **34** (1986), 1071.
- 129) G. Lennartz: *Mikrochim. Acta, Hefte 3* (1965), 405.
- 130) P. Rozenak, L. Zevin and D. Eliezer: *J. Mater. Sci.*, **19** (1984), 567.
- 131) D. J. Dyson and B. Holmes: *J. Iron Steel Inst.*, **208** (1970), 469.
- 132) G. J. Eichmann and F. C. Hull: *Trans. Am. Soc. Met.*, **45** (1953), 77.
- 133) E. P. Butler and M. G. Burke: *Acta Metall.*, **34** (1986), 557.
- 134) M. W. Bowkett, S. R. Keown and D. R. Harries: *Met. Sci.*, **16** (1982), 499.
- 135) P. Marshall: Austenitic Stainless Steels: Microstructure and Mechanical Properties, Elsevier Applied Science Publishers Ltd., New York, (1984), 23.
- 136) Y. Kaieda and A. Oguchi: *J. Mater. Sci.*, **20** (1985), 1847.
- 137) T. J. Angel: *J. Iron Steel Inst.*, **177** (1954), 1654.
- 138) P. L. Mongonon, Jr. and G. Thomas: *Metall. Trans. A*, **1A** (1970), 1577.
- 139) P. L. Mongonon, Jr. and G. Thomas: *Metall. Trans. A*, **1A** (1970), 1587.
- 140) V. Seetharaman and R. Krishnan: *J. Mater. Sci.*, **16** (1981), 523.
- 141) L. F. M. Martins, R. L. Plaut and A. F. Padilha: *ISIJ Int.*, **38** (1998), 572.
- 142) S. F. Peterson, M. C. Mataya and D. K. Matlock: *JOM*, **49** (1997), No. 9, 54.
- 143) V. Tayan, R. H. Wagoner and J. K. Lee: *Metall. Mater. Trans. A*, **29A** (1998), 2161.
- 144) G. T. Burstein, I. M. Hutchings and K. Sasaki: *Nature*, **407** (2000), 885.