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MICROSTRUCTURAL STUDIES OF ADVANCED AUSTENITIC STEELS

November 15th 1989

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Report prepared by
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ABSTRACT

This report presents the first complete microstructural and analytical electron microscopy study of Alloy AX5, one of a series of advanced austenitic steels developed by Maziasz and co-workers [1-7] at Oak Ridge National Laboratory, for their potential application as reheater and superheater materials in power plants that will reach the end of their design lives in the 1990's. The advanced steels are modified with carbide forming elements such as titanium, niobium and vanadium. When combined with optimized thermo-mechanical treatments, the advanced steels exhibit significantly improved creep rupture properties compared to commercially available 316 stainless steels, 17-14 Cu-Mo and 800 H steels. The importance of microstructure in controlling these improvements has been demonstrated for selected alloys, using stress relaxation testing as an accelerated test method.

The microstructural features responsible for the improved creep strengths have been identified by studying the thermal aging kinetics of one of the 16Ni-14Cr advanced steels, Alloy AX5, in both the solution annealed and the solution annealed plus cold worked conditions. Time-temperature-precipitation diagrams have been developed for the temperature range 600 C to 900 C and for times from 1 h to 3000 h. Particle size measurements have shown that the MC precipitates formed on matrix dislocations resist coarsening for up to 3000 h at 900 C.

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Dislocations are shown to be essential for controlling the size and distribution of the MC precipitates, with 5-8% cold work giving less rapid recovery at 900 C than the 15-25% cold work applied to Din 1.4970 steel by Kesternich. Analytical electron microscopy studies have been used to follow the compositional evolution of the precipitate phases in alloy AX5 as a function of time and temperature. The results show that by careful control of the alloy composition and the degree of cold work, it is possible to develop extremely stable precipitate distributions in both the matrix and grain boundaries. This results in the new series of advanced austenitic steels having elevated temperature strengths approaching those of the superalloys.

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I. INTRODUCTION

The advanced austenitic steels discussed in this report have been developed recently by Maziasz and co-workers [1-7], at Oak Ridge National Laboratory (ORNL), for their potential application in nuclear reactors and in steam power generating plants. The new alloys have evolved after thirty years of research on austenitic steels, particularly 316 stainless steel, for structural components and fuel cladding in nuclear reactors. For example, 316 stainless steel was used in (a) the Dounreay Fast Reactor in 1959; (b) the Prototype Fast Reactor in 1974; and (c) the Fast Flux Test Facility at ORNL. It was originally anticipated that creep and embrittlement would be the primary failure modes during irradiation until Cawthorne and Fulton [8,9] in 1966/67 identified void induced swelling in 316 stainless steel cladding that had been irradiated in the Dounreay Fast Reactor. Since then, alloy design programs have focussed on compositional modifications and processing methods designed to optimize the resistance of 316 type stainless steels to irradiation damage. An important spin-off from these programs has been the development of modified austenitic stainless steels that also have significantly improved creep rupture resistance.

The development of irradiation resistant and creep resistant microstructures has only become possible with the gradual accumulation of microanalytical and kinetic data regarding the precipitate phase evolution as a function of time in 316 stainless steels. Such data are now being collected for the modified steels. Comparison of the precipitate phases observed in components removed from service with

those identified in 316 stainless steels after short term laboratory aging treatments has permitted reasonable extrapolation of microstructures and properties for twenty year lives. In the advanced austenitic steels it is hoped to extrapolate microstructures and creep properties out to thirty year design lives.

This report presents a detailed microstructural and compositional study of one of the advanced austenitic steels, Alloy AX5, and shows how microstructures can be optimized for creep strength by controlling the composition, amount of prior cold work and the aging conditions of this 16Ni-14Cr austenitic steel modified with titanium, niobium and vanadium.

Following the introduction, Chapter two begins with a review of the categories of stainless steels, explaining why 316 stainless steels have been selected for nuclear reactor components. The historical development during the last twenty five years of austenitic steels for improved irradiation resistance is discussed in Chapter three. The compositional evolution of 316 stainless steels, leading to the development of the present advanced austenitic stainless steels is traced in detail. In Chapter four, the crystal structures, compositions and morphologies of the precipitate phases identified in 316 stainless steels are reviewed and the phases deleterious to long term creep rupture strength are identified. The elevated temperature strengths of selected alloy modifications are compared with those of existing commercial stainless steels and the implications for alloy design in the modified steels are discussed.

The experimental procedures used in this research are described in Chapter five. The use of stress relaxation tests, not only as an accelerated method for predicting creep strength, but also for relating creep lives to microstructural condition, is introduced in Chapter six. Data supporting the use of such short term tests for screening the creep strengths of new materials, are presented for selected alloy modifications.

A detailed study of one of the most promising alloy modifications, Alloy AX5, is then initiated by presenting (a) the isothermal aging kinetics of the solution annealed condition in Chapter seven, and (b) the isothermal aging kinetics of the solution annealed plus cold worked condition in Chapter eight. Both Chapters seven and eight contain detailed microstructural studies for aging times ranging from 1 h to 3000 h at temperatures of 600 C to 900 C. Analytical electron microscopy data from the phases identified in Chapters seven and eight are presented in Chapter nine, together with compositional models for precipitate phase evolution.

The Time-Temperature-Precipitation (TTP) diagrams for Alloy AX5, related developmental steels and 316 stainless steels are compared in Chapter ten. Average MC precipitate size measurements are presented as a function of aging time at two different temperatures and also compared with existing models for precipitate coarsening in Chapter eleven. The effects of (a) solution annealing treatments and (b) solution annealing plus prior cold work are summarized and the implications for the long term service applications of these new advanced austenitic stainless

steels are discussed. The overall conclusions of this research are presented in Chapter twelve..

2. STAINLESS STEELS

Stainless steels are selected primarily for the level of corrosion resistance required in a given application and secondly for their mechanical properties, ease of fabrication, total cost and product availability. The corrosion resistance, oxidation resistance and aesthetic appearance of stainless steels requires a minimum of 12%, by weight, of the element chromium, which restricts the formation of austenite (γ loop) and promotes the formation of ferrite. This can be seen by comparing the Fe-C diagram in Figure 2.1 [10] with the Fe-Cr diagrams presented in Figures 2.2a and 2.2b [11,12]. In this chapter we shall briefly review the categories of stainless steels in order to explain why alloy modifications of 316 stainless steels, known as lean stainless steels, are strong candidate materials for the next generation of reheater and superheater pipes in steam power generating plants.

2.1 Categories of Stainless Steels

Stainless steels can be classified into the following five categories, whose compositions are summarized in Table I [13].

2.1.1 Ferritic Stainless Steels

Ferritic stainless steels contain 12-30% Cr and have low carbon contents (0.08-0.2%) to give good toughness and to minimize sensitization (i.e. the depletion of chromium due to the precipitation of chromium carbides). Molybdenum may be added to improve resistance to crevice corrosion and pitting. The yield strengths range from 275-415 MPa, giving good cold-formability, but these steels cannot be hardened to give martensite. The body centered cubic (BCC) structure of these

steels means that they undergo a ductile to brittle transition, limiting their application in load bearing structures. These steels are also susceptible to embrittlement by sigma phase (σ - FeCr) and alpha prime phase (α' - Cr-rich ferrite) and are not recommended for extensive service above 325 C. The requirement that service temperatures be increased to the range 600-700 C in the next generation power plants eliminates ferritic steels from further consideration.

2.1.2 Martensitic stainless steels

The chromium contents of martensitic stainless steels range from 12-18% with carbon contents of 0.1-1.0%. Figure 2.3 shows that carbon stabilizes the austenite phase at high temperatures in a 12% chromium steel [14]. The presence of both chromium and carbon gives these steels sufficiently high hardenability that they can be air-hardened to form martensite. Subsequent tempering gives yield strengths in the range 550 to 1860 MPa. However, these steels should not be used at temperatures above 500 C due to extensive precipitation of chromium carbides, Cr_{23}C_6 or M_{23}C_6 (where M = Fe, Cr).

2.1.3 Duplex Stainless Steels

Duplex stainless steels have chromium contents of 23-30% Cr with 2.5-7.0% Ni to stabilize the austenite phase, resulting in duplex austenite/ferrite microstructures at room temperature. These steels have similar corrosion resistance to austenitic stainless steels, higher yield strengths, which increase with increasing amounts of ferrite, but lower ductilities. The disadvantage of duplex stainless steels is their susceptibility to (a) α' embrittlement when held or slow cooled through

the temperature range 300-550 C, and (b) σ phase embrittlement when aged in the temperature range 550 to 950 C, with a maximum at 700 C. The risk of embrittlement again makes these steels unsuitable for long term service applications in the temperature range 500-700 C.

2.1.4 Austenitic Stainless Steels

Austenitic stainless steels contain 17-25% Cr plus sufficient (8-20%) nickel and manganese (2%) to stabilize the austenite phase to room temperature. They have low yield strengths (250-300 MPa) and are usually strengthened by cold work, solid solution strengthening or reduction of the stacking fault energy. The solubility of carbon in Fe-Ni-Cr austenite is low, approximately 0.5 wt% at 1100 C and 0.003 wt% at 600 C in an 18Cr-8Ni steel, as shown in Figure 2.4 [13]. Consequently, on heating at temperatures between 450 and 850 C, $M_{23}C_6$ precipitates can form at grain boundaries, depleting these regions of chromium and making them susceptible to intergranular corrosive attack--a phenomenon known as sensitization. This can be prevented by keeping the carbon content low, hence the nominal carbon composition of both type 304 (18Cr-8Ni) and type 316 (16Cr-10Ni) austenitic stainless steels is a maximum of 0.08%C, which can be readily achieved commercially. [Note: the most significant difference between types 304 and 316 steels is the addition of 2% Mo to 316 stainless steel to further enhance the corrosion resistance.] Recent advances in steelmaking technology have resulted in extra low carbon contents of 0.03% maximum in the 304L and 316L grades of austenitic steels. However, even with such low carbon contents, prolonged exposure in the critical temperature range still

results in extensive precipitation of grain boundary carbides. Consequently, methods other than simply reducing the carbon content must be developed to prevent sensitization.

In practice, stronger carbide forming elements such as Ti and Nb are used to stabilize austenitic stainless steels and prevent Cr_2C_6 precipitation. Austenitic steels with additions of Ti or Nb are designated types 321 and 347 respectively. Ideally the stoichiometric ratios 4:1 and 8:1, corresponding to weight percents Ti:C and Nb:C, are required to stabilize the steel (i.e. getter the carbon). These ratios are usually increased to 5:1 (Ti) and 10:1 (Nb) to account for solution of Ti and Nb in the austenite or, more likely, the removal of Ti and Nb as nitrides, TiN and NbN. The stabilized steels are suitable for applications in the temperature range 500-700 C.

For high temperature applications such as gas turbines, improved scaling resistance is required, leading to increased additions of Cr and Ni in the 310 type stainless steels (24Cr-19Ni). For greater work hardenability, the Cr and Ni contents are lowered (16Cr-6Ni) in the 301 type stainless steels. The nominal compositions of typical austenitic stainless steels are listed in Table I.

2.1.5 Precipitation Hardened Stainless Steels

Higher strength stainless steels can be achieved by precipitation hardening both austenitic (non-magnetic) and, more frequently, martensitic stainless steels. The hardening is achieved by solution treatment at, for example, 1200 C to dissolve all the alloying elements in solution, followed by quenching and then aging at temperatures in the

range 600 C to 800 C to form precipitates. The principal strengthening agents are carbides, intermetallic compounds and Cu or Cu-Ni precipitates. These steels can be used at higher temperatures than the martensitic grades, and the precipitation strengthened austenitic steels, because of their elevated temperature strengths, have formed the basis for the alloy developments discussed in this thesis.

Fossil energy electric power plants are currently operating with steam environments at 566 C and 31 MPa pressure and employ 300-series stainless steels such as types 304, 316, 321 or 347. However, significant improvements in efficiency could be achieved if higher temperature and pressure steam were used to run the turbine generators. Consequently, the Electric Power Research Institute (EPRI) and the Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program of the U. S. Department of Energy, have initiated an alloy design program to develop superheater/reheater tube materials capable of withstanding 650 C and 35 MPa pressure steam environments [15,16]. In order to identify the alloy design criteria and compositional modifications necessary to increase the elevated temperature strength of austenitic steels, the role of alloying elements in stainless steels will first be reviewed.

2.2 Role of Alloying Elements

As we have seen in Section 2.1, alloying elements in stainless steels play three major roles in addition to improving corrosion and oxidation resistance: (1) stabilization of the austenite or ferrite

phases; (2) reduction of sensitization; and (3) strengthening either by elements in solid solution or by precipitation.

2.2.1 Cr and Ni Equivalents

The tendency of elements to stabilize ferrite or austenite can be conveniently expressed by the following empirical relationships, known as the Cr equivalent and Ni equivalent.

$$\begin{aligned} \text{Cr Equivalent} = \% \text{Cr} + 2 \times \% \text{Si} + 1.5 \times \% \text{Mo} + 5 \times \% \text{V} \\ + 5.5 \times \% \text{Al} + 1.75 \times \% \text{Ti} + 0.75 \times \% \text{W} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Ni Equivalent} = \% \text{Ni} + \% \text{Co} + 0.5 \times \% \text{Mn} + 0.3 \times \% \text{Cu} \\ + 30 \times \% \text{C} + 25 \times \% \text{N} \end{aligned} \quad (2)$$

From these equations it can be seen that the ferrite stabilizing elements include Cr, Si, Mo, V, Al, Nb, Ti and W, while the austenite stabilizing elements are Ni, Co, Mn, Cu, C and N. Similar equations are plotted in the Schaeffler diagrams (Figure 2.5), which were originally developed for air cooled weld deposits, but which can be used to estimate the phases present at room temperature in a stainless steel [17].

2.2.2 Sensitization

Although the elements Ti and Nb are predominantly used to improve resistance to sensitization in 316 stainless steels, other elements such as V and Mo may also be incorporated into the carbides, with the removal of Mo then deteriorating the corrosion resistance of the steel. It should be noted that precipitation of Cr_2C_6 , TiC and NbC occurs predominantly at grain boundaries, since the large lattice mismatch, particularly of TiC and NbC, makes nucleation in the austenite matrix

difficult. However, if nucleation sites such as dislocations are introduced into the matrix, uniform distributions of MC precipitates [where $M = (Ti, Nb, V, Mo)$], which also strengthen the matrix, can then be formed.

2.2.3 Precipitates

Austenitic stainless steels are complex alloys, whose structure may not be single phase after prolonged annealing. For example, the isothermal section of the Fe-Ni-Cr equilibrium phase diagram at 650 C shows that all the type 300 series austenitic steels fall into the two phase (γ plus σ) field (Figure 2.6) [18]. In the presence of multiple alloying elements the precipitation behavior becomes complex, with the potential formation of carbides, nitrides, carbonitrides, borides, phosphides, sulphides, borosulphides and intermetallic compounds other than σ phase. A summary of these precipitate phases is presented in Table II [19-23]. The kinetics of precipitate phase formation will be discussed in detail in Chapter 4, but is critically dependent on minor compositional changes and small variations in thermomechanical processing. For example, the elements Si, Mo, Ti, P and Mn increase the rate of formation of the embrittling σ phase; higher chromium contents increase both the rate of formation and the range of temperature over which σ phase can develop; and cold work promotes σ phase since the dislocations assist nucleation. The development of modified austenitic steels with resistance to the formation of embrittling phases, such as σ phase, during their design lives of twenty, possibly thirty, years cannot be achieved without systematic analytical studies of metastable

phase formation in these multicomponent systems. This thesis will present the first detailed thermal aging study of one of these modified steels, Alloy AX5, for times up to 3000 h at temperatures of 600, 700, 800 and 900 C in Chapters 5 to 10.

2.3 Alloy Design Philosophy

Two approaches have been explored for the development of an improved creep resistant austenitic steel. The first approach considered the modification of higher Cr and Ni containing steels for improved corrosion and oxidation resistance as well as creep strength. The main disadvantage of such steels is their cost and the use of higher amounts of the strategic element chromium. The second approach is to develop a "lean" stainless steel (14-16%Cr), which could then be chromized to allow adequate protection on the steam side at 650 C, and which must also be protected on the fire side from the extremely corrosive liquid slag that forms on the tubing at temperatures in the range 600 - 700 C [24,25]. The cost advantage has resulted in the second approach being adopted by EPRI and ORNL.

The development of an advanced austenitic steel with improved creep strength requires alloy design and compositional modifications that will (1) increase the strength of the austenite matrix; (2) provide uniform distributions of stable matrix carbides; (3) increase resistance to recovery and prevent recrystallization; (4) eliminate embrittling phases such as intermetallics; (5) reduce or control grain boundary void formation; (6) prevent grain boundary sliding or migration; and (7) control the distribution(s) of stable precipitates at grain boundaries.

Before discussing potential compositional modifications that could achieve these goals, we shall first review, in Chapter 3, the alloy developments of 316 austenitic steel that have been necessary for improved resistance to void swelling and embrittlement in nuclear reactor applications. We shall then show how this knowledge provided the basis for alloy developments designed to optimize the creep rupture properties of the advanced austenitic steels.

TABLE I: COMPOSITIONS OF STAINLESS STEELS

Type	Cr	Ni	C	Mn	P	S	Si	Mo	other elements
<u>Ferritic</u>									
405	11.50/14.50	-	0.08	1.00	0.04	0.03	1.00	0.00	-
430	16.00/18.00	-	0.12	1.00	0.04	0.03	1.00	-	-
436	16.00/18.00	-	0.12	1.00	0.04	0.03	1.00	0.75/1.25	Nb+Ta5*C min. 0.70max.
442	18.00/23.00	-	0.20	1.00	0.04	0.03	1.00	-	-
<u>Martensitic</u>									
410	11.50/13.50	-	0.15	1.00	0.04	0.03	1.00	-	-
420	12.00/14.00	-	>0.15	1.00	0.04	0.03	1.00	-	-
431	15.00/17.00	1.25/2.50	0.20	1.00	0.04	0.03	1.00	-	-
440C	16.00/18.00	-	0.95/1.20	1.00	0.04	0.03	1.00	0.75	-
<u>Duplex</u>									
329	25.00/30.00	3.00/6.00	0.10	2.00	0.04	0.03	1.00	1.00/2.00	-
<u>Austenitic</u>									
304	18.00/20.00	8.00/10.25	0.08	2.00	0.045	0.03	1.00	-	-
304L	18.00/20.00	8.00/12.00	0.03	2.00	0.045	0.03	1.00	-	-
316	16.00/18.00	10.00/14.00	0.08	2.00	0.045	0.03	1.00	2.00/3.00	-
316L	16.00/18.00	10.00/14.00	0.03	2.00	0.045	0.03	1.00	2.00/3.00	-
321	17.00/19.00	9.00/12.00	0.08	2.00	0.045	0.03	1.00	-	Ti 5*C min.
347	17.00/19.00	9.00/13.00	0.08	2.00	0.045	0.03	1.00	-	Nb+Ta10 *C min.

TABLE I: COMPOSITIONS OF STAINLESS STEELS

Type	Cr	Ni	C	Mn	P	S	Si	Mo	other elements
<u>Precipitation Strengthened</u>									
S13800	12.25/13.25	7.50/8.50	0.05	0.10	0.01	0.008	0.10	2.00/2.50	Al 0.90 /1.35
S15500	14.00/15.50	3.50/5.50	0.07	1.00	0.04	0.03	1.00	-	N 0.01 Cu 2.50 /4.50 Cu+Ta 0.15 /0.45
S17400	15.50/17.50	3.00/5.00	0.07	1.00	0.04	0.03	1.00	-	Cu 3.00 /5.00 Cu+Ta 0.15 /0.45
S17700	16.00/18.00	6.50/7.75	0.09	1.00	0.04	0.04	1.00	-	Al 0.75 /1.50

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Oak Ridge, TN.

Figure 2.1 The iron-carbon phase diagram [10].

Figure 2.2a The iron-chromium phase diagram [11].

Figure 2.2b The low temperature portion of the iron-chromium phase diagram [12].

Figure 2.3 The effect of carbon on the equilibrium phases present in a 12%Cr steel [14].

Figure 2.4 The solubility of carbon in Fe-Cr-Ni austenite [13].

Figure 2.5 Constitution diagram (Schaeffler diagram) for stainless steel weld metal [13].

1	AISI 301	2	AISI 302	3	AISI 304	4	AISI 310
5	AISI 316	6	AISI 321	7	AISI 347		

2.6 Isothermal section of Fe-Cr-Ni equilibrium phase diagram at 650 C [18].

3. DEVELOPMENT OF THE ADVANCED AUSTENITIC STEELS

Type 316 austenitic stainless steel is used for the control rods in the reactor core and in the internal heat exchanger of the liquid metal fast breeder reactor (LMFBR) shown in Figure 3.1 [26]. In the future magnetic fusion reactor (MFR), shown in Figure 3.2 [26], type 316 steels are being considered as candidate first wall and blanket materials. The implementation of these steels has required compositional modifications, which have improved both the irradiation resistance and the elevated temperature properties as discussed below.

3.1 DEVELOPMENT OF AUSTENITIC STEELS FOR IRRADIATION RESISTANCE

In the early 1960's it was observed that exposure of 316 stainless steel to thermal neutrons at temperatures above 500 C caused a reduction in high temperature ductility [27-33], and it was proposed that this was due to He atoms migrating to grain boundaries and then clustering to form He bubbles [34-37]. He generation was attributed to neutron capture by boron-10 atoms, followed by the decay of the excited B-10 nucleus and transmutation to He atoms as follows:

In Ni containing alloys, a two step reaction between Ni atoms and the thermal neutrons was proposed for the generation of He:

In addition to a reduction in high temperature ductility, the volume of the austenitic steels increased and many internal voids were observed [9]. When the void population responsible for the volume increase was

estimated, it was found that its volume was greater than the total volume of He generated. Thus He generation could not be the only reason for void swelling. It was then suggested that voids were formed by vacancy capture in the He bubbles. Vacancies and interstitial atoms can be simultaneously created when a neutron bombards a lattice atom and displaces it from its original position. The created vacancies and interstitials can migrate, recombine and annihilate, but some may survive with the vacancies clustering at defect sinks, such as He bubbles, to form voids.

Void formation was first observed in irradiated 316 steel, used as a fuel cladding material in the FBR. This caused a problem with the design of the FBR core since extra space was required to allow for swelling of the fuel cladding and core component distortion. The U.S. alloy design program for developing LMFBR cladding and duct materials was, therefore, initiated in 1967 to characterize and understand the swelling and microstructural behaviour of austenitic steels in an irradiation environment [38]. At that time types 304 and 316 steels were selected as candidate materials for studies of void swelling induced by neutron irradiation in the Experimental Breeder Reactor II. In 1968, 20% cold worked type 316 steel was specified as the reference cladding and duct material in design studies for the Fast Flux Test Facility (FFTF) and the Clinch River Breeder Reactor (CRBR) because this steel had been used for fuel cladding in the U.K. Dounreay Fast Reactor and had been extensively studied by the British [39].

By 1974, experimental results indicated that the 20% cold worked type 316 steel had potential performance limitations as a reactor core material for the FBR, and alternative alloys were being identified. The U.S. Energy Research and Development Administration (ERDA) initiated an alloy development program for reactor core materials for LMFBR applications. The near term objective of the LMFBR program was to provide the microstructural evolution and swelling data for the reference material, 20% cold worked type 316 steels, in LMFBR environments. The far term objective was to provide fully qualified reactor core materials by testing and screening from 29 commercially available alloys and 35 developmental alloys.

Ten alloys from different classes had been selected as leading candidate alloys by 1977, with the prime candidate austenitic stainless steel class being alloy D9, a 12-16Cr, 14-15Ni, 2Mo steel with Si and Ti additions. The lower Cr level in this steel was intended to reduce σ phase formation. The Si and Ti additions, at that time, were believed to lessen the irradiation-induced swelling [40-44]. It was proposed that Ti may trap residual gases such as oxygen which may cluster to form voids [45], whereas Si could bind with vacancies to prevent them from migrating to void surfaces [40]. However, when the Si content was increased above 0.5 wt%, the swelling became worse due to precipitation of Ni and Si-rich phases which reduced the matrix Ni content and promoted swelling [46,47].

From 1977 to 1978 the U.S. initiated the "Alloy Development for Irradiation Performance" (ADIP) program, which then incorporated the FBR

alloy development as part of the fusion reactor materials development program. The ADIP program was aimed at the development of advanced alloys for first wall materials in the MFR, and was divided into five parallel paths: (A) austenitic stainless steels; (B) high strength Fe-Ni-Cr alloys; (C) reactive and refractory alloys; (D) innovative materials concepts; and (E) ferritic steels. Each path was requested to offer a prime candidate alloy (PCA) in its own alloy class. Based on the experience with D9 type alloys in the FBR program, a PCA austenitic stainless steel, 14Cr-16Ni with 0.24 Ti addition, was immediately selected.

By the early 1980's, studies of the Ti-modified austenitic steel after irradiation in the High Flux Isotope Reactor (HFIR) had revealed that the Ti-rich MC carbide precipitates in this steel significantly improved the swelling and embrittlement resistance by trapping the He at the MC/matrix interfaces [48-51]. This led to the understanding that control of the alloy composition and the pre-irradiation microstructure was essential for (a) determining the microstructural evolution during irradiation, and (b) reducing void swelling and grain boundary embrittlement. It had become clear that irradiation not only induced bubble and void formation, but also induced solute segregation and either induced or enhanced precipitation of certain phases [9,52-58]. As these phenomena were all closely related to the generation of helium, it was realized that the vacancy population responsible for swelling could be significantly reduced if both vacancies and interstitials migrated to bubble sinks and annihilated there [49,59-61]. This could

be achieved if a large number of fine He bubbles were introduced into the bulk matrix during irradiation, creating sinks with sufficiently high strengths to dominate the partitioning of both vacancies and interstitials.

A second important concept in alloy design for void swelling resistance is the critical bubble size, defined as the size at which the vacancy absorption and re-emission rates are equal. Above the critical size, He bubbles can transform to voids which grow by absorbing available vacancies, but below this size the bubbles can grow only by capturing available He atoms. Since the number of He atoms generated by irradiation is limited, a high population of fine He bubbles creates severe competition for the He atoms, reduces the number of He atoms available to each bubble for growth, and suppresses void swelling.

Recent research has shown that the creation of distributions of fine He bubbles can be achieved by pre-irradiation cold work treatments [7,62] and by controlling the precipitation of MC carbides [50,63,64]. The high dislocation density introduced by cold work increases the He bubble population by providing a large number of bubble nucleation sites. Additional nucleation sites are provided by MC carbides, which, due to their large positive volume misfit with the austenite matrix, trap He-vacancy complexes at the MC/austenite interfaces during MC particle growth. The MC carbides precipitated along matrix dislocations also reduce the accumulation of He at grain boundaries, giving increased resistance to irradiation-induced grain boundary embrittlement [65-69].

Matrix phosphide precipitates have also been identified as effective in trapping He atoms and refining He bubbles in an irradiated solution annealed 15.2Ni-13.6Cr austenitic steel modified with Ti and P additions [70,71]. Other commonly observed precipitate phases, such as M_6C (η phase) and $M_{23}C_6$ (τ phase), have smaller positive volume misfits and Laves phase has a negative volume misfit. These phases are not as effective in trapping He as the MC carbides. Although $M_{23}C_6$ appears to have little effect in trapping He atoms, early microstructural observations of irradiation effects indicated that grain boundaries with $M_{23}C_6$ precipitates were more resistant to embrittlement than precipitate-free grain boundaries. This suggested that grain boundary He embrittlement could be reduced by controlling the $M_{23}C_6$ precipitation at grain boundaries and the MC precipitate distribution in the matrix [35,36,72].

However, recent alloy design research has indicated that MC precipitates at grain boundaries may give increased resistance to He embrittlement [51,73,74]. These results have lead to the selection of an optimum thermo-mechanical treatment; solution anneal (SA) + 8 hrs at 800 C + 25 % cold work (CW); where SA + 8 hrs at 800 C was designed to develop MC carbides at the grain boundaries in the prime candidate alloy (PCA). This treatment significantly improved the embrittlement resistance up to 500 C, but was not effective at 600 C due to the dissolution of the grain boundary MC carbides [75]. It was anticipated that improved resistance to embrittlement might be achieved at higher temperatures if the stability of the MC carbides could be increased.

The presence of the irradiation induced phases, γ' (Ni_3Si),

G-phase ($M_6Ni_{16}Si_7$) and phosphide needles, was discovered in austenitic steels in the 1970's [56,76-79]. These phases do not normally occur in thermally aged austenitic steels, but once induced by irradiation, they may be eliminated by thermal aging at the irradiation temperature. The precipitation of irradiation induced phases is closely related to radiation induced solute segregation (RIS) [51,80,81]. RIS is the preferential flow of solute atoms to point defect sinks, increasing their solute concentrations. In irradiated austenitic steels it was observed that the concentrations of Si and Ni were higher, while those of Cr and Mo were lower at point defect sinks than in the unirradiated steels [7,81-85]. As the solute atoms build-up at defect sinks, the irradiation induced phases are then able to nucleate. This is demonstrated by the fact that the irradiation induced phases, G and γ' are both enriched in Si and Ni. RIS can also influence the precipitation of thermal phases. It was found that M_6C , which is a minor thermal phase enriched in Si and Ni, was dominant in the irradiated austenitic steels, while the precipitation of $M_{23}C_6$ (which may be low in both Si and Ni under irradiation), σ phase and χ phase, which are the dominant thermal phases, was greatly retarded [7,86-93]. The composition of Laves and phosphide phases are more flexible [7,50]. They may or may not be enriched in Si and Ni, and are stable in both thermally aged and neutron irradiated microstructures.

It is clear from the above discussion that the compositions of the precipitate phases are dictated by the composition of the local environment, which in turn is determined by irradiation enhanced

diffusion in the case of neutron irradiation or by local solute supersaturation during thermal aging [86,94]. This was demonstrated by Williams and Titchmarsh [95], who showed that it was possible to form G phase (normally an irradiation induced phase) by thermal aging a compositionally modified alloy. It should be noted that the presence of a large number of fine He bubbles may suppress RIS and favor the formation of the thermal phases [1].

From the alloy developments described above, it was concluded that irradiation resistant austenitic steels could be achieved by (1) development of stable carbides along grain boundaries; (2) development of fine MC carbides and/or fine phosphide in the austenite matrix; and (3) prevention of the formation of intermetallic phases such as Laves, χ and σ phases, which had either no effect or a negative effect on irradiation resistance [1]. A series of modified PCA's with additions of minor alloying elements such as Nb, Ti, V, Si and P was evaluated to identify the best compositional modification and preheat treatment for achieving these objectives [16,24]. It was proposed that a distribution of MC carbides along grain boundaries could be achieved by controlled additions of Ti, Nb, V and C. Increasing the C content was necessary to avoid intermetallic phase formation, which is encouraged by (a) low C content, and (b) solid solution Ti and Nb, which favor σ and Laves phase formation, respectively. The stability of MC carbides at higher temperatures was also improved by the combined additions of Ti, Nb and V. Matrix precipitation of fine MC carbides during irradiation was best obtained by adequate pretreatment, namely SA at 1100 C, to dissolve most

of the primary carbides, followed by 20-25 % CW. Matrix phosphides were obtained by P addition, with precipitation being enhanced in the presence of Nb and V. The recrystallization resistance of the PCA steels was also improved by the combined additions of Ti, Nb and V. Significant advances have, therefore, been made in the development of irradiation resistant austenitic steels during the last twenty years. Development of advanced alloys is continuing with research focussing on more variable starting microstructures and exposure to high fluences [7]. The microstructural improvements in the new alloys have not only produced improved irradiation resistance but also superior elevated temperature mechanical properties. This technology is now being transferred to increase the operating temperature range for austenitic steels in fossil energy applications.

3.2 DEVELOPMENT OF AUSTENITIC STEELS FOR CREEP RESISTANCE

The AR&TD Fossil Energy Materials Program of the U.S. DOE is now considering the advanced austenitic steels for application as superheater/reheater materials, which can operate in severe steam conditions of 31-35 MPa pressure at temperatures of 595-650 C [16,24]. Among the commercial alloys only alloy 800H approaches the required strength at temperature of 595 C and only Inconel 617 is satisfactory at 700 C. However, these alloys contain high percentages of strategic elements such as Cr, Ni, and especially 12% Co in Inconel 617, and are too expensive for superheater tubing. In contrast, austenitic steels would provide a less expensive alternative and are being developed to withstand design stresses of 100 Mpa at 700 C for 100,000 h. The

commercially available 17-14 CuMo steel, used in the Eddystone Unit-I power plant, has been selected as the reference alloy for this development program.

The rate of creep deformation of a material depends on the competition between strain-hardening and thermal softening in the regimes of primary and secondary (or steady state) creep. Strain hardening results from the increased dislocation density introduced by the application of a load, while thermal softening results from recovery processes, such as dislocation climb. Thus, an effective method for increasing creep strength is to suppress the recovery effect by impeding dislocation movement. Similarly, it is important to restrict grain boundary sliding, which may lead to the nucleation of cavities at grain boundaries, followed by their growth and coalescence to form cracks. The fine, stable, matrix MC carbide and phosphide dispersions together with the grain boundary $M_{23}C_6$ and MC carbides developed in the modified PCA for fusion applications, appear ideal for producing the higher creep strengths required in the fossil energy applications.

As discussed in Section 2.3, the modified PCA alloys are lean 14Cr-16Ni austenitic steels with additions of Ti, V, Nb, P, Si, and Cu [25,96]. The most recent modifications of these steels are designated the CE series and the AX series alloys, and their compositions can be compared with those of the commercial alloys in Table III. The creep rupture strengths of selected alloys have been compared by Maziasz and Swindeman [3] with those of 316 stainless steel, alloy 800H and 17-14CuMo steel at 700 C and a stress of 170 MPa. These data are presented

in Figure 3.3 and show that 316 stainless steel, alloy 800h and 17-14CuMo failed in 12h, 120h and 1400h respectively, whereas alloys AX5 and AX8 showed orders of magnitude improvement. In fact, AX steels have now been tested for 20,000h at 700 C and 170 MPa, with certain modifications exhibiting less than 1% creep strain. These results are promising and extrapolation of available data suggests that the advanced alloys could easily meet a design criterion of 100 MPa for 100,000h rupture resistance at 700C.

In the next chapter we shall examine the kinetics of phase evolution during thermal aging of 316 stainless steel in order to compare the results with those from one of the most promising AX steels, alloy AX5, in Chapters 5-10. The microstructural and analytical data presented in these chapters will identify the metastable phases responsible for the improved creep rupture strengths and will lead to a basic understanding of how the alloy compositions and thermomechanical treatments can be "fine tuned" to produce austenitic steels with the required properties.

TABLE III: CHEMICAL COMPOSITIONS OF AUSTENITIC STEELS

Alloy	Chemical Analysis (wt %)														
	C	Si	Mn	Ni	Cr	Ti	Nb	V	Mo	P	S	Cu	N	B	Co
<u>Creep Tests</u>															
316ES1	0.059	0.56	1.79	13.18	16.49	0.01	0.01	0.02	2.24	0.013	0.020	0.09	0.04	-	-
800H	0.080	0.24	0.90	31.90	19.50	-	-	-	-	-	0.003	0.54	-	-	-
17-14															
CuMo	0.098	0.95	0.83	13.85	16.49	0.21	0.45	0.07	1.96	0.014	-	3.07	0.03	-	-
CE0	0.072	0.41	1.80	16.00	14.20	0.24	0.10	0.57	2.45	0.071	0.007	0.03	0.02	0.005	0.008
CE1	0.085	0.21	1.64	16.19	13.14	0.21	0.12	0.52	2.30	0.076	0.008	0.04	0.02	0.005	0.008
CE2	0.079	0.26	1.89	16.00	14.53	0.31	0.11	0.58	2.26	0.069	0.008	0.03	0.02	0.005	0.008
CE3	0.086	0.21	1.75	16.20	14.50	0.27	0.11	0.56	2.41	0.071	0.008	1.96	0.01	0.005	0.008
AX5	0.076	0.12	2.04	16.20	13.90	0.27	0.15	0.52	2.46	0.024	0.015	.005	0.02	0.005	0.008
AX7	0.075	0.12	2.05	16.00	14.00	0.18	0.15	0.50	2.50	0.070	-	1.50	-	0.005	0.008
AX8	0.074	0.12	2.05	15.90	13.90	0.24	0.09	0.15	2.48	0.043	0.015	0.14	0.02	0.005	0.008
<u>TTP diagrams</u>															
1.4970	0.090	0.46	1.70	15.00	14.60	0.46	0.05	-	1.25	0.003	0.004	0.07	0.01	0.005	0.013
E 1250	0.100	0.58	6.04	9.46	15.30	-	1.20	0.24	1.02	-	-	-	-	0.007	-
316TiM	0.057	0.03	1.41	13.96	17.52	0.29	-	-	2.51	0.005	0.004	-	.004	-	-

Figure 3.1 Liquid metal fast breeder reactor (LMFBR) [26].

Figure 3.2 Tokamak controlled thermonuclear reactor (CTR) and typical thermal cycle conversion in the magnetic fusion reactor [26].

Figure 3.3 Creep rupture data for 316 stainless steel, alloy 800H, 17-14CuMo and selected CE and AX series austenitic steels [2].

4. PRECIPITATE PHASES AND THE KINETICS OF PRECIPITATION IN THERMALLY AGED AUSTENITIC STEELS

In 316 austenitic steels, the first precipitate phases to form are carbides, ($M_{23}C_6$, MC and M_6C), followed at longer aging times by intermetallic compounds, such as Laves, χ and σ phases. The kinetics of precipitation depends critically on alloy composition and thermal history. This chapter reviews the extensive literature relating to these phases and summarizes the kinetics of their precipitation in 316 and stabilized austenitic steels.

4.1 CARBIDES

4.1.1 $M_{23}C_6$ (τ carbide)

As early as 1930 Strauss et al. [97] proposed that Cr impoverishment was responsible for intergranular corrosion, but it was not until the 1950's and 1960's that electron microscopy confirmed the relationship between Cr carbides and stress corrosion cracking. Early research on Cr carbides was conducted on type 304 steels by Mahla and Nielsen [98] and Kinzel [99], who observed that Cr carbides were nucleated along dislocation lines if the steels were cold worked before aging. Cr carbide precipitation in type 316 steels was investigated by Garofalo [100] and Garofalo et al. [101,102], who observed that coarse carbides were nucleated at grain boundaries in solution annealed steels which were aged at 900 F and 1300 F, but that little Cr carbide nucleated within the grains. However, if the steels were cold worked then aged at the same temperatures, extensive precipitation on dislocations was observed. The creep strength was found to increase due to the pinning

effect of $M_{23}C_6$ particles on the dislocations. Once 316-type steels were selected for the LMFBR during the 1960's, extensive programs were initiated to study carbide precipitation and phase stability in both thermally aged and irradiated steels [87,103-111].

The Cr carbide observed in austenitic steels is $M_{23}C_6$ [112-115]. $M_{23}C_6$ has a complex FCC unit cell with a lattice constant of 1.06 nm and contains 92 metal and 24 carbon atoms (Figure 4.1) [114]. Cr atoms in the $Cr_{23}C_6$ lattice can be replaced by smaller Fe atoms, giving $(CrFe)_{23}C_6$, but as the Fe content increases it becomes possible for larger atoms, such as Mo, to be incorporated. Consequently, Wess and Stickler [103] have proposed the formula, $Cr_{16}Fe_3Mo_2C_6$ for the $M_{23}C_6$ carbide in type 316 steels. In addition to the replacement of Cr by metallic atoms, C may also be replaced by N, B and P [23].

$M_{23}C_6$ forms preferentially at high energy interfaces, such as high angle grain boundaries and incoherent twin boundaries, in 300 series austenitic steels which have been solution treated above 1100 C, quenched and aged in the temperature range 550-800 C [116,117]. Nucleation at low energy coherent twin boundaries has been reported but Lewis and Hattersley [118] indicated that the nucleation sites were provided by extrinsic dislocations which move into the twin boundary during deformation. Kinzel [99] proposed that grain boundary $M_{23}C_6$ nucleates coherently with one of the two austenite grains and grows into this grain by following the austenite lattice plane to which it is registered. Lewis and Hattersley [118] showed that this coherently matched lattice plane was the (111) plane and that the grain boundary

$M_{23}C_6$ has the following cube-cube orientation relationship with the austenite grain.

$$(100)_{M_{23}C_6} // (100)_{\gamma} \quad \text{and} \quad \langle 100 \rangle_{M_{23}C_6} // \langle 100 \rangle_{\gamma}$$

Singhal and Martin [119] suggested that growth of grain boundary $M_{23}C_6$ occurs by movement of the grain boundary into the austenite grain with which the $M_{23}C_6$ is out of register, so that growth of $M_{23}C_6$ would depend on the ease of boundary migration. Grain boundaries may be pinned if the $M_{23}C_6$ precipitates are in register with both austenite grains.

Intragranular nucleation of $M_{23}C_6$ has been reported in the austenite matrix and on dislocations generated (1) at undissolved carbides or inclusions during quenching of solution annealed samples, (2) by prismatic punching of dislocations as carbides grow during aging, or (3) by cold work prior to aging. $M_{23}C_6$ nucleated on dislocations produced by the punching mechanism often form stringers along the dislocation lines, with the orientation of these dislocations being in $\langle 110 \rangle$ and $\langle 112 \rangle$ directions [118,120].

The morphology of $M_{23}C_6$ has been reported as dendritic, globular, geometric forms including cubes, triangles and trapezoids [98,99,121], and long laths [23,122,123]. The form of grain boundary $M_{23}C_6$ was observed to depend on the orientation of the boundary and the misfit between the two grains [121], whereas the form of intragranular $M_{23}C_6$ was determined by the surface energy, with $\{111\}$ type interfaces having the lowest surface energies. Lewis and Hattersley [118] concluded that, in three dimensions, $M_{23}C_6$ particles should be polyhedra bounded with $\{111\}$ planar interfaces. Beckitt and Clark [120] observed that $\{110\}$ type

planes were also suitable interfaces and that the shape of the $M_{23}C_6$ particles could be almost a cube constructed by four {111} planes and two {110} planes. The long lath $M_{23}C_6$ were found to have two conjugate sets of {111} plane as interfaces [122].

After prolonged aging, especially at higher temperatures, $M_{23}C_6$ becomes unstable and dissolves or transforms to other phases, which vary as a function of alloy composition. Goldschmidt [114] has summarized the possible phase evolution of $M_{23}C_6$ and this is reproduced in Figure 4.2.

4.1.2 MC Carbides

The carbide-forming tendencies of alloying elements in austenitic steels increase in the order: Mn, Fe, Cr, Mo, V, Ti and Nb [115]. Hence, in the presence of V, Ti or Nb, precipitation of $M_{23}C_6$ can be significantly reduced, due to the decreased availability of carbon. Ti forms the monocarbide, TiC, whereas Nb and V can form both monocarbide, MC, and hemiacarbide, M_2C . However, only the monocarbide has been observed in austenitic steels. Monocarbides of the transition metals are FCC with carbon atoms in the octahedral sites, forming a NaCl type lattice [124]. According to Hagg's rule, the radius ratio of carbon to metal atoms should be less than 0.59 [125]. MC carbides have a range of stoichiometry, and their lattice parameters increase with increasing C content. Goldschmidt [114] suggested that Fe hardly dissolves in TiC and NbC, but dissolves more easily in the VC lattice, due to the similar atomic sizes of Fe and V. The monocarbides VC, TiC and NbC are completely soluble in one another and the lattice parameters of binary

carbide systems are given as a function of composition in Figure 4.3 [114].

High solution treatment temperatures (1100-1300 C) are required to dissolve primary MC carbides for redistribution during aging at 650-850 C. Precipitation occurs at grain boundaries, incoherent and coherent twin boundaries, dislocations, partial dislocations associated with stacking faults and in the austenite matrix. Although Ti, V and Nb have stronger carbon affinity than Cr, $M_{23}C_6$ precipitates first at grain boundaries due to the higher diffusivity of Cr in austenite. Figure 4.4 shows a Time-Temperature-Precipitation (TTP) diagram for $M_{23}C_6$ and Nb(Ti)C in a Ni-Cr austenitic steel [126]. At lower temperatures and shorter aging times, $M_{23}C_6$ is predominant, but after prolonged aging above 800 C, Dewey et.al. [127] confirmed that MC carbides precipitated at grain boundaries previously decorated with $M_{23}C_6$. Jones observed that MC nucleated preferentially at grain boundary steps in solution annealed austenitic steels [128]. In prestrained samples, MC was observed to nucleate at extrinsic dislocations in planar grain boundaries, resulting in a linear chain appearance, and at coherent twin boundaries. Nucleation of MC was observed at incoherent twin boundaries in both deformed and undeformed samples.

4.1.2.1 Precipitation on dislocations

Precipitation of MC on dislocations introduced by (a) aging, (b) plastic deformation at room temperature, or (c) plastic deformation at the aging temperature has been extensively studied [129-133]. Early investigations of Nb-containing austenitic steels revealed that

deformation caused very fine intragranular NbC precipitation, whereas precipitation in undeformed specimens was very sparse [134-136]. Haddrill et al. [129] suggested that NbC carbides on dislocations are completely coherent with the austenite lattice and obtained a cube-cube orientation relationship by electron diffraction:

$$(001)_{\gamma} \quad // \quad (001)_{\text{NbC}} \quad \text{and} \quad [001]_{\gamma} \quad // \quad [001]_{\text{NbC}}$$

This orientation relationship was confirmed for NbC and TiC by Aswegen et al. [131] and observed by Froes and Warrington [137] for TaC in a 18Cr-12Ni-2Ta-0.1C austenitic steel. It can be maintained as the carbides grow to 20 nm, but since the MC/ γ lattice mismatch is large (up to 25%), the strain field must be accommodated for continued particle growth. Since the concentration of quenched-in vacancies is low at the aging temperature, it has been suggested that this accommodation is achieved by flux of vacancies, from grain boundaries and climbing dislocations, to the precipitate/matrix interfaces. Thus, MC carbides nucleate and grow most easily at vacancy sources [116].

As the MC carbides on dislocations coarsen, secondary dislocations, which act as additional MC nucleation sites, are punched out to relieve the local strain field [131]. According to Baker et al. [138] a punched-out dislocation creates vacancies as it moves away, and a dislocation of opposite sign remains around the particle as part of the dislocation network. The strain field may also be relieved by vacancy condensation at the particle/matrix interface to form dislocation loops [137]. Irani and Weiner [139] proposed that the vacancies needed for MC growth are provided by climb of the dislocation on which the particle

nucleated. As the dislocation climbs, it then provides further MC nucleation sites, giving a repeated climbing-nucleation process that results in sheets of fine precipitates. Chaturvedi et al. [140] reported that the NbC precipitate sheets form on (110) planes in which $a/2 \langle 100 \rangle$ dislocation climb has been observed.

4.1.2.2 Precipitation on Stacking Faults

Precipitation of MC carbides on stacking faults in austenitic steels was first observed by Aswegen and Honeycombe [130]. On aging at 700 C after a solution anneal, dislocations were observed to dissociate and form stacking faults, which continued to grow and which developed fine NbC precipitates during prolonged aging. Aswegen et al. [131] observed that the MC particles within the stacking fault band were arranged in stringers and suggested that they were nucleated on partial dislocations which lead the stacking faults. The nucleation of MC and growth of the stacking fault would occur simultaneously, with movement of the partial dislocations being induced by the difference in elastic modulus between the precipitate and matrix; i.e. the higher modulus of the precipitate would repel the partials to a new position which could then provide new nucleation sites.

The stacking faults on which MC precipitation was observed by Silcock and Tunstall [141] were reported as extrinsic, Frank type. They showed that the outer dislocation bounding the stacking fault was a Frank partial and deduced that the inner dislocation of the stacking fault was a Shockley partial. They suggested that the stacking fault was formed by the dissociation of a $a/2 [110]$ type sessile dislocation

at the intersection of the $(\bar{1}11)$ and (111) planes as postulated by Hirsch [142]

This reaction produces a fault lying in the (111) plane which is not the slip plane of $a/2 [110]$ dislocation. As the MC carbides nucleate and grow on the Frank partial, the need for vacancies to accommodate the volume change causes the Frank partial to climb, emit vacancies and bow out around the particles until the bowed segments attract each other and finally move away from the precipitates. In this manner, the Frank partials repeatedly acted as nucleation sites giving a planar colony of strings of MC carbides, as shown in Figure 4.5. The requirements for this growth were suggested to be (1) a low stacking fault energy so that dissociation of the dislocations was easy; (2) segregation of atoms to dislocations to heterogeneously nucleate MC; (3) persistence of simple orientation relationships between the precipitate and matrix; and (4) a volume increase when the precipitate forms in the matrix so that vacancies are needed for growth. According to this mechanism the ratio of the distance, D , between the rows of particles to the distance, L , between the particles in a row should be 0.5. However $D/L > 0.5$ has been observed for precipitation in Si specimens [143,144], leading Nes and Washburn [145] to suggest that the precipitates are dragged by the climb of the partial dislocations. Calculations by Nes [146], incorporating this drag effect, have shown that the row spacing agrees well with the observed value in a Nb-containing austenitic steel.

Since a perfect $a/2$ $[110]$ dislocation lying in the $(\bar{1}11)$ or (111) plane cannot dissociate according to Eqn. (6), Silcock and Tunstall [141] suggested that this $a/2$ $[110]$ dislocation was produced by climb of loops formed by the vacancy flux from the precipitation of NbC on dislocations. The part of the loop with burgers vector $a/2$ $[110]$ may lie in a (111) plane which is not its slip plane, becoming an exact Lomer-Cottrell sessile dislocation which can dissociate to form either an intrinsic or extrinsic Frank fault. It was suggested that the formation of an extrinsic fault occurred only when vacancies were required for NbC carbide growth. Alternatively, it was suggested that the dislocations on which stacking fault precipitation occurred were secondary dislocations produced in accommodating the volume expansion of nucleated MC particles [141]. Finally, Froes et al. [133] suggested that the dislocation which climbs to provide the nucleation sites for stacking fault precipitation is a primary dislocation which is being reorientated to a sessile position by quenched in vacancies.

4.1.2.3 Role of Vacancies

The concentration of quenched in vacancies may play a role in the occurrence of stacking fault precipitation. Froes et al. [133] compared the density of stacking faults in a 18Cr-12Ni-2Ta austenitic steel quenched to room temperature and aged at 700 C to that directly quenched to 700 C and aged. The stacking fault density in the former specimen was three times greater than in the latter, and was attributed to the higher vacancy density in the quenched-to-room-temperature specimen.

However, the stacking fault growth rate in both specimens was the same, although a longer time was required for the development of stacking faults in the direct aged specimens. This suggested that the vacancies needed for growth of stacking fault precipitates nucleated at partial dislocations were provided by the associated climbing partial and that the growth rate was independent of the matrix vacancy concentration.

4.1.2.4 Role of Plastic Deformation

Since stacking faults are produced by dislocation reactions, it is reasonable to expect that stacking fault precipitation would be enhanced by plastic deformation. Van Aswegen et al. [131] observed that plastic deformation in an as-quenched 18Cr-10Ni-1Nb austenitic steel resulted in extended dislocation nodes, prismatic dislocation loops and dislocation dissociations forming stacking faults. On aging, prior deformation resulted in more rapid stacking fault growth, than in undeformed specimens. Chaturvedi et al. [140] showed that prior deformation clearly increased the stacking fault density on aging a manganese austenitic steel.

4.1.2.5 Solution Annealing Temperature

It is well known that in any precipitation process the driving force for nucleation of a new phase depends on the supersaturation of the solute atoms in the solid solution. Stacking fault precipitation would not violate this rule. Chaturvedi et al. [140] found that the stacking fault density increased with matrix Nb and C content in manganese austenitic steels with varying Nb and C levels. Froes et al. [133] also reported that in a 18Cr-12Ni austenitic steel containing 2%

Ta and 0.1% C, extensive stacking fault precipitation was observed. However in a 18Cr-12Ni austenitic steel containing 0.6% Ta and 0.085% C, no indication of stacking fault precipitation was observed. Pickering [147], using a solution treatment temperature of 1000 C, found no stacking fault precipitation occurred on aging, in contrast with the extensive stacking fault precipitation observed on aging when Van Aswegen et al. [131] used a solution treatment temperature of 1300 C. These different results can be attributed to the different solution annealing temperatures, with higher temperatures dissolving more primary MC, which is subsequently available for precipitation during aging.

4.1.2.6 Aging Temperature

The extent of stacking fault precipitation will also depend upon the aging temperature, since the solubilities of MC carbides in austenite decrease with decreasing temperature. VC, NbC, TiC and TaC have higher solubilities in austenite than ZrC, which has not been observed in association with stacking faults [148]. Van Aswegen et al. [131] reported no stacking fault precipitation in a 18Cr-10Ni-1Nb austenitic steel aged at 850 C, but well developed stacking fault precipitation at 600 and 700 C. The stacking fault density was also higher and the stacking fault length was shorter at the lower aging temperatures. Borland [149] reported a lower stacking fault density in a N-containing 18Cr-12Ni-1Nb austenitic steel aged at 765 C compared to 700 C. It is clear that a critical solute supersaturation is required for stacking fault precipitation.

4.1.2.7 Stacking Fault Energy

Although stacking fault energy (SFE) influences the ease of dislocation dissociation, it may not be as important for stacking fault precipitation, which has been observed in alloys with a wide range of stacking fault energies (e.g. in 18Cr-10Ni steel, $\text{SFE} = 10 \text{ mJ m}^{-2}$; 35Ni-15Cr steel, $\text{SFE} = 50 \text{ mJ m}^{-2}$; and even in Inconel 625 alloy, $\text{SFE} = 100 \text{ mJ m}^{-2}$) [116,150]. Repeated MC precipitation has been observed on both climbing undissociated dislocations and Frank partial dislocations in austenitic steels, but it should be noted that undissociated dislocations, due to their larger strain fields, are more suitable sites than Frank partials, which in turn are favored over the stacking fault plane. Borland [149] concluded that MC nucleation on undissociated dislocations prevented their dissociation, so that MC precipitation on Frank partials must occur only after these dislocations have dissociated.

4.1.2.8 Matrix Precipitation

Matrix precipitation, not in association with dislocations, has been observed for VC [139,151,152], NbC [152,153] and TaC [133,137]. Silcock and Denhem [152] suggested that the large VC/ γ misfit strain could be reduced by nucleation of VC particles at solute-vacancy clusters. Froes et al. [133] suggested that matrix TaC particles nucleated at vacancy aggregates and reduced their strain fields by vacancy absorption. Shepherd [153] reported that the density of matrix NbC decreased when the vacancy concentration was reduced by either quenching from a lower solution annealing temperature or using a slower cooling rate. He suggested that vacancies go directly into the NbC

nucleus to reduce the nucleation barrier. A critical carbon level (0.1 wt% for VC and 0.04 wt% for TaC) was observed for the precipitation of matrix MC carbides, suggesting that matrix MC precipitation was associated with solute-carbon-vacancy complexes. A critical aging temperature was also observed for VC and NbC precipitation, above which no matrix precipitation was observed [151,153].

Matrix VC precipitation occurs preferentially in steels containing high V and C contents, aged in the range 600-800 C [151], with the early stages of precipitation having line contrast along $\langle 100 \rangle$ directions and being referred to as matrix dot precipitates. The particle shape of TaC is also masked by strain contrast, which is used to detect the early stages of growth. In the later stages of growth, matrix TaC are plate-like with edges bounded by {111} planes [137]. The morphology of matrix NbC is varied, with small particles being polyhedral and large particles plate-like [153].

Some elements were observed to enhance matrix precipitation of MC carbides. P atoms, being about 20% smaller than Fe atoms, may interact with vacancies to form vacancy loops and voids, which promote nucleation of matrix MC [116]. Shepherd [153] suggested that P atoms can trap vacancies, delaying their migration to sinks and aiding the formation of solute-vacancy complexes. N may also be important in the formation of vacancy defects. In a Cr-Ni austenitic steel containing 0.5 wt% N, Frank loops were detected on aging at 650 and 850 C. In contrast, no loops were observed in a N-free steel.

4.1.3 M_6C (η carbide)

This carbide was originally observed in high speed steels as Fe_4W_2C [154]. The carbon atoms may be replaced by nitrogen or oxygen to form the nitride and oxide, respectively, or by vacancies to form inter-metallic compounds. The metal atoms may be replaced by Si [114] and a formula of M_3SiX , where X is vacant site, has been identified [23]. The following isomorphs of η -carbide are known: $M_3M'_3C$, $M_2M'_4C$ and $M_6M'_6C$ [155], where M and M' are metallic elements, which may or may not be carbide-forming elements. The crystal structure of η -carbide is shown in Figure 4.6. The FCC unit cell contains 96 metal atoms and 16 carbon atoms, with metal atoms occupying the octahedral and tetrahedral units and carbon atoms between the octahedral units.

The composition of η -carbide varies with matrix composition and environmental conditions. η -carbide observed in 18W-8Cr-1V high speed steels has the formula Fe_3W_3C , but Mo can readily substitute for W to give Fe_3Mo_3C . Weiss and Stickler [113] reported that η -carbide formed in 316L austenitic steels, thermally aged for more than 1500 h at 650 C, by the following process

Lee et al. [87] identified η -carbide after thermal aging for 10,000 hrs at 650 C in solution annealed type 316 steel, and in the temperature range 600-650 C for 20% cold worked 316 steel. The average composition of η -carbide was 31Cr-25Ni-23Mo-11Fe-6Si, but a much smaller quantity developed in the solution annealed specimen. η -carbide formation appears to be promoted by lower carbon contents and prior cold work.

M_6C has a similar crystal structure and lattice parameter to $M_{23}C_6$ carbide making it difficult to distinguish by electron diffraction [87,103]. Lee et al. [87] found that tilting to the [001] zone axis gave much weaker (200) and (420) reflections for the η -carbide than $M_{23}C_6$. Maziasz [156] also showed that η -carbide contains much higher Si, Ni and Mo but lower Cr contents than $M_{23}C_6$, so that the two phases could be identified by analytical electron microscopy.

4.2. INTERMETALLIC COMPOUNDS

Intermetallic compounds are intermediate phases, some of which have fixed ratios of the component metal atoms, while others exist over a range of composition without changing their crystal structure and physical properties. The component metal atoms of many intermetallic compounds do not obey their normal chemical valence rules ($MgZn_2$), although some do ($MgCu_2$). A discontinuity in the chemical, electrical, mechanical and magnetic properties occurs at intermetallic positions in binary phase diagrams.

The intermetallic phases in austenitic steels are Laves, χ and σ phases, with topologically close-packed crystal structures having limited coordination numbers of 12, 14, 15 and 16 [157], and tetrahedral interstitial sites [158,159]. These structures have been extensively reviewed by Wernick [160] and Sinha [161].

The rules controlling the formation of intermetallic compounds have been generalized by many researchers. Abegg [162] indicated that the tendency of two elements to form intermetallics increases with increasing electronegativity factor (separation in the Periodic Table),

but is significant only for non-close-packed intermetallics. Hume-Rothery [163] pointed out that the formation of many intermetallics can be generalized by the ratio of number of valence electrons to atoms (e/a ratio) in the compounds, known as the electron concentration factor. Laves and Witte [164] and Laves [165] observed that the formation of AB_2 intermetallics required the component atoms to have a limited range of the atomic radius ratio, or size factor, for more effective space filling. In most cases a combination of all three factors is needed to determine the structure of intermetallics.

4.2.1 Laves phase

In austenitic alloys, the Laves intermetallic phase has the form, AB_2 , where A is the larger Mo or Nb atom and B is the smaller Fe, Cr or Ni atom. The ideal radius ratio r_A/r_B for Laves phase formation is 1.225, but in practice Goldschmidt [114] reports ratios varying from 1.05 to 1.68, indicating that a contraction or expansion of atomic radius is needed to achieve the ideal ratio of 1.225. Wiegand and Doruk [166] reported that Laves phase has some solubility for carbon, whereas Thier et al. [167] reported no solubility for carbon.

Laves phases have three different crystal structure types; $MgCu_2$, $MgZn_2$ and $MgNi_2$. The $MgCu_2$ structure is cubic containing eight A atoms and sixteen B atoms per unit cell; $MgZn_2$ is hexagonal containing four A atoms and eight B atoms per unit cell; and $MgNi_2$ is hexagonal but contains eight A atoms and sixteen B atoms per unit cell. The A and B atoms are each arranged in tetrahedral networks, so that the crystal structure can be regarded as two interpenetrating networks, which are

shown for the MgCu_2 structure in Figure 4.7. The Laves phase which forms depends on the electron concentration factor. Nontransition metal Laves phases with e/a ratio of (a) 1.33-1.75 are MgCu_2 type; (b) 1.8-1.9 are MgNi_2 type; and (c) 1.8-2.2 are MgZn_2 type. For Laves containing only transition metals, with unfilled d-orbitals, it is difficult to assign a unique valence to each element. However, it was observed that for a given element A combining with elements B along a transition series, the structures of the resultant Laves phases would be MgCu_2 , MgZn_2 , then MgCu_2 , in sequence [166]. Bardos et al. [168] indicated that Laves phase cannot form if the average group number (AGN) > 8 , where $\text{AGN} = e/a$ ratio calculated by counting the total number of electrons outside the inert gas shell. By this rule, a B atom such as Ni cannot form Laves phases with A atoms of Cr, V or Ti. However when Si is present as a B atom, Laves phases of Ni combined with Cr, V or Ti do form. This is attributed to Si acting as an electron acceptor, decreasing the e/a ratio.

In austenite containing strong carbide-forming elements, two types of Laves phases may be formed: (1) MgZn_2 type (NbFe_2 , TiFe_2 and MoFe_2); and (2) MgCu_2 type (ZrFe_2 and HfFe_2). Beattie and Hagel [169] solution annealed, quenched and aged Fe-, Ni- and Co- based austenitic alloys, and observed Laves phases forming intragranularly and also intergranularly at 700-760 C in the Ni- and Co-based alloys only. Matrix composition was, therefore, suggested to be important in the formation of Laves phase. Chaturvedi and Honeycombe [170] investigated Laves phase precipitation in carbon-free Fe-Mn-Nb steels aged between 600-800

C. In all cases, NbFe_2 or NbMn_2 were observed to preferentially nucleate on quench-induced dislocations around undissolved particles. The matrix was observed to be strengthened by the extensive Laves precipitation, but Ni content did not influence the precipitation kinetics. The lattice constants of Laves phase were reported to be $a = 0.4828 \text{ nm}$ and $c = 0.7860 \text{ nm}$.

In Mo-containing austenitic steels hexagonal Laves phase has been reported as a minor phase with the formula MoFe_2 and lattice parameters $a = 0.4744 \text{ nm}$ and $c = 0.7725 \text{ nm}$ [171]. Weiss and Stickler [113] observed that MoFe_2 Laves phase, with composition 45Mo-38Fe-11Cr-5Ni, precipitated intragranularly and occasionally on grain boundaries in type 316 steel aged at 815 C and below. Lee et al. [87] reported Laves phase (43Mo-33Fe-13Cr-6Ni-5Si) after 10,000 hrs aging at 600 C in type 316 steel and at 650-750 C in Ti-modified 316 steel. The Bristol Group [23] reported that Laves phase occurred after prolonged thermal aging, usually at grain boundaries and closely related to grain boundary M_{23}C_6 in type 316 steels. The morphology of Laves phase in austenitic steels has been reported as equiaxed particles [103], hexagonal platelets [170,172] and laths [172]. The orientation relationships between Laves phase and the austenite matrix have been reported by Denham and Silcock [172] as:

$$(0001)_{\text{Laves}} // (111)_{\gamma} ; [\bar{1}\bar{1}00]_{\text{Laves}} // [\bar{1}10]_{\gamma} \quad \text{for } \text{NbFe}_2$$

and by Nutting and Parsons [173] as

$$(10\bar{1}3)_{\text{Laves}} // (111)_{\gamma} ; [\bar{1}2\bar{1}0]_{\text{Laves}} // [\bar{1}2\bar{1}]_{\gamma} \quad \text{for } \text{MoFe}_2.$$

The formation of Laves phase in austenitic steels was observed to be enhanced by cold work, which increases the diffusivity of Laves-forming elements, and by high solution treatment temperatures. High carbon contents suppress Laves precipitation as a low carbon matrix is required for nucleation. Aging temperature appeared to have little influence on the particle size or the amount of Laves phase precipitated [103].

4.2.2. χ phase

χ phase was first observed in steels containing Cr, Ni and Mo [174] and can behave either as an intermetallic compound or a carbide, i.e. carbon can dissolve in this phase [114]. In austenitic steels it usually contains Fe, Cr and Mo, and has an ordered b.c.c. α -Mn type lattice containing 58 atoms per unit cell [175] with a lattice parameter of $a = 0.8920$ nm. A typical composition of χ phase in a Fe-Cr-Ni-Mo system is $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ [175]. However, as the lattice can tolerate metal interchange, the composition may vary considerably [114]. In Type 316 steel the stoichiometry of χ phase has been reported as $(\text{Fe},\text{Ni})_{36}\text{Cr}_{18}\text{Mo}_4$ [175] and the lattice parameter varies from 0.8862 nm to 0.8878 nm [103,174]. When carbon is dissolved in the lattice, the χ phase may convert to the carbide, M_{18}C , and the composition may shift to higher amounts of the stronger carbide-forming elements such as Mo [114].

Weiss and Stickler [103] showed that χ phase nucleates, in order of increasing difficulty, at grain boundaries, incoherent twin boundaries, within the grains and occasionally on coherent twin boundaries in 316 steels. χ phase precedes the formation of σ phase and occurs in the temperature range 700-880 C, compared to 680-980 C for σ

phase and 480-900 C for $M_{23}C_6$. After longer aging times, $M_{23}C_6$ begins to dissolve, enriching the surrounding matrix with Mo and Cr, and the number of χ and σ precipitates increases. χ phase may nucleate independently at grain boundaries or closely associated with $M_{23}C_6$, in both cases enhancing the dissolution of $M_{23}C_6$ [103].

The morphology of χ phase has been observed as globular and rod shape, similar to σ phase. The orientation relationship between χ phase and austenite was reported as [103,176]

$$(111)_{\gamma} \quad // \quad (110)_{\chi} ; \quad [01\bar{1}]_{\gamma} \quad // \quad [\bar{1}10]_{\chi}$$

High solution annealing temperature tends to decrease the size of χ precipitates, whereas cold work accelerates the formation of χ phase [103].

4.2.3. σ phase

σ phase was first observed by Bain and Griffith [177] in systematic studies of Fe-Cr-Ni alloys in 1927, and usually contains two transition elements, AB, where A elements are from Group VB or VIB and B elements are from the first or second long series in the Periodic Table. The transition elements which may form σ phase with Fe in austenitic steels are V, Nb, Mo and Cr etc. σ phase does not have a definite stoichiometry, unlike its topologically close-packed counterpart Laves phase, and the B atom content may range from 20 at% to 80 at% [161]. In addition, the temperature range over which σ phase is stable may be quite different in different alloy systems. For example, in the Fe-Cr system, FeCr σ phase is formed congruently at about 815 C from the primary α -solution and is stable to room temperature. In the Fe-Mo

system, FeMo σ phase is formed by peritectic reaction at 1540 C but on subsequent cooling undergoes a eutectoid decomposition at 1180 C [178].

The crystal structure of σ phase is a complex tetragonal lattice containing 30 atoms per unit cell [160]. The lattice parameters vary from $a = 0.8799$ - 1.0120 nm and $c = 0.4544$ - 0.5420 nm in the different alloy systems. In austenitic steels the σ phases, FeCr and FeMo, have lattice parameters of $a = 0.8799$ nm, $c = 0.4544$ nm and $a = 0.9188$ nm, $c = 0.4812$ nm respectively [178]. σ phase has a stacking sequence of four layers located at $z = 0, 1/4, 1/2$ and $3/4$ as shown in Figure 4.8 [161], where the $z = 1/2$ layer is obtained by rotating the $z = 0$ layer by 90 about a two-fold axis perpendicular to the plane of the paper. The atomic layer at $z = 3/4$ is a repetition of the layer at $z = 1/4$. There are five different crystallographic sites for the 30 atoms in the unit cell, designated as A, D (CN=12), B (CN=15) and C, E (CN=14) in Figure 4.8, where CN = coordination number. X-ray and neutron diffraction studies show that in FeCr σ phase, ordering of Fe atoms occurs on A and D sites and of Cr on B and E sites, while occupation of the C sites is mixed. However, in FeMo σ phase, the A, B and E sites are occupied by Mo, while the C and D sites are occupied by Fe [160].

The radius ratio of A and B atoms in σ phase varies from 0.82 to 1.15, with no particular preferred radius ratio. When $r_A/r_B < 1$, the atom distribution in the lattice seems to be random. The e/a ratio is approximately constant, with most σ phase occurring at an e/a ratio of 6.0-7.1. The effect of Si and P on the stability of σ phase has been extensively reviewed [160,161]. Si stabilizes σ phases and may

substitute for the smaller B atoms (e.g. Fe) and expand the composition and temperature ranges of stability for Cr(FeSi) σ phase. This was explained by Si acting as electron acceptor, providing more electron states available for filling, thus permitting more transition elements to dissolve in the σ phase. P additions have the same effect as Si. However, Al has a destabilizing effect, attributed to its electron donor behavior [178].

σ phase causes embrittlement in austenitic steels, and has received much more attention than the other intermetallic phases. Lewies [179] reported that σ phase grew as thin plates with the plate faces (001) being parallel to (111) planes of the austenite matrix. In many cases σ phase was associated with TiC carbides and it was suggested that growing TiC punches out dislocations which then further nucleate TiC. As larger TiC grow by consuming smaller ones on the same dislocation, segregation of TiC may cause a small portion of the dislocation to dissociate giving a stacking fault with (111) fault plane. σ phase, nucleating on this stacking fault, prefers to grow with its (001) plane parallel to the (111) fault plane due to the smaller mismatch, resulting in a thin plate morphology. The orientation relationships observed between σ phase and austenite are [179,180]

$$(111)_{\gamma} // (001)_{\sigma} ; [0\bar{1}1]_{\gamma} // [140]_{\sigma}$$

and $(111)_{\gamma} // (001)_{\sigma} ; [\bar{1}10]_{\gamma} // [\bar{1}10]_{\sigma}$.

Although it has been suggested that $M_{23}C_6$ nucleation can restrict the nucleation and growth of σ phase [181], σ phase nucleated from $M_{23}C_6$

is frequently reported [114,119,182,183]. Goldschmidt [114] suggested that σ phase can be formed by the decarburization of $M_{23}C_6$ (Figure 4.2). σ phase can also be formed from ferrite, due to its enrichment in Cr, and develops more rapidly in duplex ferrite/austenite steels.

Singhal and Martin [183] suggested that in alloys of low (Ni+Cr) content σ phase formed directly from austenite, whereas in high (Ni+Cr) austenites, σ phase grew by consumption of the metastable ferrite phase. In the high (Ni+Cr) alloys, $M_{23}C_6$ precipitated first at grain boundaries, but dissolved as grain boundary ferrites nucleated and the thermodynamically more stable σ phase developed. Nucleation of σ phase on matrix dislocations was not observed. White and Le May [182] reported that in type 316 steel the phase transition sequence at grain and twin boundary was $M_{23}C_6 \rightarrow$ ferrite $\rightarrow \sigma$ phase and intragranular σ formed at the ferrite/austenite interfaces. Duhaj et al. [184] observed that σ phase nucleated at coherent twin boundaries, but it most probably originated from the incoherent portion of the twin boundary and then grew into the coherent portion [185]. Weiss and Stickler [103] reported that in type 316 and 316L steels, σ nucleation sites are triple points, grain boundaries, incoherent twin boundaries and intragranular oxide inclusions, in order of increasing difficulty. Spruiell et al. [104] reported σ nucleation sites at the interfaces between recrystallized and unrecrystallized regions. Thus, nucleation at high energy surfaces appears more frequent than at low energy defects such as dislocation and coherent twin boundaries.

σ phase is normally well developed after aging for up to 1500 hrs at 750 C [116]. Ni retards the formation of σ phase, as does C, which cannot dissolve in the lattice [166]. Ti [119] and Mo [169] accelerate the formation of σ phase, which formed after only 30 minutes at 870 C in an austenitic steel containing both Ti and Mo. High solution treatment temperatures retard the formation of σ phase [186,187], attributed to the larger grain size giving longer diffusion paths for the σ -forming elements to the grain boundaries, and results in smaller σ phase particles [103]. However, very high solution temperatures, resulting in δ -ferrite formation, can accelerate σ phase formation [166]. Cold work prior to aging accelerates σ phase formation [103,104,180,184,186,188] by either increasing the diffusion rate or promoting recrystallization which refines the grain size and provides more grain boundaries and triple junctions. Repeated cold work and recrystallization significantly enhances the formation of σ phase by introducing σ phase nuclei during the pretreatment [104].

Commercial 316 stainless steel does not contain the carbide forming elements Ti, Nb or V, hence, $M_{23}C_6$ and M_6C are the only carbides that form. $M_{23}C_6$ forms within 10 minutes in the temperature range 750 C to 900 C, while M_6C appears after 2000-3000 h at approximately 650 C. The intermetallics, Laves and χ begin to form after 100 h at 700-800 C, but σ phase formation requires at least 1000 h at the same temperatures. Maziasz and McHargue [4] have summarized the kinetics of phase formation

in solution annealed (SA) 316 stainless steel and his TTP diagram is reproduced in Figure 4.9.

Commercial 347 stainless steel, which contains no Mo, is strengthened by Nb and Ta additions, and 17-14CuMo, which is closest in composition to the new lean austenitic steels, contains Nb, Ti, V and Cu. However, as we have seen in Figure 3.3, despite its improved creep rupture strength over 316 stainless steel, the precipitation of copper in 17-14CuMo does not provide the same long term stability as precipitation of matrix carbides in the advanced austenitic steels.

The extension of creep rupture lives in the developmental steels clearly requires a delicate balance of carbide forming elements, for greater matrix and grain boundary strength, together with minor compositional modifications to retard or prevent the nucleation and growth of the intermetallic phases and particularly σ phase. In the next chapter we shall review the compositional modifications investigated for precipitate phase control and optimization of the creep rupture properties as well as the experimental procedures adopted in this thesis for the study of the advanced austenitic steels.

4.1. The $M_{23}C_6$ structure showing the unit cell for $(Cr, Fe, W, Mo)_{23}C_6$ [114].

Figure 4.2 Phase evolution from M_7C_3 carbides in high chromium steel [114].

Figure 4.3 Lattice parameters of MC carbides as a function of composition for binary carbide systems [114].

Figure 4.4 Time-Temperature-Precipitation (TTP) diagram for M_{23}C_6 and Nb(Ti)C precipitates in a Cr-Ni austenitic steels [126].

Figure 4.5 Stages in the growth of an extrinsic stacking fault due to the climb of a Frank partial aided by NbC precipitates, E: stacking fault, F: Frank partial, J: jog emitting vacancies [141].

Figure 4.6 Unit cell for M_6C (η -carbide) structure [114].

Figure 4.7 The MgCu_2 structure (AB_2) [160].

Figure 4.8 Four layer stacking arrangement in the σ phase structure. The heavily outlined square represents the unit cell projected parallel to the basal plane [161].

Figure 4.9 TTP diagram showing precipitate phase formation in aged SA 316 as a function of time [4].

5 EXPERIMENTAL PROCEDURES

5.1 Alloy Compositions

Two series of alloy compositions emerged from the AR&TD Fossil Energy Materials Program for new superheater and reheater materials. The first was the CE series of alloys, followed by the AX series, both of which were based on the lean stainless composition of 16% Ni and 14% Cr (compared to 16% Cr and 14% Ni in 316 stainless steel). The alloys were made by vacuum induction melting followed by electroslag remelting.

The compositions of these steels (wt%) are given in Table III. The carbon content of the CE steels ranged from 0.07 to 0.09 wt% and was held at 0.075 in the AX steels. This carbon level is comparable to those of 316 stainless steel (0.08 max) and 800 H (0.08) but lower than that of 17-14 CuMo steel (0.1). Alloys CE0, CE1 and CE2 are stabilized with Ti, Nb and V additions, whereas CE3 is both stabilized with Ti, Nb and V and also Cu modified (1.96 Cu). The silicon content was reduced from 0.95 in 17-14 CuMo and 0.56 in 316 stainless steel, to 0.41 in CE0, 0.20-0.25 in CE1-3, and finally to 0.12 in the AX series, to retard σ phase formation. For both series, the Ti content was 0.25, Mo was 2.25-2.50, V was 0.5 (except for V = 0.15 in AX8), and Nb was 0.1 (except for AX5 and AX7 where Nb = 0.15). The phosphorus level was 0.07 in all alloys except AX8 and AX5, where it was reduced to 0.04 and 0.02, respectively. Alloys CE3 and AX7 contained Cu additions of 1.96 and 1.50 for comparison with 17-14 CuMo (3.07 Cu). Apart from their Ni and Cr contents, CE3 and AX5 also had increased V and reduced Nb, compared to 17-14 CuMo.

5.2 Load Relaxation Tests

Load relaxation tests have been used by Carolan et al. [189,190] to evaluate the elevated temperature ($>0.4T_m$) flow strength, as a function of strain rate and temperature, of the modified alloys. Plates, 0.10 cm thick, of the modified alloys were supplied for these tests in the mill annealed condition. The plates were solution treated at 1150 C in an argon atmosphere for 45 minutes and then cooled to room temperature by an argon stream, giving a grain size of approximately 100 μm . After solution treatment, dog-bone type tensile specimens with a gage length of 2.28 cm and gage width of 0.15 cm were machined and given a 15 minute solution anneal at 1150 C to remove any residual stresses. 2% or 5% cold work levels were introduced by tensile deformation in an Instron model 1102 Universal Mechanical Testing Machine. The specimens were then aged for either 30 days at 800 C (to simulate a service life of 50,000 h at 700 C), or 2 days at 850 C.

The principles of load relaxation tests have been well documented by Li [191], who has shown that reliable data can be collected at strain rates as low as 10^{-8} s^{-1} if the temperature is controlled within $\pm 0.1 \text{ C}$. Load relaxations were made close to the 0.2% yield strain to identify the flow properties associated with a given microstructure and to eliminate the effects of work hardening during loading. The results were plotted as the logarithm of true stress vs strain rate. Short term strength was evaluated by the 0.2% proof stress at a strain rate of 10^{-4} s^{-1} , and long term strength was evaluated by comparing flow strengths at a strain rate of 10^{-8} s^{-1} . Carolan et al. [189] have shown that load

relaxation and creep data were comparable from specimens with similar thermomechanical treatments indicating that the load relaxation test may be a simple and rapid method for extrapolating the long term creep rupture strengths.

The load relaxation mechanical testing was carried out by Carolan and Li [190] at Cornell University and the reader is referred to Appendix I for details of the individual test results. Tests were conducted at 650 C and 700 C on alloys CE0, CE2 and CE3 with the heat treatments given in Table IV. The electron microscopy data collected from these samples will be discussed in Chapter 6.

5.3 Creep Rupture Tests

Constant load creep rupture tests were conducted by Maziasz and Swindeman [2] on round bar specimens, 6.35 mm in diameter, of the advanced and commercial alloys listed in Table III. The initial stress was 170 MPa at a temperature of 700 C and tests were conducted on alloys with varying thermo-mechanical treatments as well as the as-received (mill-annealed) condition. The mill-annealed condition involved solution treatment at 1200 C, followed by either cold or warm working for flattening and final dimensioning.

5.4 Thermal Treatments for Alloy AX5

Alloy AX5 was annealed for 1 hour at 1250 C in a high purity argon atmosphere, to ensure that all the stabilizing elements were in solution, quenched, and half the material was cold rolled by 5.6%. Transmission electron microscopy (TEM) disc blanks were then removed from both the solution annealed and cold worked materials and were

encapsulated in quartz tubes, back filled with argon. These samples were aged at temperatures of 600 C, 700 C, 800 C and 900 C for times of 1, 10, 300, 1000, and 3000 h respectively.

5.5 Thin Foil Electron Microscopy

Thin foil TEM specimens were prepared from SA and SA plus cold worked AX5 by electropolishing in a 7:1 volume ratio of methanol and sulfuric acid at -15 C and 120 mA current. Specimens were then washed in methanol and distilled water. The specimens were observed using a Philips 420T scanning transmission electron microscope.

5.6 Extraction Replicas

Carbide extration replicas were prepared by etching samples in a solution of 9:1 volume ratio of methanol and hydrochloric acid and then carbon coating. Carbon films were removed by etching in the same solution for two to five minutes, washing in methanol and then floating off the carbon films in distilled water. The specimens were observed in the Philips 420T scanning transmission electron microscope and also in the Philips 400T electron microscope equipped with a field emission gun. Both microscopes were fitted with energy dispersive X-ray spectrometers.

5.7 Precipitate Size Measurements

MC precipitate sizes were measured in-foil using a method similar to that used by Kesternich [192]. Moire fringe images between the austenite matrix and MC carbides were observed with the foil normals oriented in the [011] direction and the excited diffraction vector, $g = \bar{1}\bar{1}1$ or $1\bar{1}\bar{1}$, in the two beam condition. In this orientation the

majority of MC precipitates were plate-like. One side of the rectangle, a , was measured by counting the number of fringes and the other side, b , using a magnifying graticule. The particle size was then taken as the side of the equivalent square, i.e. $(ab)^{0.5}$. The experimental Moire fringe spacing, D , was found to be 1.341 nm for the mixed (Ti,Mo,V,Nb)C and compared well with theoretical spacings of 1.249 nm and 1.520 nm for pure TiC and VC, respectively. The resolution limit for in-foil measurements is two Moire fringe spacings, i.e. 2.7 nm. However, by checking the measurements against those of extracted precipitates it was possible to resolve particles of approximately 1.5 nm (equivalent to 1 Moire fringe spacing) in size. More than 500 precipitate sizes were measured for times of 1, 10, 300, 1000 and 3000 h at 700 C and 900 C.

TABLE IV: STRESS RELAXATION TESTS

Sample	%CW ⁺	Heat Treatment [*]		Test Temperature (C)
		Days	T (C)	
CE3 26	0	30	800	650
CE3 25	5	30	800	650
CE3 02	0	2	850	650
CE3 12	5	2	850	650
CE3 10	5	2	850	700
CE3 64	5	3	900	700
CE2 07	5	2	850	650
CE0 01	0	2	850	650
CE0 10	5	2	850	650
17-14-49	5	2	850	650

⁺CW - Cold Work;

^{*}All samples were solution annealed for 1 hour at 1150 C

6 STRESS RELAXATION TESTS

The stress relaxation test method has proved a very promising technique for preliminary screening of the creep rupture properties of the advanced austenitic steels and for comparing their performance with those of commercial alloys such as 800H and 17-14 CuMo steel. The rapid accumulation of stress relaxation data can also provide a guide to the long term creep rupture tests which should be performed on new materials and also to the microstructural conditions which will give optimized creep performance.

In this chapter we shall present transmission electron microscopy studies of alloys CE0, CE2, CE3 and 17-14 CuMo steel after stress relaxation testing at 650 C and 700 C. The specimens were in either the solution annealed (0% cold work) or 5% cold worked condition and were given one of two aging treatments. The first was the standard stabilizing aging treatment of two days at 850 C [19], while the second treatment of 30 days at 800 C, gave stabilization and simulated a service life of 50,000 h at 700 C [110]. Details of the individual stress relaxation tests are given in Table IV, and the mechanical property data, which were collected by Carolan and Li at Cornell University, are presented in ref. 190. These tests showed that alloy CE3 which contained the stabilizing elements Ti, Nb and V plus a copper addition performed better than 17-14 CuMo steel and the modifications CE0 and CE2 which were stabilized without a copper addition.

The microstructural studies suggested that the role of the element copper in the stabilized steels was greater than simply a strengthening

mechanism produced by precipitates of copper metal. Instead, the addition of copper to alloy CE3 gave a much finer MC precipitate distribution than observed in alloy CE0 (without a copper addition). This was attributed to the copper increasing the stacking fault energy in the dislocated austenite matrix of cold worked CE3, resulting in an enhanced nucleation rate and consequently a finer distribution of the MC carbides.

This observation suggested that it was not the addition of 1.96% Cu which significantly improved the stress relaxation and creep rupture properties of alloy CE3, but rather the refined MC precipitate distribution. Hence, a copper addition may not be necessary if a fine matrix MC distribution could be produced by thermal aging for shorter times at lower temperatures or by stress aging during a creep test. The creep rupture data presented in Figure 3.3 appear to support this conclusion as alloys AX7 (1.5% Cu), AX8 (0.14% Cu) and AX5 (0.005% Cu) all show improved creep rupture strengths compared to alloy CE3, when tested under identical conditions with a stress of 170 MPa at 700 C. As a result of the microstructural information gained from these preliminary screening experiments, alloy AX5 was selected for the detailed aging kinetics study described in Chapters 7 through 9 of this report.

The electron microscopy observations leading to our understanding of the relationship between the copper alloying addition and the matrix MC distribution will now be illustrated by first considering the effects

of cold work, aging time, aging temperature and alloy composition on the stress relaxation behavior of the CE series alloys.

6.1 The Effect of Cold Work

The effect of cold work has been studied in samples CE3 26 and CE3 25 which have been given 0% and 5% cold work, prior to aging for 30 days at 800°C and stress relaxation testing at 650°C. Figure 6.1 shows that CE3 26 (no prior cold work) contained large phosphide precipitates (labelled P in Figure 6.1a), MC precipitates on matrix dislocations (labelled M in Figure 6.1c) and many stacking faults (Figure 6.1e). The 5% prior cold work applied to sample CE3 25 resulted in finer phosphide and more extensive MC matrix precipitation (Figure 6.1b). Stacking faults were also observed, but appeared to be narrower than in CE3 26 and were also associated with MC matrix precipitates (Figures 6.1d, 6.1f). $M_{23}C_6$ precipitates were found associated with the stacking faults in CE3 26 (arrowed in Figure 6.1g). Rather than the usual cube-cube orientation relationship with austenite, these precipitates exhibited the orientation relationship shown in Figure 6.1h:

$$(11\bar{1})_{\gamma} \quad // \quad (1\bar{1}1)_{M_{23}C_6} \quad ; \quad [011]_{\gamma} \quad // \quad [011]_{M_{23}C_6}$$

6.2 The Effects of Aging Time and Aging Temperature

The effects of aging time after 5% prior cold work are shown in Figure 6.2. After 2 days aging at 850°C and testing at 700°C, sample CE3 10 showed more extensive MC precipitation on dislocations and less splitting of the dislocations into partials (Figures 6.2a, 6.2c, 6.2e) than in CE3 25 (aged 30 days at 800°C and tested at 650°C, Figures 6.1b, 6.1d, 6.1f). Increasing the aging temperature to 900°C for 3 days in

sample CE3 64 resulted in the presence of small spherical precipitates (Cu particles) and coherency strain fields (possibly γ' or Cu precipitates) in the matrix (Figures 6.2b, 6.2d, 6.2f).

6.3 The Effect of Copper Content

The microstructures of CE3 10 (1.96% Cu), tested at 700 C, and 17-14 CuMo steel (3.07% Cu), tested at 650 C, (both 5% cold worked and aged for 2 days at 850 C) can be compared in Figures 6.2 and 6.3. The most significant difference between these samples is the increase in copper precipitation in the 17-14 CuMo alloy, arrowed in Figures 6.3c and 6.3d.

6.4 The effects of alloy composition and prior cold work on the MC precipitate distributions

An important question in this research is the effect of prior cold work on the evolution of MC precipitate distributions during both aging of the alloy and during elevated temperature creep rupture testing. (It should be noted that the short testing time makes it unlikely that significant precipitate phase coarsening or evolution will occur during the stress relaxation test itself). Carbide extraction replicas from alloys CE0 01 (0%CW), CE0 10 (5%CW) and CE3 12 (5%CW), all of which have been aged for 2 days at 850 C and tested at 650 C, are shown in Figure 6.4. Comparison of Figures 6.4a and 6.4b clearly shows that 5% cold work produces a larger number of finer precipitates in CE0 10 (Figure 6.4b). This observation was confirmed by precipitate number counts from several micrographs of CE0 01 and CE0 10 imaged under identical conditions. Figures 6.4b and 6.4c show that the MC precipitates are again finer in alloy CE3 12 when both alloys are in the cold worked state.

The replica data are consistent with observations of the MC precipitates in thin foils. These results confirm that: (1) larger numbers of finer precipitates were produced in the prior cold worked samples, and (2) finer precipitates were produced in alloy CE3 12 (containing 1.96% Cu) than in alloy CE0 10, for the same level of cold work.

The effects of alloy composition on MC precipitation is compared for alloys CE0 10, CE2 07 and CE3 12, all aged for 2 days at 850 C with 5%CW and tested at 650 C, in Figures 6.5, 6.6 and 6.7. The bright and dark field images of MC precipitation on dislocations clearly show increased precipitation in alloy CE3, containing 1.96% copper, and smaller precipitates than in alloys CE0 and CE2. The effect of prior cold work on alloy CE3 is also clearly demonstrated by comparing CE3 02 (0% CW) in Figure 6.8 with CE3 12 (5% CW) in Figure 6.7. Significantly greater amounts of finer MC precipitates were observed in the prior cold worked material (CE3 12) confirming the carbide extraction replica data shown for alloy CE0 in Figure 6.4.

6.5 Summary

The stress relaxation data for the alloys listed in Table IV are presented in Appendix 1 and show that the relative creep strengths of the alloys may be ranked as follows:

(a) CE3 12 > CE3 10 > 17/14 CuMo > CE2 07, demonstrating that the combined additions of copper and the stabilizing elements Ti, V and Nb, impart greater elevated temperature strengths than either the copper or stabilizing elements alone, for the aging treatments used in this study.

(b) CE3 12 > CE3 10 > CE3 25, indicating a deterioration in creep strength with long term aging;

(c) CE3 12 > CE3 02, showing that prior cold work improved the creep strength.

The superior stress relaxation and creep rupture strength of CE3 compared to alloys CE2, CE0 and 17/14 CuMo steel can be explained by the copper addition increasing the stacking fault energy and enhancing the precipitation of fine MC carbides. This can be seen by considering the free energy for nucleation of the carbides [193]:

$$\Delta G^{\circ} = -\Delta G_w V + \sum A_{pi} \gamma_{pi} - A_d \gamma_d \quad (7)$$

where ΔG° = overall free energy barrier to nucleation, ΔG_w = free energy change per unit volume, V = volume of the precipitate phase, A_{pi} = surface areas of the precipitated phase, γ_{pi} = interfacial energies per unit area of the surfaces of the precipitated phase, A_d = surface area or length of the defect on which nucleation occurs, and γ_d = interfacial energy per unit area or line tension per unit length of the defect on which nucleation has occurred. The first and third terms on the right hand side assist nucleation, whereas the second term represents the barrier to nucleation. The increase in stacking fault energy resulting from the presence of copper, γ_d , will make the third term more negative and thus lower the overall free energy for nucleation of the MC precipitates.

It should be noted that this effect contrasts with the conventionally accepted view that increasing the stacking fault energy decreases the nucleation rate of precipitates [131,133,139,141,146,194]. Hornbogen

[195] has shown that for semi-coherent precipitation or precipitation in non-cold worked materials, decreasing the stacking fault energy increases the nucleation rate of precipitates. The lower stacking fault energy enhances partial dislocation formation, and alleviates the lattice mismatch between the matrix and a semi-coherent precipitate, reducing γ_p . However, the present case involves nucleation of coherent MC precipitates in a cold worked matrix, with many pre-existing nucleation sites, and precipitate/matrix interfacial energies that are unchanged by a change in the stacking fault energy. Instead, the higher stacking fault energy will increase the defect site nucleation energy, γ_d , and increase the overall free energy change for nucleation as described above.

The effect of cold work in improving the creep rupture strength of the advanced austenitic steels arises from the extensive dislocation precipitation of fine MC carbides as well as the presence of small MC carbides at the grain boundaries.

It appears from the present study that although additions of copper increase the creep rupture strengths of stabilized and non-stabilized austenitic steels, the dominant factor governing the elevated temperature strength is the MC carbide sizes and distribution. It is suggested that the precipitation of copper particles in 17-14 CuMo may not be the strength determining factor and that alternative methods for controlling the MC distribution, such as optimizing the thermomechanical processing, should be investigated. For this reason, together with the promising creep rupture data presented in Figure 3.3, it was decided

to make a detailed microstructural investigation of alloy AX5 (0.005% Cu) in both the solution annealed and cold worked conditions in order to (a) identify thermal aging treatments which may further enhance the creep rupture strengths of the advanced austenitic steels; (b) determine whether further alloy design is required to eliminate the formation of intermetallic phases during long term aging and (c) identify the temperature range and times for which the various metastable precipitate phases, and in particular the MC carbides, are stable.

The remaining chapters of this report will focus on an analytical electron microscopy study of alloy AX5.

Fig. 6.1a Large phosphide precipitates (P) in CE3 26.

Fig. 6.1b Fine matrix MC (M) and phosphide precipitates (P) in CE3 25.

Fig 6.1c MC (M) on matrix dislocations in CE3 26.

Fig. 6.1d Stacking faults in CE3 25.

Fig. 6.1e Stacking faults in CE3 26.

Fig. 6.1f Precipitation of MC at a stacking fault in CE3 25.

Fig. 6.1g $M_{23}C_6$ precipitates (arrowed) associated with stacking faults in CE3 26

Diffraction pattern

$[011]_{\gamma} // [011]_{M_{23}C_6}$

$(111)_{\gamma} // (111)_{M_{23}C_6}$

$BM_{23}C_6 = B_{\gamma} = [011]$

Fig. 6.1h Diffraction pattern

Fig. 6.2a More extensive matrix precipitation and dislocation substructure in CE3 10.

Fig. 6.2b Matrix dislocation substructure near grain boundary in CE3 64.

Fig. 6.2c MC precipitation on dislocations in CE3 10.

Fig. 6.2d Fewer MC precipitates on dislocations in CE3 64.

Fig. 6.2e MC matrix precipitates in CE3 10.

Fig. 6.2f Coherency strain fields in CE3 64.

Fig. 6.3a Matrix precipitation in 17-14 CuMo.

Fig. 6.3b MC and phosphide precipitates (P) in 17-14 CuMo.

Fig. 6.3c Copper precipitates (arrows) on dislocations in 17-14 CuMo.

Fig. 6.3d Spherical copper precipitates in 17-14 CuMo.

Fig. 6.4 Carbide extraction replicas showing the precipitate distributions in (a) CE0 01, (b) CE0 10 and (c) CE3 12.

Fig. 6.5 Bright field (a); dark field (b); images for MC precipitates on dislocations in CE0 10.

Fig. 6.6 Bright field (a); dark field (b); images for MC precipitates on dislocations in CE2 07.

Fig. 6.7 Bright field (a); dark field (b); images for MC precipitates on dislocations in CE3 12.

Fig. 6.8 Bright field (a); dark field (b); images for MC precipitates on dislocations in CE3 02.

7 AGING KINETICS OF SOLUTION ANNEALED ALLOY AX5

This chapter presents transmission electron micrographs from thin foils and extraction replicas of alloy AX5 in the solution annealed condition after aging for 1, 10, 300, 1000 and 3000 hours at 600, 700, 800 and 900 C.

7.1 Solution Annealed AX5

The one hour solution annealing treatment at 1250 C resulted in a grain size of approximately 200 μm and the dissolution of most of the precipitates. Undissolved carbides (approximately 0.1 μm in size) were occasionally observed at grain boundaries and associated with dislocation tangles in the austenite matrix. EDX data indicated that the undissolved precipitates contained mainly Ti and Nb. The solubility product expressions given below indicate that TiC and NbC should dissolve at a solution temperature of 1250 C, hence it is possible that these precipitates may be nitrides or remnants of very large carbonitride precipitates. [19,196]

$$\log [\text{Ti}][\text{C}] = -6780/T + 2.97 \quad (8)$$

$$\log [\text{Nb}][\text{C}] = -9350/T + 4.55 \quad (9)$$

Few dislocations were observed in the austenite matrix except adjacent to undissolved carbides, where dislocations were produced during the quench as a consequence of the different thermal expansion coefficients of the carbides and austenite.

7.2 Aging at 600 C

After aging the solution annealed material for 1 h and 10 h at 600 C, the only precipitates observed in thin foil specimens and extraction

replicas of alloy AX5 were undissolved (Ti,Nb)C. These MC carbides can be seen in both the matrix and at grain boundaries (arrows) in Figures 7.1a (1 h) and 7.1b (10 h). Increasing the aging time to 300 h resulted in rafts of MC precipitates at grain boundaries as seen in the extraction replica in Figure 7.2a. MC precipitates also formed on dislocations in the matrix and can be identified by the Moire fringe images shown in the thin foil micrograph in Figure 7.2b. It is interesting to note that the MC precipitates in the rafts are arranged in equally spaced stringers, suggesting that the MC precipitates nucleated on intrinsic dislocations at the grain boundary.

Grain boundary $M_{23}C_6$ was not detected in the 300 h aged microstructure, but was found in association with grain boundary rafts of MC carbides after 1000 h (Figure 7.3a). The associated diffraction patterns (Figures 7.3b and 7.3c) indicated that the grain boundary MC and $M_{23}C_6$ are in cube-cube orientation relationship. Grain boundary $M_{23}C_6$ precipitates were abundant after 3000 h at 600 C (arrowed in Figure 7.4), but precipitation of $M_{23}C_6$ on matrix dislocations was not observed at 600 C. It should be noted that the few matrix MC precipitates observed at 600 C were found only on the matrix dislocations introduced by either the quenching stresses or punched out by growing grain boundary carbides or at incoherent twin boundaries. No phosphide or M_6C precipitates have been identified at 600 C.

7.3 Aging at 700 C

Grain boundaries containing undissolved (Ti,Nb)C, and rafts of fine MC precipitates, which contained small amounts of Mo, were observed

after only 1 h at 700 C (Figure 7.5a). MC precipitates on an inclined grain boundary can be seen in the thin foil micrograph in Figure 7.5b (1 h). Aging for 1 h at 700 C also resulted in MC precipitates on matrix dislocations. The MC carbides had an average width of approximately 3 nm and could only be identified by the Moire fringe images shown in Figure 7.6. Faulted structures associated with punched out dislocations indicated the first stage of phosphide precipitation in the austenite matrix (Figure 7.7). Grain boundary $M_{23}C_6$ precipitates were not detected after 1 h at 700 C.

However, after 10 h aging at 700 C, grain boundary precipitation of $M_{23}C_6$ and MC was extensive (Figure 7.8a). The early stages of phosphide precipitation were again observed in the matrix (Figure 7.8b), together with MC carbides only in regions containing dislocations (Figure 7.8c). Increasing the aging time to 300 h, 1000 h and 3000 h resulted in further precipitation of $M_{23}C_6$ and MC (labelled M) carbides at the grain boundaries, shown for 1000 h in Figure 7.9a). After 3000 h, well developed phosphide precipitates were observed in the austenite matrix (labelled (P) in Figure 7.9b). Phosphide precipitates in the specimens aged for times longer than 300 h were always associated with dislocation tangles and dense patches of MC precipitates, suggesting that the dislocations punched out by the phosphides provided the nucleation sites required by the MC carbides (M). The evolution of MC precipitates on matrix dislocations is shown for times of 1, 10, 300, 1000 and 3000 h in Figures 7.10a through 7.10e. These micrographs shows that dislocations climbing away from MC precipitates may also act as

nucleation sites for additional MC precipitation, resulting in dense MC patches and dislocation tangles.

$M_{23}C_6$ precipitates were occasionally observed on dislocations in the austenite matrix. Laves phase was observed in addition to $M_{23}C_6$ and MC carbides, at grain boundaries after 1000 h.

7.4 Aging at 800 C

Grain boundary $M_{23}C_6$ and MC carbides, together with matrix phosphides and MC precipitates on dislocations were observed at all aging times. After 1 h at 800 C, fine precipitates, thought to be phosphides, (labelled P in Figure 7.11a) and twins (labelled B in Figure 7.11b) were observed with MC precipitates located at the incoherent twin boundaries (Figure 7.11b). Small $M_{23}C_6$ precipitates were observed at grain boundaries (labelled C in Figure 7.11c) with dislocations being punched into both austenite grains. Stacking faults could be observed in regions of higher dislocation density and the Moire fringe contrast associated with the fault (arrowed in Figure 7.11d) suggests planar MC precipitation in the stacking fault plane.

After 10 hours at 800 C, the grain boundary $M_{23}C_6$ precipitates were typically 1 μm in size. Figures 7.12a and 7.12b show a $M_{23}C_6$ carbide (C) with associated grain boundary MC precipitates (M). The diffraction pattern (Figure 7.12c) indicates a cube-cube orientation relationship between both precipitates and the adjacent austenite matrix.

The evolution of the phosphide precipitates is shown for aging times of 300, 1000 and 3000 h in Figures 7.13a through 7.13c. The phosphides grow to approximately 1 μm in length and in all cases are

associated with misfit dislocations. Virtually no MC matrix precipitation was observed, except at dislocations generated by the phosphide precipitates and the grain boundary precipitates. Typical MC precipitation on dislocations is shown in Figure 7.14 for 1000 h aging.

$M_{23}C_6$ were the dominant grain boundary precipitates for all aging times, and were up to 2 μm in size after 3000 hours. Figure 7.15 shows some of the smaller (0.05 - 0.10 μm) titanium-vanadium-molybdenum containing MC carbides, which were present at the grain boundaries after 3000 h aging. χ phase was observed in small quantities at grain boundaries after 1000 h aging.

7.5 Aging at 900 C

Phosphide precipitates, MC precipitates on matrix dislocations and grain boundary MC precipitates were present for all aging times at 900 C. In all cases the matrix MC and phosphides were closely associated and surrounded by dislocation tangles. Grain boundary $M_{23}C_6$ carbides were abundant for times up to 300 h, but only occasionally observed in the 1000 h and 3000 h samples, indicating that the $M_{23}C_6$ was going back into solution. Phosphide precipitates present after only 1 h aging are shown in Figure 7.16a and grain boundary $M_{23}C_6$ carbides, which were approximately 1 μm in size are shown in Figure 7.16b. Matrix MC, which again precipitated only on dislocations, were up to 0.2 μm in size after 1000 h. The evolution of the MC carbides for times of 1, 10, 300 and 1000 h is shown in Figures 7.17a through 7.17d. Grain boundary MC precipitates containing only titanium, presumed to be TiC, were observed in addition to the titanium carbides containing niobium. For times

greater than 300 h there was evidence of recovery and in the 1000 h and 3000 h indications that grain boundaries may be starting to unpin and migrate beyond the predominantly MC carbides (Figure 7.18).

7.6 Summary

The aging kinetics study of solution annealed alloy AX5 indicates that the MC carbides, which strengthen the austenite matrix and improve the creep rupture properties, have difficulty nucleating without a pre-existing dislocation substructure. Consequently, MC are found only on quenched in dislocations, stacking fault partials or dislocations generated by growth of other phases, such as grain boundary carbides and matrix phosphides. This results in an inhomogeneous distribution of dense MC patches within the austenite matrix. The ready availability of solute results in significant coarsening of the MC precipitates with aging time and increasing temperature.

MC precipitates form rapidly, i.e. in less than 1 h at 700 C at both grain boundaries and in the matrix. Although indications of phosphide precipitation are observed as early as 1 h at 700 C, they are not well defined until 300 h at 700 C. Phosphides are observed at 700 C, 800 C and 900 C, but not 600 C. In the absence of a pre-existing dislocation substructure, the phosphides appear to nucleate first with MC precipitates subsequently nucleating on the punched out dislocations. Hence for solution annealed or solution annealed and lightly cold worked materials, the phosphides may be beneficial in creating additional dislocations which act as nucleation sites for the MC. The application

of a creep stress may favor the initial formation of a uniform phosphide distribution which then promotes a uniform distribution of MC carbides.

Although MC precipitation occurs first at grain boundaries, the dominant grain boundary precipitate is $M_{23}C_6$ after 1000 h aging at 600 C or 10 h aging at 700 C. $M_{23}C_6$ is abundant for all times at 800 C and up to 300 h at 900 C after which it begins to dissolve and is replaced by Ti- and Nb-rich MC. Laves phase was observed at grain boundaries only after prolonged aging (1000 h at 700 C). To date, χ phase has been identified in the 800 C samples annealed for 1000 h only, but σ phase has not been detected in solution annealed alloy AX5.

Fig. 7.1a Extraction replica, SA, 1h, 600 C: undissolved (Ti,Nb)C in the matrix and at grain boundaries.

Fig. 7.1b Extraction replica, SA, 10h, 600 C: undissolved (Ti,Nb)C at grain boundaries.

Fig. 7.2a Extraction replica, SA, 300h, 600 C: rafts of MC precipitates at grain boundaries.

Fig. 7.2b Thin foil, SA, 300h, 600 C: MC precipitates on dislocations in the matrix.

Fig. 7.3a Extraction replica, SA, 1000h, 600 C: grain boundary $M_{23}C_6$ in association with rafts of MC carbides.

Fig. 7.3b Diffraction pattern showing cube-to-cube relationship between $M_{23}C_6$ and MC carbides.

Fig. 7.3c Diffraction pattern showing cube-to-cube relationship between $M_{23}C_6$ and MC carbides.

Fig. 7.4 Thin foil, SA, 3000h, 600 C: extensive grain boundary $M_{23}C_6$ precipitation.

Fig. 7.5a Extraction replica, SA, 1h, 700 C: undissolved and precipitated grain boundary MC carbides.

Fig. 7.5b Thin foil, SA, 1h, 700 C: inclined grain boundary containing MC carbides.

Fig. 7.6 Thin foil, SA, 1h, 700 C: Moire fringe images showing MC carbides on dislocation.

Fig. 7.7 Thin foil, SA, 1h, 700 C: early stages of matrix phosphide precipitation.

Fig. 7.8a Thin foil, SA, 10h, 700 C: grain boundary $M_{23}C_6$.

Fig. 7.8b Thin foil, SA, 10h, 700 C: matrix phosphide precipitation.

Fig. 7.8c Thin foil, SA, 10h, 700 C: MC precipitation on matrix dislocations.

Fig. 7.9a Thin foil, SA, 1000h, 700 C: grain boundary $M_{23}C_6$ precipitation.

Fig. 7.9b Thin foil, SA, 3000h, 700 C: matrix phosphides with MC carbides precipitated on associated dislocations.

Fig. 7.10a Thin foil, SA, 700 C, 1h: MC precipitates on matrix dislocations.

Fig. 7.10b Thin foil, SA, 700 C, 10h: MC precipitates on matrix dislocations.

Fig. 7.10c Thin foil, SA, 700 C, 300h: MC precipitates on matrix dislocations.

Fig. 7.10d Thin foil, SA, 700 C, 1000h: MC precipitates on matrix dislocations.

Fig. 7.10e Thin foil, SA, 700 C, 3000h: MC precipitates on matrix dislocations.

Fig. 7.11a Thin foil, SA, 1h, 800 C: undissolved carbide (U) and fine phosphides (P).

Fig. 7.11b Thin foil, SA, 1h, 800 C: MC precipitates on incoherent twin boundaries.

Fig. 7.11c Thin foil, SA, 1h, 800 C: grain boundary $M_{23}C_6$ precipitates.

Fig. 7.11d Thin foil, SA, 1h, 800 C: MC precipitates at stacking faults.

Fig. 7.12a Thin foil, SA, 10h, 800 C: $M_{23}C_6$ (C) and MC (M) grain boundary precipitates.

Fig. 7.12b Diffraction pattern showing cube-cube orientation relationship between grain boundary $M_{23}C_6$, MC precipitates and the austenite matrix.

Fig. 7.12c Analysis of Diffraction pattern.

Fig. 7.13a Thin foil, SA, 800 C, 300h: phosphide precipitates and associated MC carbides (M).

Fig. 7.13b Thin foil, SA, 800 C, 1000h: phosphide precipitates and associated MC carbides (M).

Fig. 7.13c Thin foil, SA, 800 C, 3000h: phosphide precipitates and associated MC carbides (M).

Fig. 7.14 Thin foil, SA, 1000h, 800 C: MC precipitates on matrix dislocations.

Fig. 7.15 Thin foil, SA, 3000h, 800 C: grain boundary (Ti,Mo,V)C carbides (M).

Fig. 7.16a Thin foil, SA, 1h, 900 C: phosphide precipitates.

Fig. 7.16b Thin foil, SA, 10h, 900 C: grain boundary M_2C_6 carbides.

Fig. 7.17a Thin foil, SA, 900 C, 1h: matrix MC carbides on dislocations.

Fig. 7.17b Thin foil, SA, 900 C, 10h: matrix MC carbides on dislocations.

Fig. 7.17c Thin foil, SA, 900 C, 300h: matrix MC carbides on dislocations.

Fig. 7.17d Thin foil, SA, 900 C, 1000h: matrix MC carbides on dislocations.

Fig. 7.18 Thin foil, SA, 1000h, 900 C: wavy grain boundary beginning to unpin and migrate.

8: AGING KINETICS OF SOLUTION ANNEALED PLUS COLD WORKED ALLOY AX5

This chapter presents transmission electron micrographs from thin foils and extraction replicas of alloy AX5 in the solution annealed plus 5.6% cold worked condition after aging for 1, 10, 300, 1000 and 3000 h at 600, 700, 800 and 900 C.

The intragranular microstructural features of these specimens are quite different from those of the solution annealed specimens, which are characterized by sparsely distributed phosphides and patches of associated MC carbides on dislocations. The cold worked material shows a much finer MC precipitate distribution on the dislocations introduced into the austenite matrix by the 5.6% deformation. These MC carbides remain stable even after 3000 h at 900 C.

8.1 Aging at 600 C

The 5.6% cold work performed after the solution annealing treatment of 1 h at 1250 C introduced a dislocation density of approximately 10^{14} lines m^{-2} . After aging for 1 h and 10 h (Figure 8.1a) the austenite matrix was still heavily dislocated and undissolved (Ti,Nb)C, (Ti,Nb)N or (Ti,Nb)CN were observed in the matrix and at grain boundaries. Precipitation of MC carbides on the matrix dislocations could not be clearly identified until Moire fringe images were detected after 300 h aging (arrowed in Figure 8.1b). The first appearance of grain boundary $M_{23}C_6$ was observed after 300 h. Extensive MC precipitation on matrix dislocations, together with grain boundary (Ti,Nb)C and $M_{23}C_6$ precipitates were observed after 1000 h (shown in Figure 8.1c) and 3000 h. No

phosphide precipitates were observed in the cold worked specimens at 600 C.

8.2 Aging at 700 C

MC carbides were present on dislocations in the matrix (Figure 8.2) and also observed together with $M_{23}C_6$ at grain boundaries after 1 h at 700 C. However, grain boundary precipitation was sparse with only occasional clusters of fine MC and $M_{23}C_6$ precipitates, identified by EDX spectra and diffraction pattern and arrowed in Figure 8.3. The evolution of MC precipitation on matrix dislocations is shown in Figures 8.4a through 8.4e, for times of 1, 10, 300, 1000, and 3000 h.

$M_{23}C_6$ grain boundary carbides were more abundant after 10 h aging (Figure 8.5a), when they appeared as both filamentary grain boundary carbides, 0.8 μm in length by 0.05 μm wide, (Figure 8.5b) and also as rafts of precipitates approximately 0.2 μm in size. Observations of extensive grain boundary $M_{23}C_6$ precipitates were made in thin film specimens after 300 h, 1000 h and 3000 h, as shown in Figures 8.6a through 8.6c. It is interesting to note that as the $M_{23}C_6$ precipitates accumulate at the grain boundaries, the regions between the precipitates are also filling in with fine MC carbides. EDX analyses showed that the $M_{23}C_6$ carbides contained small quantities of vanadium and molybdenum and were often associated with the adjacent MC carbides as reflected by the presence of minor amounts of titanium and niobium in certain analyses. The undissolved precipitates shown clearly in Figures 8.5a and 8.5b contained predominantly Ti and Nb or Ti, Nb and Mo. In contrast, the MC carbides precipitating directly on the dislocations in both the

matrix and at grain boundaries also contained significant amounts of vanadium and molybdenum, and occasionally (V,Mo)C carbides were also observed.

After 1000 h at 700 C both Laves phase and M_6C were detected at grain boundaries in addition to MC and $M_{23}C_6$. The rod-shaped Laves phase was found in association with the Nb-rich undissolved precipitates at both the grain boundaries and in the matrix (arrowed in Figure 8.7). The molybdenum-rich M_6C carbides were observed at grain boundaries for aging times of 300 h and higher and contained up to 12 at% vanadium. The MC carbides precipitated on dislocations formed stringers (as shown in Figure 8.8) and contained the three stabilizing elements Ti, Nb and V, in contrast to the undissolved carbides which did not contain vanadium. Vanadium and molybdenum enrichment dominated the early stages of MC growth, but after 1000h the molybdenum and vanadium contents were reduced and the carbides became richer in titanium and niobium. This suggests that the displaced molybdenum and vanadium then become available for the formation of Laves phase and M_6C carbides containing vanadium.

Evidence for the early stages of phosphide precipitation started to appear in thin foils after 1000 h aging but these precipitates were not clearly identified in extraction replicas (Figure 8.9) and in thin foils (Figure 8.3e) until the 3000 h aging treatment. Figures 8.9 and 8.3e also show the fine MC distribution present in the matrix after 3000 h aging. Rod-shaped Laves phases were again observed closely associated with coarse, undissolved, precipitates.

In addition to precipitating on matrix dislocations and at grain boundaries, MC carbides also precipitated at incoherent twin boundaries (shown after 10 h in Figure 8.10a) and precipitated on the partial dislocations associated with stacking faults (Figure 8.10b). Precipitation of coarse $M_{23}C_6$ (C) carbides at stacking faults was also occasionally observed and is shown for 3000 h aging in Figure 8.10c.

8.3 Aging at 800 C

Grain boundary $M_{23}C_6$ and MC carbides were abundant after 1 h at 800 C (Figure 8.11) and were present for all aging times. Extensive precipitation of MC carbides was also observed on matrix dislocations (Figure 8.12a), including those in the regions adjacent to grain boundaries (Figure 8.12b). Hence precipitate free zones were only occasionally observed at grain boundaries in contrast to 316 stainless steel where such zones are frequently observed. MC precipitates formed on extrinsic dislocations in the regions of the grain boundaries between the $M_{23}C_6$ particles. Energy dispersive X-ray (EDX) spectroscopy and convergent beam electron diffraction analyses in thin film specimens after 1 h and 1000 h identified two types of grain boundary carbides, $M_{23}C_6$ containing Cr, Fe, Mo and Ni, and MC carbides containing Ti, V and Mo.

Increasing the aging time from one hour to 3000 hours produced very little coarsening of the matrix MC precipitates as shown in Figure 8.13. These results are in agreement with those of Kesternich [192], who showed that TiC precipitates in a 15% cold worked 15Cr-15Ni-0.3Ti steel increased in size from approximately 4 nm after 0.2 h to only 8

nm after 2500 h aging at 750 C. However, Carolan [197] has observed ripening of MC precipitates in a 16Ni-14Cr modified austenitic alloy containing 0.4 % Si. The lattice parameters of the matrix MC carbides, determined from the diffraction patterns of the specimen aged for 3000 h, ranged from 0.428 nm to 0.432 nm (note $a_{VC} = 0.416$ nm, $a_{TC} = 0.432$ nm). There was insufficient recovery of the dislocation substructure in the 1000 and 3000 h aged specimens to result in rapid coarsening of the MC precipitates.

M_6C carbides were detected after 300 h and Laves phase after 1000 h. The grain boundary carbides were again predominantly $M_{23}C_6$, shown in Figure 8.14 for 1000 h aging. Extraction replicas from the 300 h sample suggested that phosphide precipitates may be present but only MC carbides, which appeared to have grown together along dislocations (arrowed in Figure 8.15) could be identified using EDS. Analyses of the precipitates extracted after 300 h aging has identified grain boundary MC, $M_{23}C_6$ and M_6C carbides. The compositions of these carbides are similar to those observed after 1000 h at 700 C. EDX spectroscopy and convergent beam diffraction also identified the presence of grain boundary $M_{23}C_6$ carbides, (Ti,Nb)C carbides, Mo-rich M_6C carbides and Laves precipitates in the samples aged for 1000 and 3000 h at 800 C.

8.4 Aging at 900 C

Grain boundary $M_{23}C_6$ and MC carbides, plus MC on matrix dislocations were observed after 1 hour aging and both types of MC were found for up to 3000 h aging. Figure 8.16a shows the presence of MC carbides between the $M_{23}C_6$ carbides at a grain boundary in the 10 h aged microstructure

and Figure 8.16b shows the corresponding matrix distribution of MC carbides. The $M_{23}C_6$ carbides were less abundant after 300 h at 900 C and appeared to be going back into solution. The grain boundary carbides extracted after 300 h and 1000 h are shown in Figures 8.17a and 8.17b respectively. These times coincided with some recovery of the dislocation substructure in the matrix and the appearance of wavy grain boundaries, suggesting boundary migration. Such a boundary is shown for the 1000 h aged microstructure in Figure 8.18. However, Figure 8.19 clearly indicates that many MC carbides still remained on dislocations in the austenite matrix after 1000 h and similar observations were made for the 3000 h aging treatment. In some regions the dislocation structure near grain boundaries was well preserved even after 3000 h (Figure 8.20), which may be attributed to the precipitation of stable MC carbides on the dislocation networks. Recrystallization, which might be expected when aging a deformed alloy at 900 C, was not observed in cold worked alloy AX5 after 3000 h at 900 C. Such resistance to recrystallization will clearly improve the high temperature creep resistance of alloy AX5. For comparison, Kesternich [192] showed that 15 % cold worked Din 1.4970 steel recrystallized after aging for 20 h at 900 C. The superior performance of AX 5 alloy may be attributed an optimized level of cold work (5.6%), which produces sufficient dislocations for uniform MC precipitation but stores too little strain energy for rapid recrystallization.

M_6C carbides were observed in the 300 h extraction replicas, but only grain boundary MC carbides have been detected to date in the 1000

h and 3000 h aged samples. No phosphide precipitates were detected in the 900 C aged samples. The presence of the matrix MC carbides on dislocations after 3000 h at 900 C clearly accounts for the remarkable creep strengths observed in this steel.

8.5 Summary

The precipitate phases observed in cold worked alloy AX5 are similar to those in solution annealed AX5, with the dominant phases being MC carbides in the austenite matrix and both MC and $M_{23}C_6$ carbides at the grain boundaries. However some distinct features of the cold worked specimens may be summarized as follows: (1) the distribution of matrix MC carbides is uniform and random compared with the few dense patches in the solution annealed specimens; (2) grain boundary $M_{23}C_6$ carbides precipitate earlier at 600 C and 700 C than in the solution annealed specimens; (3) the matrix MC are finer in the cold worked material; (4) phosphides have only been observed after 1000 and 3000 h at 700 C in the cold worked material.

The observation that matrix MC precipitation was much less in solution annealed alloy AX5 is in agreement with Kesternich and Meertens' observations of no intergranular TiC precipitation in DIN 1.4970 steel, unless aging treatments in the temperature range 650 to 900 C were preceded by cold work [198]. They concluded that precipitation of TiC was dislocation controlled up to 800 C for 25% prior cold work and 900 C for 15% cold work. Above these temperatures recrystallization was observed together with rapid coarsening of the TiC precipitates. The choice of 5.6% cold work has prevented recrystalliza-

tion at 900 C and retarded recovery for approximately 1000 h at 900 C, resulting in a very stable distribution of MC precipitates on dislocations for all the conditions studied in this research.

Fig. 8.1a Thin Foil, CW, 10h, 600 C: dislocated matrix and undissolved (Ti,Nb)C at grain boundaries.

Fig. 8.1b Thin foil, CW, 300h, 600 C: Moiré fringe images (arrowed) of fine MC precipitates on matrix dislocations.

Fig. 8.1c Extraction replica, CW, 1000h, 600 C: grain boundary $M_{23}C_6$ and MC precipitates.

Fig. 8.2 Thin foil, CW, 1h, 700 C: Moiré fringe images showing MC precipitates on matrix dislocations.

Fig. 8.3 Extraction replica, CW, 1h, 700 C: $M_{23}C_6$ (arrowed) at grain boundary.

Fig. 8.4a Thin Foil, CW, 1h, 700 C: Evolution of MC precipitates on matrix dislocations.

Fig. 8.4b Thin Foil, CW, 10h, 700 C: Evolution of MC precipitates on matrix dislocations.

Fig. 8.4c Thin Foil, CW, 300h, 700 C: Evolution of MC precipitates on matrix dislocations.

Fig. 8.4d Thin Foil, CW, 1000h, 700 C: Evolution of MC precipitates on matrix dislocations.

Fig. 8.4e Thin Foil, CW, 3000h, 700 C: Evolution of MC precipitates on matrix dislocations.

Fig. 8.5a Extraction replica, CW, 10h, 700 C: Grain boundary M₂₃C₆ precipitates.

Fig. 8.5b Extraction replica, CW, 10h, 700 C: Fibrous grain boundary M₂₃C₆ carbides.

Fig. 8.6a Thin foil, CW, 300h, 700 C: Evolution of grain boundary precipitates.

Fig. 8.6b Thin foil, CW, 1000h, 700 C: Evolution of grain boundary precipitates.

Fig. 8.6c Thin foil, CW, 3000h, 700 C: Evolution of grain boundary precipitates.

Fig. 8.7 Extraction replica, CW, 1000h, 700 C: Laves phase associated with MC carbides.

Fig. 8.8 Thin foil, CW, 1000h, 700 C: Moire fringe images showing MC carbides on dislocations.

Fig. 8.9 Extraction replica, CW, 3000h, 700 C: Matrix phosphide precipitates.

Fig. 8.10a Thin foil, CW, 10h, 700 C: MC precipitates at incoherent twin boundaries.

Fig. 8.10b Thin foil, CW, 1000h, 700 C: MC precipitates on partial dislocations.

Fig. 8.10c Thin foil, CW, 1000h, 700 C: $M_{23}C_6$ precipitates on stacking faults.

Fig. 8.11 Extraction replica, CW, 1h, 800 C: Grain boundary $M_{23}C_6$ and MC precipitation.

Fig. 8.12a Thin foil, CW, 1h, 800 C: MC precipitation on dislocations in the matrix.

Fig. 8.12b Thin foil, CW, 1h, 800 C: $M_{23}C_6$ and MC carbides with no precipitate free zone at a grain boundary.

Fig. 8.13 Thin foil, CW, 3000h, 800 C: Matrix MC precipitates.

Fig. 8.14 Thin foil, CW, 1000h, 800 C: Grain boundary containing $M_{23}C_6$, MC and M_6C carbides.

Fig. 8.15 Extraction replica, CW, 300h, 800 C: Matrix MC precipitates. Arrows indicate coallescence of MC along a dislocation line. No phosphides detected.

Fig. 8.16a Thin foil, CW, 10h, 900 C: Grain boundary MC between $M_{23}C_6$ carbides.

Fig. 8.16b Thin foil, CW, 10h, 900 C: Matrix MC precipitates.

Fig. 8.17a Extraction replica, CW, 300h, 900 C: Grain boundary containing M₂₃C₆ and MC carbides.

Fig. 8.17b Extraction replica, CW, 1000h, 900 C: Grain boundary containing MC carbides only.

Fig. 8.18 Thin foil, CW, 1000h, 900 C: Wavy grain boundary containing MC carbides.

Fig. 8.19 Thin foil, CW, 1000h, 900 C: Matrix MC precipitates.

Fig. 8.20 Thin foil, CW, 3000h, 900 C: Dislocation structure near a grain boundary.

9: COMPOSITIONAL ANALYSES OF THE EXTRACTED PRECIPITATE PHASES

The precipitate phases identified in both the solution annealed and solution annealed plus cold worked samples were extracted on replicas and analysed using energy dispersive X-ray analysis in either a Philips 420 scanning transmission electron microscope or a Philips 400T equipped with a field emission gun. In this chapter we shall present analytical data for times of 1, 10, 300, 1000 and 3000 h at 700 C, followed by data for 1000 h at 700 C, 800 C and 900 C.

Compositional analyses of the precipitates extracted from the solution annealed specimens at 700 C are presented in Table V and from the cold worked specimens in Table VI. The comparison for a constant aging time of 1000 h at 700, 800 and 900 C is presented for solution annealed AX5 in Table VII and cold worked AX5 in Table VIII.

9.1 Undissolved MC Carbides

Tables V through VII show that titanium is the major component of the undissolved carbides with niobium being the secondary element. The undissolved carbides range from pure TiC, to (Ti,Nb)C containing up to 42 at% Nb (e.g. Ti:Nb atomic percent ratios of 99.2:0.8 to 58.8:41.5). Up to 8% Mo, 3% Cr and 2% Fe was observed but no vanadium was incorporated into undissolved carbides containing more than 50% Ti. Molybdenum was incorporated after only 1 h aging but Fe and Cr were found only after aging for 1000 and 3000 h at 700 C. A typical spectrum from an undissolved carbide is shown in Figure 9.1 (Note: the copper peak comes from the copper grid supporting the specimen). Three types of high-Ti MC carbides were identified: type A containing approximately

60% Ti, type B containing approximately 75% Ti and type C containing more than 85% Ti. Figure 9.2 shows that type B has been observed only after 1000 and 3000 h at 700 C, and that type C appears the most stable as it is observed for all aging times at 700 C.

9.2 Matrix and Grain Boundary MC

Studies of the matrix MC showed that the earliest MC to form in cold worked alloy AX5 (1 h at 700 C, Table VI) comprised two types, the first contained only 13% Ti, but incorporated 15% V, 21% Cr and 44% Mo, and the second, which also occurred at grain boundaries, contained 37% Ti, 13% V, 21% Nb and 23 % Mo. The appearance of Mo-rich matrix MC carbides (without chromium) was confirmed after 10 h aging at 700 C (Table VI and Figure 9.3a) and MC precipitates containing only the elements Mo and V were also observed. After 1000 h at 700 C, the MC composition stabilized to 35-40% Ti, 18-23% V, 15% Nb and 20-25% Mo (with small quantities of Cr and Fe) (Figure 9.3b), and remained unchanged after 3000 h. Comparison with Table V showed that the titanium and niobium contents were a little lower, (25-35%) and (7-11%) respectively, the vanadium contents increased to the range (23-34%) vanadium, and the molybdenum was a little higher (22-28%) in solution annealed AX5. The MC with the lowest vanadium levels incorporated up to 20% chromium. The matrix and grain boundary MC carbides of solution annealed AX5 had similar compositions for all aging times.

Increasing the temperature to 800 C and 900 C for the 1000 h aging treatment resulted in a decrease in the vanadium and molybdenum contents for both the solution annealed and cold worked specimens. In the

solution annealed sample this corresponded to an increase in the titanium and niobium levels, whereas in the cold worked samples Nb-rich precipitates were observed at 800 C and MC containing chromium were found at 900 C. Schematic representations of the MC compositions in CW AX5 for 10 h and 1000 h at 700 C plus 1000 h at 900 C are shown in Figures 9.3a to 9.3c.

The precipitate compositions are different for the cold worked and solution annealed conditions at 700 C, and comparisons of the Mo, V, Ti, Cr and Nb contents of these carbides as a function of aging time are presented in Figures 9.4a through 9.4e. Figure 9.4a shows that in the cold worked alloy there are two types of MC carbide: the first has essentially a constant molybdenum level as a function of aging time and the second has a high molybdenum level (~45 at%) during the early stages (1 and 10 h) of aging. The Mo-rich precipitates are V-rich and may also contain Cr but they have lower Ti and Nb levels than the first type of MC. During the later stages of aging (>1000 h) the Mo- and V-rich precipitates have not been observed, indicating that these elements have been gradually replaced with Ti, Nb and a smaller amount of Cr with increasing time and increasing temperature. As the Mo is rejected from the Mo-rich MC phase it then becomes available for the formation of M_6C and Laves phase. The parallel development of M_6C and Laves phases has restricted the amount of the Laves phase produced so that its presence appears not to be embrittling during the creep rupture tests. When the aging temperature is increased to 900 C the Cr content of the matrix MC rises accompanying the dissolution of the grain boundary $M_{23}C_6$ carbides.

It should be noted that the Mo-rich MC carbides have not yet been observed in the solution annealed material. Figures 9.4a through 9.4e show that the Mo, V and Cr levels are lower and the Ti and Nb levels higher in CW AX5 compared to SA AX5 for aging times greater than 1000 h.

Mo-enriched MC carbides have been reported in Ti-modified type 316 steel, 17-14 CuMo and CEO steel [199-201]. The composition of MC carbides in creep ruptured CEO alloy after 6174 h testing at 700 C and 170 Mpa (Figure 9.5) is similar to that in alloy AX5 aged for 1000 h at 700 C. Maziasz [199] has systematically analyzed the MC composition in type 321 steel, type 347 steel, Ti-modified type 316 steel and Nb-modified type 316 steel and concluded that pure NbC dissolves little Mo whereas Ti-enriched MC dissolves significant amounts of Mo, up to 55 wt%. This number is consistent with 58 wt% or 46 at% Mo observed in MC carbides during their early aging stages of growth in cold worked AX5 (e.g. after 10 h at 700 C). The enrichment of Mo and V in MC during the early stages of growth is consistent with their fast diffusivities and their compositions in the alloy (2.4 wt% Mo and 0.52 wt% V) compared to 0.27 wt% Ti and 0.15 wt% Nb. It should be noted that the matrix Ti and Nb levels will be reduced below these values due to the presence of the large undissolved carbides.

In summary, it seems that the presence of Mo was important for the nucleation and early growth of MC precipitates, and it should be emphasized that the incorporation of Mo into the MC lattices together with the extensive MC precipitation at grain boundaries and on matrix

dislocation significantly suppressed the development of Fe₂Mo Laves phase in alloy AX5.

9.3 M₂₃C₆

M₂₃C₆ carbides were present at the grain boundaries in both solution annealed and cold worked AX5 and were occasionally observed on stacking faults. Their compositions varied from 59-71% Cr, 16-24% Fe, 6-15% Mo, 3-7% V, and 3-8% Ni. There was no systematic variation of composition with either aging time or temperature. The appearance of small quantities of Ti and Nb in the analyses arises from the presence of fine grain boundary MC precipitates which become associated with the M₂₃C₆ during the extraction. The Cr, Fe and Mo contents of M₂₃C₆ in AX5 steel are similar to those reported by (a) Maziasz, who found that M (at%) = 63Cr-23Fe-8Mo-4Ni-1Mn in 20% cold worked 316 steel after aging for 4400 h at 560 C [6]; (b) Weiss and Stickler [103] who reported that M₂₃ = Mo₂Cr₁₆Fe₅ (M = 69.6Cr-21.7Fe-8.7Mo (at%)); and (c) Kautz and Gerlach [202] who identified M₂₃C₆ as (Cr₁₇Fe_{4.3}Mo_{1.3})C₆ i.e. (M = 74Cr-19.5Fe-6.5Mo (at%)).

9.4 M₆C

M₆C carbide has been observed after prolonged aging (1500 h at 650 C) in 316 type austenitic steels [103], but enhanced precipitation of Si-enriched M₆C occurs at earlier times in irradiated type 316 steels [87,156]. M₆C formed by prolonged aging is characterized not only by Si but by high Mo content. Examples were given as 8Si-0.8P-24.5Mo-0.6V-30Cr-1Mn-5Fe-30.7Ni (wt %) reported by Pedraza and Maziasz [6] in 20% cold worked type 316 steel after 4400 h at 600 C, and as 7Si-23Mo-0.8Ti-

31Cr-0.8Mn-11Fe-25Ni-1V (wt%) reported by Lee et al. [87] in type 316 steel after 10000 h at 600-650 C.

In alloy AX5, M_6C carbides were observed at grain boundaries, often closely associated with $M_{23}C_6$ carbides, for aging times greater than 300 h. Both M_6C and $M_{23}C_6$ have similar morphologies and crystal structures, with the small difference in lattice constants making it difficult to distinguish them by diffraction analysis. A typical EDX spectrum of M_6C is shown in Figure 9.6, identifying the carbide by the strong Mo peak and smaller Cr and Fe peaks. The M_6C carbide contains (39-41%) Mo, (33-42%) Cr, (10-12%) V, (6-12%) Fe (at%) and up to 6% Si, with no systematic variation in composition as a function of aging time or temperature, and may contain small quantities of nickel and phosphorus. The low levels of Ti and Nb reported in Tables VI and VIII probably reflect associated fine grain boundary MC carbides.

Since grain boundary M_6C carbide is often found with grain boundary $M_{23}C_6$ and appears only after extensive precipitation of $M_{23}C_6$, it is quite possible that the grain boundary M_6C evolved from $M_{23}C_6$ as suggested by Goldschmidt (Figure 4.2) [114] and Weiss and Stickler [103]. In alloy AX5, precipitation of M_6C occurs at higher temperatures (700-900 C) and earlier times (300 h at 800 and 900 C) than in 316 stainless steels. It has been observed predominantly in cold worked AX5 and reported only for 1000 h at 800 C in solution annealed AX5.

9.5 Laves phase

The Laves intermetallic phase was observed mainly at grain boundaries as globular, plate-like and rod shaped precipitates, and was

only observed after prolonged aging (>1000 h) in both solution annealed and cold worked alloy AX5. The globular and plate-like precipitates were closely associated with grain boundary $M_{23}C_6$, while the rods formed at the large undissolved grain boundary and matrix MC carbides (Figure 8.7). High energy planar defects such as grain boundaries and phase interfaces were the preferred nucleation sites for Laves phases agreeing with the observations of the Bristol group [23].

In the present study Laves phase was identified from diffraction patterns and EDX spectra. It should be noted that the diffraction patterns from Laves phase may be confused with those from χ phase. For example, Figure 9.7 shows a diffraction pattern, indexed as Laves phase with $B = [031]$ (where B is electron beam direction), which may be confused with χ phase with $B = [023]$. This problem can be easily resolved by comparing the EDX spectra in Figures 9.8 and 9.9. The Laves phase has high Fe and Mo/Nb peaks and smaller Cr, Ti and V peaks, whereas the χ phase has high Fe and Cr peaks with a smaller Mo peak.

The EDX spectra and diffraction patterns of Laves phase in alloy AX5 show that it is $MoFe_2$ with the $MgZn_2$ hexagonal crystal structure. The compositions shown in Tables V, VI and VIII are similar to those reported for aged type 316 steel as 32Mo-47Fe-14Cr-7Ni (at%) [103] and as 32Mo-42Fe-18Cr-7Ni-13Si-1Mn [87]. Small amounts of all three stabilizing elements appeared in the Laves phase in AX5, and could again arise from contamination by MC carbides. However, as Nb can form the Laves phase $NbFe_2$ and Cr has a similar atomic radius to Fe, the Laves phase in AX5 may also be represented as $(Mo,Nb)(Fe,Cr,Ni)_2$. Ni, which

replaces Fe and is often observed in Laves phase in austenitic steels [6,23,50,87,106], was observed in the solution annealed material after 1000 h at 700 C. However, Lee et al. [87] have reported that Ni was strongly rejected from Laves phase in type 316 steel after prolonged aging (10000 h at 600-650 C). Ti and V can also form the Laves phases TiFe_2 , V(Fe,Ti) and NbTiV , which have the MgZn_2 type lattice [161]. Thus Ti may play the role of either Mo as in TiFe_2 or Fe as in V(Fe,Ti) and V seems to replace Mo, which has a similar atomic size.

9.6 Phosphides

The addition of phosphorus to austenitic steels has been observed to increase their yield strengths and ultimate strengths [203,204]. The improvement in room temperature yield strength was explained by the solid solution strengthening effect and the high temperature strength was explained by the strain aging effect [204]. Since the atomic radius of phosphorus is about 15% less than that of iron, it was suggested that phosphorus was substitutionally dissolved in austenite [205]. In addition to solid solution strengthening, the addition of phosphorus may also affect the precipitation processes. It was observed that fine dispersions of M_{23}C_6 could be produced in the austenite matrix by the addition of phosphorus, which increased either the effective carbon supersaturation or the number of nucleation sites [206]. Rowcliffe and Nicholson [207] investigated the effects of P using a 18Cr-10Ni-3P-0.01C (wt %) austenitic steel and reported that the major precipitate phase was chromium phosphide (Cr_3P). Very little carbide was observed because of the low carbon content of this alloy. The Cr_3P phase had a tetrago-

nal crystal structure (Table II) and a lath shape morphology. Nucleation sites were reported to be at grain boundaries and on matrix dislocations.

Bentley and Leitnaker [208] investigated the phosphide phase in type 321 steel after 17 years aging at about 600 C and reported a rod-shaped iron phosphide (Fe_2P) with a hexagonal crystal structure ($a = 0.608 \text{ nm}$, $c = 0.364 \text{ nm}$) and a composition of 27Fe-4Cr-17Ni-27Ti-7P-18As, enriched in Fe and Ti. The orientation relationship between the phosphide and the austenite matrix was reported as:

$$\begin{array}{ccccccc} (0001) & // & (001) & ; & [\bar{1}210] & // & [110] \\ & \text{P} & & & \gamma & & \text{P} & & \gamma \end{array}$$

Lee et al. [87] also reported a needle-shaped iron phosphide in solution annealed type 316 and Ti-modified type 316 steel irradiated in EBR-II in the temperature range 500-625 C. The crystal structure and orientation relationship with the austenite matrix were consistent with that observed by Bentley and Leitnaker [208]. However the composition was reported as 29Fe-19Cr-27Ni-5P-4S-16Si, enriched in Ni and Si. Needle-shaped phosphides with the same crystal structure and composition have also been reported nucleated on dislocations in a 16Cr-14Ni-2.5Mo (wt %) austenitic steel and in a 14Cr-16Ni (wt %) austenitic steel, both containing minor additions of Ti, Si and P [70,71]. Phosphide precipitation was found to be significantly enhanced by the presence of Ti and Si. Recently, phosphide needles have been observed by Maziasz [1] in 14Cr-16Ni-2.5Mo (wt %) modified PCA containing Ti, Nb, V, P and

Si. Their compositions were quite complex, containing primarily Fe, Ti, P and trace amounts of Nb and V.

The presence of 0.02 wt% P in alloy AX5 results in matrix phosphide precipitation in the solution annealed specimens and a much finer distribution after longer times in the cold worked specimens. EDX analyses gave a composition of 18Si-20P-20Ti-4Cr-20Fe-8Ni-5Nb-5Mo for the phosphides extracted from solution annealed AX5 after 3000 h at 700 C and 32P-23Ti-4Cr-24Fe-9Ni-5Nb-3Mo for those extracted after 1000 h at 800 C, indicating that they are (Fe,Ti)P (Tables V and VII). A typical EDX spectrum in Figure 9.10 shows that the phosphides are enriched with Fe and Ti, agreeing with the observations of Bentley and Leitnaker [208] and Mazisz [1] but contain higher P levels than those observed in type 321 steel.

Phosphides may nucleate at clusters of phosphorus atoms [23], phosphorus-vacancy complexes or, since the phosphorus atom is smaller than the iron atom, at the compressive strain fields associated with edge dislocations, which are preferred segregation sites for phosphorus atoms. Phosphide precipitation has not yet been identified at grain boundaries, which are also preferred phosphorus segregation sites. They have been observed only after 1000 and 3000 h aging in cold worked AX5, probably reflecting the competition with the matrix MC for elements such as titanium and niobium.

9.7 σ and χ phases

It is well known that σ and χ phases cause embrittlement in austenitic steels and that they contain high Fe, Cr and lower Mo peaks in

their EDX spectra (Figures 9.11 and 9.9). High Cr contents are considered to promote the formation of sigma phase. Sticka [209] studied the effects of aging on the embrittlement of several austenitic steels and concluded that elements such as Mo and V also promoted sigma phase formation, whereas elements such as Ni and Co suppressed sigma precipitation. Hull [210] proposed that the susceptibility of austenitic steels to embrittlement by σ/χ phases could be assessed by the Cr equivalent of the alloy, which is expressed in wt% as follows:

$$\text{Cr Equivalent} = \text{Cr} + 0.31 \text{ Mn} + 1.76 \text{ Mo} + 0.97 \text{ W} + 2.02 \text{ V} + 1.58 \text{ Si} + \\ 2.44 \text{ Ti} + 1.70 \text{ Nb} + 1.22 \text{ Ta} - 0.226 \text{ Ni} - 0.177 \text{ Co}$$

The higher the Cr equivalent the more susceptible the steel to embrittlement.

The Cr equivalent of Weiss and Stickler's type 316 and 316L steel and of Grot and Spruiell's Ti-modified type 316 steel has been calculated to be 19.1, 20.7 and 20.1 respectively [105]. All these steels suffered severe sigma precipitation. Recognizing that carbon suppresses sigma precipitation, which only occurs once the carbon content has dropped to a low level after extensive carbide precipitation, Grot and Spruiell [105] suggested that the Cr equivalent of the austenite matrix after carbide precipitation would determine the susceptibility to sigma phase embrittlement. For two heats of type 321 steels, Leitnaker and Bentley [22] calculated the Cr equivalent to be 17.97 and 17.31 after subtracting out the Ti required to form TiC . The former (17.97) suffered σ precipitation but the latter (17.31) did not. Thus, they suggested that in type 321 steel a value of 17.8 may be a

reasonable minimum Cr equivalent for eliminating sigma phase. Recently Kesternich and Meertens [198] reported no sigma precipitation in Din 1.4970 steel which had a Cr equivalent of 16.

In the present study the initial Cr equivalent of alloy AX5 is 17.35. After subtracting the Ti, V and Nb contents required for MC precipitation, the Cr equivalent drops below 16.5. Thus alloy AX5 with such a low Cr equivalent would not be expected to suffer sigma precipitation, and none has been identified in this study.

However, χ phase appeared to be present at grain boundaries in the solution annealed AX5 after aging for 1000 h at 800 C. The composition of 52Fe-24Cr-19Mo-6Ni is very similar to the composition 51Fe-26Cr-15Mo-5Ni-2Mn observed by Maziasz [1] for 316 steel, which had been thermally aged for 2770 h at 800 C. To date χ phase has not been identified in cold worked AX5.

9.8 Summary

The compositions of the $M_{23}C_6$, Laves and M_6C phases have been determined and found to be constant as a function of aging time and temperature. χ phase has been identified only in the solution annealed specimen and its composition is similar to that determined by Maziasz for SA 316 steel. $M_{23}C_6$ is a Cr-rich phase, Laves is Fe and Mo-rich, M_6C is Cr and Mo-rich, and χ is Fe and Cr-rich. The phosphides are predominantly Fe-Ti phosphides. The MC carbides have the widest composition range which includes: undissolved TiC and (Ti,Nb)C, matrix (Mo,V)C and Mo-rich (Ti,Mo,V)C during the early stages of growth, followed by grain boundary and matrix (Ti,Mo,V)C with lower Mo and a

stable composition as growth proceeds. These MC remain stable for up to 3000 h at 900 C when recovery processes result in the $M_{23}C_6$ going back into solution and (Ti,Nb)C, which may incorporate a little Cr, becoming dominant.

The compositional evolution of the precipitate phases in SA AX5 and CW AX5 is shown schematically in Figure 9.12. The solution annealing treatment places most of the alloying elements in solution leaving only a few undissolved carbide or carbo-nitride precipitates. Figure 9.12a shows that during the quench from the solution annealing temperature, the alloying elements Ti, V, Mo, Nb, segregate to the grain boundaries and to dislocations introduced around the undissolved particles. When the alloy is cold worked by 5.6%, dislocations are introduced into the matrix, represented by the two dislocation lines shown in Figure 9.12b. Subsequent heating to the aging temperature will immediately result in solute segregation to these dislocations (Figure 9.12b).

The first precipitates to form at grain boundaries and on dislocations are MC containing Ti, V, Mo and Nb (Figure 9.12c). In the cold worked material MC precipitation on the dislocation lines is extensive with some precipitates being (a) Mo-rich (b) containing only vanadium and molybdenum, and (c) containing Ti, V, Mo and Nb (Figure 9.12d). The higher dislocation density in CW AX5 results in competition for the solute between the carbides on the dislocations themselves and also between the carbides on dislocations and at the grain boundaries.

$M_{23}C_6$ follows the MC precipitation at grain boundaries in both SA AX5 and CW AX5 (Figures 9.12e and 9.12f). The low dislocation density in SA AX5 results in few nucleation sites for the matrix MC precipitates, which consequently do not form. The first matrix precipitates to develop in SA AX5 are the phosphides, which incorporate the elements Ti and Fe with smaller amounts of Mo, V, Cr and Nb (Figure 9.12e). In contrast, MC precipitates rapidly develop on the dislocations in CW AX5. After the initial period of nucleation and growth, which is favored by high molybdenum contents for many precipitates, the Mo-rich MC appear to lose Mo and incorporate more Ti and Nb reaching a stable composition (Figure 9.12f). This composition remains constant for up to 3000 h at 900 C.

After prolonged aging, coarsening of the MC precipitates occurs on the few dislocation sources in SA AX5. Laves phase develops at the grain boundaries predominantly in association with the undissolved carbides, but also as isolated particles (Figure 9.12g). In the cold worked AX5, the flux of molybdenum from the MC precipitates to the grain boundaries results in the simultaneous appearance of both M_6C and Laves phase after 1000 h at 700 C (Figure 9.12h). The M_6C frequently form adjacent to the $M_{23}C_6$ carbides and may be developed by incorporation of molybdenum into this phase as proposed by Goldschmidt [114]. Both M_6C and χ phase have been observed in SA AX5 after 1000 h at 800 C (Figure 9.12i). The Cr for the χ phase may be supplied by the $M_{23}C_6$ carbides if they lose Cr as they incorporate Mo and form M_6C . Figure 9.12i also

shows the coarsening and coalescence of the MC precipitates on dislocations punched out from the phosphide precipitates.

The competition for solute between the MC carbides on dislocations in CW AX5 prevented significant development of the phosphide precipitates, which contain Ti, Nb, Fe and Ni, until 3000 h at 700 C, shown in Figure 9.12j. For all the aging conditions studied, σ phase was not detected.

When the aging temperature is increased, for example, to 900 C for 1000 h, the $M_{23}C_6$ carbides, Laves and χ phases go back into solution increasing the matrix Cr and V levels (Figures 9.12k and 9.12l). Some Cr is incorporated into the matrix MC, which also lose V and Mo, becoming Ti and Nb rich (Figure 9.12l). The dislocation substructure begins to recover and wavy grain boundaries, suggesting unpinning are observed. The Ti-rich MC grow rapidly by matrix diffusion of solute in solution annealed AX5 (Figure 9.12k).

Table V: Compositional Analyses of Precipitates Extracted from the Solution Annealed Specimens Aged at 700 C

Ppt.	Type*	Composition (atomic %)								
		Si	P	Ti	V	Cr	Fe	Ni	Nb	Mo
1h										
MC	U/GB/M	-	-	87.8	-	-	-	-	12.2	-
	U	-	-	58.5	-	-	-	-	41.5	-
	U/M	-	-	89.3	-	-	-	-	8.3	2.4
10 h										
MC	U	-	-	99.2	-	-	-	-	0.8	-
	U	-	-	90.4	-	-	-	-	8.5	1.1
	GB/M	-	-	34.2	19.0	5.8	-	-	15.2	24.8
M ₂₃ C ₆	GB	-	-	-	2.6	64.1	22.9	3.2	-	7.2
1000 h										
MC	M	-	-	34.5	27.9	-	-	-	11.1	26.5
	M	-	-	22.0	33.3	10.4	-	-	6.7	27.6
	M	-	-	29.4	33.9	-	0.9	-	9.5	26.4
	M	-	-	24.8	23.3	19.1	1.2	-	9.6	22.0
	GB	-	-	56.9	-	1.7	-	-	33.4	8.0
	U/GB	-	-	83.6	-	-	-	-	15.4	1.0
M ₂₃ C ₆	GB	-	-	0.9	3.3	67.3	20.2	3.2	-	7.4
	GB	-	-	-	2.9	68.0	20.2	3.2	-	5.8
Laves	GB	12.5	-	1.1	5.6	9.0	20.7	18.2	-	32.9
3000 h										
MC	M	-	-	25.6	30.1	8.3	1.7	-	8.5	25.8
	M	-	-	24.3	33.3	7.7	-	-	8.4	26.3
	U	-	-	85.9	-	3.1	-	-	6.8	4.2
M ₂₃ C ₆	GB	-	-	-	3.0	68.7	18.5	7.9	-	7.0
	GB	-	-	2.1	4.0	60.4	19.0	3.5	-	10.9
	GB	-	-	5.6	4.8	60.4	16.0	2.6	2.3	8.4
Phos.	M	17.6	19.8	19.6	-	4.4	19.9	7.8	5.3	5.1

U - Undissolved M - Matrix; GB - Grain boundary;
Phos - Phosphide; Ppt. - Precipitate.

Table VI: Compositional Analyses of Precipitates Extracted from the Cold Worked Specimens Aged at 700 C

Ppt.	Type*	Composition in atomic %							
		Si	Ti	V	Cr	Fe	Ni	Nb	Mo
1 h									
M ₂₃ C ₆	GB	-	1.9	5.3	59.3	16.5	2.5	-	14.5
MC	U/GB/M	-	59.1	-	-	-	-	34.2	-
	GB/M	-	36.9	13.2	6.0	-	-	20.7	23.2
	M	-	13.0	15.3	21.4	-	-	5.9	44.4
	GB	-	44.1	8.7	4.5	1.4	-	24.9	16.4
10 h									
M ₂₃ C ₆	GB	-	-	3.5	65.7	23.8	-	-	7.1
	GB	-	2.3	5.6	60.9	21.8	-	1.4	8.0
MC	U/GB	-	89.7	-	-	-	-	10.2	-
	U/M	-	61.2	-	-	-	-	30.6	8.2
	M	-	16.8	24.9	-	-	-	12.2	45.9
	M	-	-	43.1	-	-	-	-	56.9
1000 h									
M ₂₃ C ₆	GB	-	-	3.0	71.3	16.5	-	-	9.2
	GB	-	5.4	7.3	53.1	16.5	-	2.5	15.2
MC	U	-	83.6	-	-	-	-	16.4	-
	U	-	84.3	-	-	2.1	-	11.1	2.5
	M	-	72.2	-	-	-	-	22.6	5.2
	M	-	38.5	21.3	-	-	-	16.6	23.7
	M	-	37.5	19.9	6.1	-	-	15.5	21.0
	GB/M	-	36.2	19.1	5.9	2.8	-	14.8	21.2
M ₆ C	GB	-	-	11.5	41.6	6.6	-	-	40.4
	GB	-	4.9	12.1	34.9	6.4	-	2.8	38.7
Laves	GB	-	-	-	16.9	46.3	-	1.4	35.4
	GB	-	4.7	3.6	15.6	40.1	-	2.8	33.3
3000 h									
M ₂₃ C ₆	GB	-	1.2	2.8	69.0	17.0	3.2	-	6.8
	GB	-	-	3.0	69.7	18.2	2.7	-	6.4
MC	U/M	-	96.0	-	1.2	-	-	1.9	0.9
	GB	-	75.7	-	1.1	-	-	20.6	2.6
	M	-	38.2	23.1	-	-	-	15.2	23.5
	M	-	35.5	20.8	8.6	-	-	14.1	20.9
	M	-	37.2	18.6	6.7	1.3	-	15.5	20.7
	M ₆ C	GB	6.2	5.3	9.8	30.6	10.3	0.6	1.5
Laves	GB	9.6	4.7	0.9	18.2	38.5	3.8	1.1	23.2

* as in Table V.

Table VII: Compositional Analyses of Precipitates Extracted from the Solution Annealed Specimens Aged for 1000 h

Ppt.	Type*	Composition								
		Si	P	Ti	V	Cr	Fe	Ni	Nb	Mo
700 C										
MC	M	-	-	34.5	27.9	-	-	-	11.1	26.5
	M	-	-	22.0	33.3	10.4	-	-	6.7	27.6
	M	-	-	29.4	33.9	-	0.9	-	9.5	26.4
	M	-	-	24.8	23.3	19.1	1.2	-	9.6	22.0
	GB	-	-	56.9	-	1.7	-	-	33.4	8.0
	U/GB	-	-	83.6	-	-	-	-	15.4	1.0
M ₂₃ C ₆	GB	-	-	0.9	3.3	67.3	20.2	3.2	-	7.4
	GB	-	-	-	2.9	68.0	20.2	3.2	-	5.8
Laves	GB	-	-	1.3	6.2	10.1	23.4	20.7	-	38.4
800 C										
MC	U/GB	-	-	88.3	-	-	-	-	9.0	2.7
	GB	-	-	56.5	-	5.5	-	-	26.3	11.7
	M	-	-	41.5	20.5	-	-	-	14.5	23.5
	M	-	-	35.2	22.2	5.2	-	-	12.7	24.6
M ₆ C	GB	1.3	5.2	1.5	10.5	32.1	10.8	0.5	0.3	37.8
X	GB	-	-	-	1.1	25.3	55.4	5.5	-	12.6
	GB	-	-	-	-	23.5	52.2	5.6	-	18.7
Phos.	M	-	32.0	22.7	-	3.7	24.5	8.7	5.5	2.9
900 C										
MC	GB/M	-	-	66.0	-	-	-	-	25.2	8.8
	M	-	-	57.6	-	-	2.5	-	20.4	19.5
	M	-	-	49.4	14.1	-	-	-	17.1	19.4

* U = Undissolved; M = Matrix; GB = Grain boundary;
Phos = Phosphide; Ppt. = Precipitate.

Table VIII: Compositional Analyses of Precipitates Extracted from the Cold Worked Specimens Aged for 1000 h

Ppt.	Type*	Composition in atomic %								
		Si	P	Ti	V	Cr	Fe	Ni	Nb	Mo
700C										
MC	U	-	-	83.6	-	-	-	-	16.4	-
	U	-	-	84.3	-	-	2.1	-	11.1	2.5
	M	-	-	72.2	-	-	-	-	22.6	5.2
	M	-	-	38.5	21.3	-	-	-	16.6	23.7
	M	-	-	37.5	19.9	6.1	-	-	15.5	21.0
	GB/M	-	-	36.2	19.1	5.9	2.8	-	14.8	21.2
M ₂₃ C ₆	GB	-	-	-	3.0	71.3	16.5	-	-	9.2
	GB	-	-	5.4	7.3	53.1	16.5	-	2.5	15.2
M ₆ C	GB	-	-	-	11.5	41.6	6.6	-	-	40.4
	GB	-	-	4.9	12.1	34.9	6.4	-	2.8	38.7
Laves	GB	-	-	-	-	16.9	46.3	-	1.4	35.4
	GB	-	-	4.7	3.6	15.6	40.1	-	2.8	33.3
800 C										
MC	M	-	-	99.2	-	-	-	-	-	0.8
	GB/M	-	-	42.0	-	-	3.4	-	48.1	6.5
	M	-	-	38.5	-	-	-	-	57.2	4.3
	M	-	-	24.3	7.8	-	-	-	61.2	6.6
M ₂₃ C ₆	GB	-	-	-	3.0	70.4	16.3	2.7	-	7.6
Laves	GB	4.1	4.4	0.4	0.7	14.3	43.9	4.8	1.5	25.9
900 C										
MC	GB	-	-	93.9	-	-	-	-	5.4	0.7
	GB	-	-	94.0	-	-	-	-	6.0	-
	GB	-	-	95.4	-	1.4	-	-	3.2	-
	GB	-	-	93.9	-	1.6	-	-	3.9	0.7
	M	-	-	82.8	-	11.9	0.9	-	1.9	2.5
	M	-	-	37.6	15.5	14.0	-	-	15.8	17.0
	M	-	-	36.8	12.8	17.5	1.5	-	15.0	16.4

* as in Table VII.

Fig. 9.1 EDX spectrum of undissolved MC carbide.

Fig. 9.2 Ti content of undissolved MC carbide as a function of aging time at 700 C.

Fig. 9.3 Composition of precipitated MC carbides in CW AX5 alloy (a) 10h, 700 C (b) 1000h, 700 C (c) 1000h, 900 C.

Fig. 9.4a Mo content of precipitated MC carbides as a function of aging time at 700 C.

Fig. 9.4b V content of precipitated MC carbides as a function of aging time at 700 C.

CW: x Mo-rich MC ; • Matrix
 ▲ Grain boundary
 ■ Matrix & Grain boundary
 SA: ○ Matrix ; Δ Grain boundary
 □ Matrix & Grain boundary

Fig. 9.4c Ti content of precipitated MC carbides as a function of aging time at 700 C.

CW: x Mo-rich MC ; • Matrix
 ▲ Grain boundary
 ■ Matrix & Grain boundary
 SA: ○ Matrix ; Δ Grain boundary
 □ Matrix & Grain boundary

Fig. 9.4d Cr content of precipitated MC carbides as a function of aging time at 700 C.

Fig. 9.4e Nb content of precipitated MC carbides as a function of aging time at 700 C.

Fig. 9.5 Composition of MC carbides in CE0 alloy after 6174 h creep test at 700 C and 170 Mpa.

Fig. 9.6 EDX spectrum of M_6C carbides in AX5 steel.

Fig. 9.7 Diffraction pattern of Laves phase obtained from extraction replica, $B = [031]$.

Fig. 9.8 EDX spectrum of Laves phase in AX5 steel.

Fig. 9.9 EDX spectrum of χ phase in 316 steel [23].

Fig. 9.10 EDX spectrum of phosphides in AX5 steel.

Fig. 9.11 EDX spectrum of σ phase in 316 steel [23].

Pages 158 and 159 not available.
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10: TIME-TEMPERATURE-PRECIPITATION (TTP) DIAGRAMS

Although quantitative microanalyses were made for only selected aging times and temperatures, qualitative analyses were obtained for most of the aging conditions of both solution annealed and cold worked alloy AX5. The combination of these analyses with diffraction data from the thin foils have enabled TTP diagrams to be developed for each phase. The TTP diagrams for grain boundary MC, $M_{23}C_6$, M_6C and Laves phase, plus matrix MC and phosphides are presented in Figures 10.1 through 10.6.

10.1 TTP Diagrams for Alloy AX5

Figure 10.1 confirms that grain boundary MC carbides were present in both solution annealed and cold worked AX5 for all the aging conditions studied. Grain boundary $M_{23}C_6$ precipitation kinetics were slow at 600 C (Figure 10.2), as 300 h aging was required before these carbides were identified in the cold worked microstructures, and even longer (1000 h) for the solution annealed specimens. At 700 C the $M_{23}C_6$ again appeared earlier (1 h) in the cold worked alloy than the solution annealed alloy (10 h), but at 800 C, $M_{23}C_6$ carbides were observed in both solution annealed and cold worked microstructures for all aging times. After 1000 h and 3000 h at 900 C there was occasional evidence of $M_{23}C_6$ but the majority of the carbides appeared to have gone back into solution.

The M_6C carbides (Figure 10.3) were not observed at 600 C, but appeared in the 1000 h aged microstructure at 700 C, and in the 300 h microstructures at 800 C and 900 C for cold worked AX5. To date they have been observed only after 1000 h at 800 C for solution annealed AX5.

Laves phase (Figure 10.4) was identified after 1000 h at 700 C and 800 C in cold worked AX5, but only for 1000 h at 700 C in SA AX5. Data collection is continuing for this phase.

TTP diagrams for the matrix MC carbides and phosphides are presented in Figures 10.5 and 10.6. MC carbides were clearly visible on matrix dislocations after 300 h at 600 C for both the solution annealed and cold worked samples, and were observed for all subsequent aging conditions. However, it should be noted that these carbides only occurred where dislocations were present, and hence the volume fraction was significantly greater and the sizes were finer in the cold worked, heavily dislocated specimens than in the solution annealed material.

The phosphide precipitates were not observed at 600 C, and have been identified in the cold worked samples only after 1000 h and 3000 h at 700 C. They appeared to be present in the solution annealed material for all aging times at 700 C, 800 C and 900 C.

It should be noted that no sigma phase has been identified and χ phase has been identified only for 1000 h at 800 C in solution annealed alloy AX5 (Figure 10.4).

10.2 TTP Diagrams for Related Alloys

The aging kinetics of the 16Ni-14Cr austenitic steel can be compared with the TTP diagram for a typical 316 stainless steel in Figure 4.9 and modified austenitic steels in Figures 10.7 through 10.9. The TTP diagram in Figure 4.9 was compiled for SA 316 steel by Maziasz and McHargue [4], using data from references 7,103,104,106,156 and 211 through 214. Additional data has been developed by Lai [110].

TTP diagrams for stabilized austenitic steels have been developed by Murray et al. [215] for Esshete 1250 steel (Figure 10.7) and Padilha et al. [216] for steel DIN 1.4970 (redrawn in Figures 10.8 and 10.9), and Grot and Spruiell [105] for titanium stabilized 316 steel. The compositions of these steels are given in Table III. Esshete 1250 is a Nb-V stabilized 15Cr-10Ni steel, which was solution treated in the range 1050 - 1150 C. (No indication of any cold or warm work prior to the aging treatments was given.) DIN 1.4970 steel is a 15Cr-15Ni-1.25Mo steel stabilized with titanium and containing 30-100 ppm B. Figure 10.8 shows the TTP diagram for the steel after 25% cold work followed by a solution anneal at 1130 C for 30 minutes. In the temperature range 850 - 1100 C, the first precipitate to form was M_2B . Kesternich and Meertens [198] have shown this phase to be $(Cr,Fe)_2B$ with thin film EDX analyses of 78%Fe-21%Cr-1%Mo, and energy loss spectroscopy indicated that boron was the only light element present. $(Cr,Fe)_2B$ precipitates have not been identified in the present work by EDX analyses, or their characteristic faulted appearance, in either the AX5 or CEO samples. Although the role of boron in this alloy is not yet clear, Maziasz has noted that boron and phosphorus enhanced MC formation and that carbon and boron decreased Laves phase formation in modified 316 steels [1,217].

The TTP diagram developed by Grot and Spruiell [105] for 316 stainless steel containing 0.29% Ti showed that the first precipitate phase was TiC but no boride phase was reported. Their C-curve for $M_{23}C_6$ precipitation was similar to that in Figure 4.9. Within the $M_{23}C_6$

envelope were C-curves for σ and χ phases with the noses of these curves occurring at 16 and 20 hours, respectively at 750 C. The effect of prior cold work (20% RA) was to accelerate the formation of $M_{23}C_6$ and σ phase and retard the formation of χ phase, agreeing with our present observations.

10.3 Comparison of AX5 and Related Austenitic Steels

10.3.1 $M_{23}C_6$

The precipitation kinetics of grain boundary $M_{23}C_6$ in alloy AX5 is compared with that of SA type 316 steel, Esshete 1250, Din 1.4970 and Ti-modified type 316 steel in Table IX. The comparison shows that the precipitation of $M_{23}C_6$ in cold worked alloy AX5 is similar at all temperatures to that in Din 1.4970 (25% CW + 1130 C 30 min) and in Esshete 1250. The precipitation of $M_{23}C_6$ was accelerated at 600 C in the 316 type stainless steels, which contained higher Cr levels (18Cr-13Ni), compared to alloy AX5 (14Cr-16Ni), Esshete 1250 (15Cr-10Ni) and Din 1.4970 (15Cr-15Ni). The acceleration of $M_{23}C_6$ precipitation in Din 1.4970 (1130 C 30 min + 15 % CW) can be attributed to heavy cold work after the solution anneal at 1130 C for 30 min. In all the alloy systems precipitation of $M_{23}C_6$ was accelerated as the temperature increased from 600 C to 900 C, due to the faster diffusion of chromium at higher temperatures. Cold work appeared to accelerate the precipitation of grain boundary $M_{23}C_6$ in alloy AX5 at 600 and 700 C, but at higher temperatures (800 and 900 C) the effects of cold work were less pronounced, probably because the difference between the solute diffusivities in the matrix and along dislocations becomes smaller.

10.3.2 MC precipitation

The kinetics of MC precipitation has been studied in type 321 steel [105], Ti-modified type 316 steel [105], Essete 1250 [215] and Din 1.4970 steel [216]. (It should be noted that MC precipitation is not observed in 316 stainless steel as this alloy does not contain stabilizing elements). In type 321 steel and Ti-modified type 316 steel, for both the solution annealed and cold worked conditions, precipitation of MC preceded the formation of grain boundary $M_{23}C_6$. However, Figure 10.7 shows that for Essete 1250 steel $M_{23}C_6$ appeared earlier than (Nb,V)C carbides for the temperature range 600-850 C. For Din 1.4970 steel (Figures 10.8, 10.9), M_2B and (Ti,Mo)C were the only precipitates observed above 900 C. $M_{23}C_6$ precipitation precedes MC in Figure 10.8 (25% CW + 1130 C 30 min) below 850 C, and in Figure 10.9 (1130 C + 15% CW) below 750 C. Thus, cold work following a solution annealing treatment promotes the formation of (Ti,Mo)C precipitates in this steel.

In alloy AX5, grain boundary MC were observed for all the aging times and temperatures studied and matrix MC were found after 300 h at 600 C and for all times in the temperature range 700 - 900 C. Precipitation of grain boundary $M_{23}C_6$ was preceded by grain boundary MC at 600 C and 700 C. This may be due to: (a) the higher amount of stabilizing elements, (0.27 Ti + 0.15 Nb + 0.52 V = 0.94 wt%) in AX 5 alloy compared with 0.51 wt% (0.46 Ti + 0.05 Nb) in Din 1.4970 steel; (b) the presence of vanadium in AX5; and (c) the higher level of

molybdenum in AX5; all of which increase the stability of the MC carbides at lower temperatures (600 C).

The grain boundary (Ti,V,Mo)C nucleated at extrinsic dislocations and topographical defects in AX5, agreeing with observations by Jones et al. [218,219] of NbC precipitation in a 20Cr-25Ni-0.5Nb austenitic steel. They observed that after a 1350 C solution treatment, increasing the degree of cold work (0,5,10%), prior to aging for 0.5 h at 930 C, decreased the mean matrix precipitate size, but increased the mean grain boundary precipitate size. The latter was attributed to the increased density of extrinsic dislocations at grain boundaries. The size variation of precipitates within the same sample was attributed to the variation in density of these defects from boundary to boundary. It should be noted however that, unlike alloy AX5, precipitate free zones developed adjacent to the grain boundaries in the 20Cr-25Ni steel.

10.3.3 M_6C

M_6C precipitation was reported after approximately 2000 h in the temperature range 600-700 C for SA type 316 steels (Figure 4.9) but was not observed in Esshete 1250 and Din 1.4970 steels. In cold worked alloy AX5, grain boundary M_6C was identified after shorter times and at higher temperatures - i.e. 1000 h at 700 C and after 300 h at 800 and 900 C. It should be noted that the Mo content of the 316 type steels (2.05 wt%) and alloy AX5 (2.4 wt%) is higher than that in Esshete 1250 steel (1.02 wt%) or Din 1.4970 steel (1.25 wt%) suggesting that higher Mo content promotes precipitation of the Mo-rich M_6C carbides. Grain boundary M_6C may evolve by incorporation of Mo into $M_{23}C_6$ as shown in

Figure 4.2, and in the absence of extensive Laves precipitation, competition for the Mo is reduced, with M_6C rapidly forming at 800 C and 900 C.

10.3.4 Laves and χ phases

Laves phase was reported in SA type 316 steel after only 200 h at 700 -800 C, but was delayed until 1000 h at 700 C in both SA and CW alloy AX5, and 1000 h at 800 C in CW AX5. χ phase appeared after 1000 h at 800 C in SA AX5. Laves and χ phases were significantly suppressed in AX5 compared to 316 steels and were not observed in Esshete 1250 or Din 1.4970 steels. The prolonged aging required for the precipitation of intermetallic phases in austenitic steels has been attributed to (1) the necessity of developing a low carbon content in the austenite matrix, and (2) the lower diffusion coefficients of the intermetallic forming elements. However, in alloy AX5, all the carbide phases, $M_{23}C_6$, M_6C and MC, contain appreciable Mo, which is one of the major constituents of Laves phase (Fe_2Mo). Thus the extensive precipitation of all three carbides at grain boundaries combined with the MC precipitation on matrix dislocations probably consumes most of the Mo content, suppressing the formation of Laves phase. In contrast, MC precipitates do not form in 316 stainless steel and the Mo is available to form Laves and χ phases. The absence of Laves phase in Esshete 1250 and Din 1.4970 steels is accounted for by the lower Mo (1.02 and 1.25 wt%, respectively) and higher C contents (0.1 and 0.09 wt%, respectively) of these steels.

10.3.5 Phosphides

Phosphorus additions were deliberately made to the AX and CE series advanced austenitic steels in order to develop phosphide precipitates for the improvement of resistance to both irradiation and creep. However, alloy AX5, which contained the lowest phosphorus level (0.024 wt%) also showed excellent creep rupture strength. In cold worked AX5, uniformly distributed phosphide precipitates were detected after 1000 h at 700 C and were abundant only after 3000 h. Although phosphides were observed in SA AX5 for all aging times and temperatures except 600 C, it's occurrence was occasional and randomly distributed becoming abundant only after 3000 h at 700 C and after 1000 h at 800 C.

The phosphides in alloy AX5 contained mainly Fe, Ti and P, similar to phosphides reported in: (a) type 321 steel after 17 years at -600 C [208]; (b) type 316 and Ti-modified type 316 irradiated in EBR-II [87]; and (c) alloy CE0 after creep testing [2]. Thus phosphides precipitation can be regarded as either irradiation and/or stress enhanced or occurring after prolonged aging.

Maziasz has suggested that the formation of Ti-containing phosphides is dictated by the competition with MC carbides for Ti [1]. Consequently, Nb and V were deliberately added to the AX and CE series alloys to replace the Ti in the MC carbides, leaving more matrix Ti available to promote phosphide precipitation. This concept was supported by the fact that phosphides were not detected in Ti-modified type 316 steel even after 10000 h at 600-900 C [87], but were extensive in AX5 after only 1000 h at 700 - 800 C. Clearly Ti has a higher

carbon than phosphorus affinity so that phosphide precipitation can be suppressed if the available Ti is removed as MC carbides. The appearance of phosphides only after prolonged aging also suggests that they may require low matrix carbon concentrations like the intermetallic compounds which cannot dissolve C in the lattice.

10.3.6 σ Phase

The most important discovery in the phase identification is the absence of sigma phase for times up to 3000 h at temperatures in the range 700 - 900 C for alloy AX5. The nose of the sigma phase curve in 316 steels (Figure 4.9) and Esshete 1250 (Figure 10.7) occurred after approximately 1500 h at 800 C but σ phase has not been identified in the AX alloys or Din 1.4970 steel. Alloys AX5 and AX8 have now been creep tested for 20,000 h at 700 C and a stress of 170 MPa, showing less than 1% creep strain. This remarkable improvement in strength is attributed in part to the low silicon and higher carbon contents which are responsible for the elimination of the sigma phase.

10.4 Summary and Conclusions

The minor compositional modifications of the elements Ti, V, Nb, Mo, C, P, and Si, combined with a low level of cold work (5.6%) have produced an optimized microstructure for alloy AX5. The cold work is essential for: (a) producing the fine, uniform matrix MC and, after longer aging, phosphide distributions; (b) introducing the fine MC precipitates at grain boundaries between the $M_{23}C_6$ and M_6C phases; and (c) delaying the onset of recovery at 900 C. The early formation of M_6C has prevented extensive Laves and χ precipitation and the elimination of

embrittling σ phase has increased the creep rupture strength by orders of magnitude. In view of the excellent creep resistance of AX5 and AX7 it is suggested that high phosphorus levels (0.07 wt %) are not needed and that a low level (<0.02 wt %) would improve the weldability of the AX series steels.

TABLE IX: PRECIPITATION KINETICS FOR $M_{23}C_6$ IN AX5 AND RELATED ALLOYS

	600	700	800	900 (C)
SA type 316	~20	<0.2	<0.1	<0.1
SA type 316 + Ti	~20	~2	~3	-
20 % CW type 316	~20	~0.2	<0.2	-
Esshete 1250	~100	~9	<2	<1
Din 1.4970 25 % CW + 1130 C 30 min.	~300	~2	~0.2	-
Din 1.4970 1130 C 30 min. + 15 % CW	~10	~0.3	~0.8	-
SA AX5	<1000	<10	<1	<1
CW AX5	< 300	<1	<1	<1

Fig. 10.1 TTP diagram of grain boundary MC carbides.

Fig. 10.2 TTP diagram of grain boundary M_2C_6 carbides.

Fig. 10.3 TTP diagram of grain boundary M₆C carbides.

Fig. 10.4 TTP diagram of Laves Phase.

Fig. 10.5 TTP diagram of MC carbides on matrix dislocations.

Fig. 10.6 TTP diagram of Phosphide precipitates.

Fig. 10.7 TTP diagram for Esshete 1250 steel [215].

Fig. 10.8 TTP diagrams for DIN 1.4970 steel, 25% cold worked plus 1130 °C for 0.5 h [216].

Fig. 10.9 TTP diagrams for DIN 1.4970 steel 1130 C for 0.5 h plus 15% cold work [216].

11: A NEW EXPLANATION FOR THE MC CARBIDE SIZES

11.1 MC Carbide Sizes

The average MC matrix precipitate size has been determined from the Moire fringe images of individual MC precipitates on dislocations, following the method employed by Kesternich [192], and checked against measurements of extracted carbides. As described in Chapter 5, the precipitate size was taken as the side length, a , for particles with square cross sections and as $(ab)^{0.5}$ for particles with rectangular cross sections. The data are presented for the cold worked specimens at 700 C and 900 C. Histograms of the size distributions are shown in Figures 11.1a through 11.1e and 11.2a through 11.2e for 1, 10, 300, 1000 and 3000 h at 700 C and 900 C, respectively. The average particle sizes as a function of time and temperature are shown in Figure 11.3. The average MC carbide size increases steadily from 2.6 nm after 1 h at 700 C to 8.7 nm after 3000 h aging. At 900 C the carbides are 8.6 nm after only 1 h aging but remain at a constant size of approximately 10.5 nm between 10 h and 3000 h. These measurements indicate that the MC carbides are extremely stable, even at 900 C.

Kesternich [192] has measured the TiC precipitate size distributions and average precipitate diameters in DIN 1.4970 steel, solution treated at 1100 C and cold worked 15% prior to aging, for times ranging from 0.2 h to 2000 h at 750 C. These data are also presented in Figure 11.3. The observed time dependence of precipitate growth was smaller than $t^{0.1}$ at aging times beyond 20 h, and could not be explained by: (a) diffusion controlled coarsening ($t^{1/3}$ dependence) [220], (b) pipe

diffusion ($t^{1/5}$ dependence) [221], (c) diffusion controlled growth [222] or interface controlled ripening [223] ($t^{1/2}$ dependence), (d) interface controlled growth (t dependence) [222], or (e) the dislocation climb model by Silcock and Tunstall [141]. This led Kesternich to propose the following qualitative model, consisting of two mechanisms, to explain the TiC precipitate growth. Firstly a dislocation recovery mechanism, in which dislocation sweeping concentrated sufficient solute to result in TiC nucleation at locations where dislocations interacted or annihilated each other. The locally enhanced solute supersaturation may also provide sufficient driving energy for a short period of rapid interfacially controlled growth. Secondly, once the precipitates have grown large enough to effectively pin the dislocations, dislocation annealing stops and growth of the TiC particles ceases. The decrease in precipitate size as the degree of cold work prior to aging increased, could be explained by the increased density of nucleation sites together with the interfacial reaction limited growth of the TiC precipitates.

Figure 11.3 shows that the average MC precipitate size in CW AX5 shows a similar time dependence to that observed by Kesternich [192] for Din 1.4970 and also cannot be explained by the above growth or coarsening theories. The results show that following an initial period of rapid precipitate growth, the growth rate steadily decreases until at 900 C growth has effectively ceased after approximately 300 h. The initial precipitate growth occurs more rapidly at 900 C than 700 C, but the data at both temperatures appear to be approaching an asymptotic value of 10.5 nm. In the following section we shall show how we have

been able to successfully curve fit our experimental data and develop the first correlation between MC precipitate size and aging time for the advanced austenitic steels.

11.2 A New Correlation for MC Precipitate Growth in CW AX5

Inspection of the experimental data in Figure 11.3 suggested that the data could be fit by a hyperbolic function. When the data at both 700 and 900 C were taken into account the following relationship between the mean precipitate size, D , aging time, t , and temperature, T , was identified:

$$D = D_o \exp - \left[\frac{A + \frac{B}{T}}{\ln \frac{t}{t_o}} \right]$$

where D_o is the limiting precipitate size = 10.5 nm, $A = -12.61$, $B = 1.54 \times 10^4$ and t_o is the incubation time = 0.1 h.

The solid lines in Figure 11.3 for the temperatures 700, 750 and 900 C, represent a plot of this correlation, which fits the experimental data for 700 and 900 C very well.

The precipitate growth rate is given by:

$$\frac{dD}{dt} = D_o \frac{A + \frac{B}{T}}{t \left[\ln \frac{t}{t_o} \right]^2} \exp - \frac{A + \frac{B}{T}}{\ln \frac{t}{t_o}}$$

Calculation of the precipitate growth rate after 100 h aging gives values of 9.63×10^{-3} , 3.92×10^{-2} and 4.61×10^{-2} nm h⁻¹ for the temperatures 900, 750 and 700 C respectively. The slowest growth rate is found at the highest temperature and corresponds to a precipitate size

increase of approximately 10 nm in 1000 h. The initial stage of growth, during which the growth rate is highest at the highest temperatures is brief, corresponding to times less than approximately 0.3 h.

Kesternich's precipitate size measurements at 750 C fall below the curves fit to the CW AX5 data, and fit to the expression:

$$D = D_o \exp - \left[\frac{0.6733}{\ln \frac{t}{t_o}} \right]$$

where $D_o = 6.25$. This expression is shown as the dashed line in Figure 11.3. Data at other temperatures are required to give an expression similar to that for CW AX5, above. Further adjustments to the fit have not been attempted due to the difficulty in obtaining accurate particle size measurements from the compressed scales in Kesternich's paper [192]. However, it is clear that the limiting particle size in this case is approximately 6.25 nm, below the value of 10.5 nm for CW AX5.

11.3 Discussion

It is clear from the above expressions that particle coarsening in the advanced austenitic steels is not a steady state phenomenon governed by an Arrhenius type relationship. For example, at longer aging times (1000 h) the growth rate of particles at 900 C is slower than that at 700 C even though the diffusivities of solute in austenite would be greater in the austenite matrix at 900 C. Instead it appears that there is rapid particle growth immediately following nucleation (i.e. between times of 0.1 to 0.3 h) resulting from solute segregation to the dislocations. The precipitates pin the dislocations and subsequently grow by competing for the available solute. The precipi-

tate growth rate decreases as the solute in the austenite matrix is depleted and finally remains constant once the solute is exhausted.

The limiting precipitate size at aging times (>3000 h) will depend on the number of nucleation sites. Alloy AX5 had been cold worked 5.6%, giving the same dislocation substructure and number of nucleation sites for the 700 and 900 C aging treatments (note: the microstructural studies in Chapter 8 have shown that MC precipitation can take place at 600 C). Hence, the 700 and 900 C specimens have the same limiting particle size. In contrast, the Din 1.4970 steel studied by Kesternich had been cold rolled by 15% prior to aging at 750 C introducing significantly more nucleation sites. Consequently it is not surprising that the limiting particle size is smaller than that in AX5, particularly since the levels of the carbide forming elements Ti and Mo are lower than in AX5 and Din 1.4970 does not contain Nb or V.

Further credence is lent to the solute exhaustion hypothesis when the diffusivity data for Ti, Nb and V in austenite are considered. Using the diffusivity data presented in Table X, titanium will diffuse approximately 19 nm in 0.2 h and 42 nm in 1 h at 700 C, compared to 265 nm in 0.2 h and 593 nm in 1 h at 900 C. Typical distances between dislocations are 150 - 300 nm as shown in Figures 8.4b and 8.4d for 10 and 1000 h, respectively, at 700 C. Hence, it is clear that the available solute will rapidly become exhausted leaving a fine distribution of MC precipitates which will creep strengthen the austenite matrix.

The difference in the MC matrix precipitate distributions in the solution annealed and cold worked alloy AX5 can now be easily explained. The solution annealed material contains very few matrix dislocations, so that the few precipitates that nucleate are continually supplied with solute and become larger in size than those in cold worked AX5. The larger precipitates in SA AX5 may punch out additional dislocations providing more nucleation sites for MC precipitates, but as these particles grow, coalescence may occur and clusters of larger precipitates are observed. In contrast the MC precipitates in CW AX5 remain small and uniformly distributed according to the solute exhaustion mechanism described above. Once the solute has been exhausted, precipitate growth will effectively cease until an alternative mechanism, such as recovery or nucleation of an intermetallic phase provides a driving force for dissolution of the MC.

The low level of cold work in alloy AX5 has significantly reduced the stored elastic strain energy, delaying the onset of recovery compared to Din 1.4970, with 15% cold work, which shows significant recovery at 900 C. The selection of the 5.6% level of cold work, together with the tailoring of the alloy composition are extremely important alloy and microstructural developments which have resulted in the fine, uniform MC distributions which are responsible for the improved irradiation and creep resistance of these advanced austenitic steels.

TABLE X DIFFUSIVITIES ($\text{mm}^2 \text{s}^{-1}$) OF STABILIZING ELEMENTS
IN AUSTENITE

	Ti*[224]	V*[225]	Nb*[226]
700 C	$4.91 * 10^{-13}$	$0.67 * 10^{-13}$	$4.04 * 10^{-13}$
800 C	$8.87 * 10^{-12}$	$1.96 * 10^{-12}$	$8.69 * 10^{-12}$
900 C	$9.78 * 10^{-11}$	$3.22 * 10^{-11}$	$11.1 * 10^{-11}$

* $D_{\text{Nb}} (\text{cm}^2/\text{sec}) = 0.83 \exp[-266.5(\text{KJ}/\text{mole})/\text{RT}]$
 $D_{\text{Ti}} (\text{m}^2/\text{sec}) = 1.5*10^{-5} \exp[-60(\text{Kcal}/\text{mole})/\text{RT}]$
 $D_{\text{V}} = 365 (\text{mm}^2/\text{sec}) \exp[-293(\text{KJ}/\text{mole})/\text{RT}]$

Fig. 11.1a Histogram of MC size distribution in cold worked AX5 steel, 1h, 700 C.

Fig. 11.1b Histogram of MC size distribution in cold worked AX5 steel, 10h, 700 C.

Fig. 11.1c Histogram of MC size distribution in cold worked AX5 steel, 300h, 700 C.

Fig. 11.1d Histogram of MC size distribution in cold worked AX5 steel, 1000h, 700 C.

Fig. 11.1e Histogram of MC size distribution in cold worked AX5 steel, 3000h, 700 C.

Fig. 11.2a Histogram of MC size distribution in cold worked AX5 steel, 1h, 900 C.

Fig. 11.2b Histogram of MC size distribution in cold worked AX5 steel, 10h, 900 C.

Fig. 11.2c Histogram of MC size distribution in cold worked AX5 steel, 300h, 900 C.

Fig. 11.2d Histogram of MC size distribution in cold worked AX5 steel, 1000h, 900 C.

Fig. 11.2e Histogram of MC size distribution in cold worked AX5 steel, 3000h, 900 C.

Fig. 11.3 Average MC carbide size in CW AX5 at 700 and 900 C and in Din 1.4970 at 750 C as a function of aging time.

CONCLUSIONS

12.1 MC Carbides

1. The lower creep strains and significant improvements in creep rupture lives of the AX series alloys compared to 316, 800H and 17-14 CuMo steels, resulted from the controlled introduction of a fine, uniform distribution of MC precipitates on dislocations in the austenite matrix.
2. The optimization of the mechanical and creep rupture properties of the AX series alloys was achieved by: (a) careful control of the solution treatment temperature (1250 C--to ensure that the solute was in solution in the austenite), (b) the levels of the stabilizing element additions, (c) the degree of cold work (5.6%), which influenced the initial dislocation substructure, and (d) the reduction of silicon levels to prevent the formation of intermetallic compounds.
3. Dislocations were essential for the nucleation of the MC precipitates and virtually no MC was observed in the matrix unless cold work preceded aging (i.e. few matrix MC were observed in solution annealed AX5).
4. The uniform dispersions of MC carbides on matrix dislocations in CW AX5 were stable for up to 3000 h at 900 C.

12.2 Grain Boundaries

5. MC nucleated on extrinsic dislocations at grain boundaries.
6. Precipitate free zones were only occasionally observed at grain boundaries in cold worked and aged alloy AX5.

7. From the earliest stages of growth, bimodal precipitate distributions of large $M_{23}C_6$ (and later M_6C plus Laves phase) with fine MC between the $M_{23}C_6$ carbides developed at the grain boundaries in cold worked AX5.

8. Grain boundary precipitation of MC, $M_{23}C_6$, M_6C and Laves phases prevented grain boundary migration and improved the creep resistance of alloy AX5.

9. More extensive precipitation of M_6C carbide was observed at grain boundaries in alloy AX5 than in 316 stainless steel.

12.3 Precipitate Compositions and Precipitation Sequence

10. During the early stages of precipitation, MC carbides rich in vanadium and molybdenum were observed, in addition to (Ti,Nb,V,Mo)C.

11. The Mo-rich MC carbides lost Mo and incorporated Ti, Nb and Cr at longer aging times.

12. The Mo then became available for the precipitation of M_6C and Laves phase.

13. Laves phase appeared after 1000 h at 700 C and 800 C.

14. M_6C appeared after 1000 h at 700 C and 300 h at 800 and 900 C.

15. Significant phosphide precipitation was observed only in solution annealed AX5 after 1000 h at 700 and 800 C.

16. The matrix phosphide precipitates may enhance the creep rupture strength, but the major contribution appeared to result from the MC carbide distribution.

17. As the presence of phosphides may result in liquation cracking during welding, it is recommended that the level of phosphorus be

reduced to 0.02 wt% or less to optimize the properties of the advanced austenitic steels.

18. Sigma phase has not been observed in AX5 and this is attributed to the low silicon content of this alloy.

19. The boride phase has not been observed at grain boundaries.

20. The $M_{23}C_6$ precipitates began to dissolve after 1000 h at 900 C, when recovery was first observed, and were replaced by Ti-rich and Nb-rich MC carbides.

21. Intergranular and intragranular precipitation of the intermetallic χ phase was suppressed by cold work in AX5 alloy. This may contribute to the improved creep rupture strength of alloy AX5.

12.4 Role of Copper

22. The role of copper in 17-14 CuMo and the CE series advanced austenitic steels may not just be strengthening by the precipitation of copper particles but may also modify the stacking fault energy resulting in a refined matrix MC carbide distribution.

12.5 Aging Kinetics

23. The aging kinetics determined for alloy AX5 may be used as a guide for: (a) welding studies to indicate the conditions under which sensitization may occur in alloy AX5. For example, 1 h at 700 C, which gives extensive $M_{23}C_6$ in 316 stainless steel, is insufficient to produce copious $M_{23}C_6$ at grain boundaries in AX5; (b) the thermal aging conditions required to produce a given microstructural condition; (c) determination of the type and stability of the metastable precipitate phases developed

during aging; and (d) extrapolation to the microstructural conditions expected during a given service life.

12.6 MC Precipitate Sizes

24. The matrix MC carbides were found to reach a limiting precipitate size during aging at 900 C.

25. A new correlation, which describes the MC precipitate size distribution in CW AX5 and Din 1.4970, has been developed.

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