

Sigma-phase formation in Nitronic 50 and Nitronic 50W stainless steels

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The formation of the sigma-phase has been studied in two heats of a nitrogen-strengthened austenitic stainless steel, Nitronic 50 and Nitronic 50W, a weld filler wire composition. It was found that the presence of cold-work greatly enhanced the rate of sigma precipitation in the temperature range of 600–1000° C. The nucleation and growth of the sigma-phase was accompanied by recrystallization of the deformed austenite. The final austenite grain size was generally very small (0.5–4 μm), since grain growth was inhibited by the intergranular sigma precipitates. Precipitation of $M_{23}C_6$ carbides was suppressed by the rapid formation of the sigma-phase. In samples solution annealed prior to ageing, the kinetics of sigma precipitation were much slower, and for a heat containing 0.04 wt% carbon (Nitronic 50W), the sigma precipitation was retarded by the formation of intergranular $M_{23}C_6$. Grain boundaries in solution annealed and aged samples of both alloys also contained Z-phase (NbCrN) precipitates, which formed in the range of 700–1000° C. Retained delta-ferrite in the Nitronic 50W heat transformed directly to sigma-phase during ageing of the cold-worked specimens, but underwent more complex reactions in the solution annealed plus aged samples. Precipitation sequences at the ferrite–austenite interfaces in these latter specimens varied with ageing temperature. Sigma-phase chemistries in all samples were determined in the analytical electron microscope. In the solution-annealed and aged specimens, the sigma-phase chemistries were generally not of equilibrium values, and a wide variation in sigma composition was seen in each sample. In the cold-worked and aged samples, equilibrium sigma chemistries were attained. On comparing data from different samples, compositional changes in the sigma phase were observed, with molybdenum increasing and chromium decreasing as ageing temperatures increased.

1. Introduction

Nitronic 50, also known as 22–13–5, is a weldable, nitrogen-strengthened austenitic stainless steel [1, 2] with strength and corrosion resistance superior to 304 and 316 stainless steels [3]. The alloy contains high chromium, nitrogen, nickel and manganese and some molybdenum, niobium, vanadium and silicon. The weld filler wire alloy, Nitronic 50W, is of a similar composition, but with more chromium and less nickel. The presence of several alloying elements results in complex phase transformation sequences [4] and numerous equilibrium phases [5, 6] including sigma-phase. Sigma is a hard, brittle phase [7], which has been shown to have deleterious effects on mechanical properties such as toughness and ductility [8, 9]. The formation of sigma-phase in stainless steel is promoted by increasing amounts of chromium, molybdenum and silicon [10], and by the presence of ferrite [11]. In addition, studies have shown [12] that the presence of cold-work greatly enhances the rate of sigma precipitation, and that increasing amounts of carbon retard the nucleation of this phase [13, 14]. The high chromium contents of both Nitronic 50 and Nitronic 50W, and the presence of delta-ferrite in the latter material,

make the alloys prone to sigma-phase formation. This study was initiated to characterize the susceptibility of the alloys to sigma formation. The variables chosen were the type of matrix (austenitic or duplex), carbon content, and the presence or absence of cold work. This last variable was of particular interest since Nitronic 50 is sometimes used in a heavily worked condition [1, 15].

2. Experimental procedure

Two heats of material were used for this study, one of Nitronic 50 and one of Nitronic 50W. The composition of the Nitronic 50 conformed to specifications for ASTM alloy XM-19, which require a maximum carbon level of 0.045 wt%. The composition of the Nitronic 50W conformed to a General Electric Company specification which allowed up to 0.4 wt% Nb. This element is usually not included in Nitronic 50W. The alloys were vacuum induction melted and poured under one atmosphere nitrogen. Compositions of the two heats as determined by X-ray fluorescence are given in Table I. The major differences between the heats were the presence of more carbon in Nitronic 50W, and a lower chromium–nickel ratio in Nitronic 50.

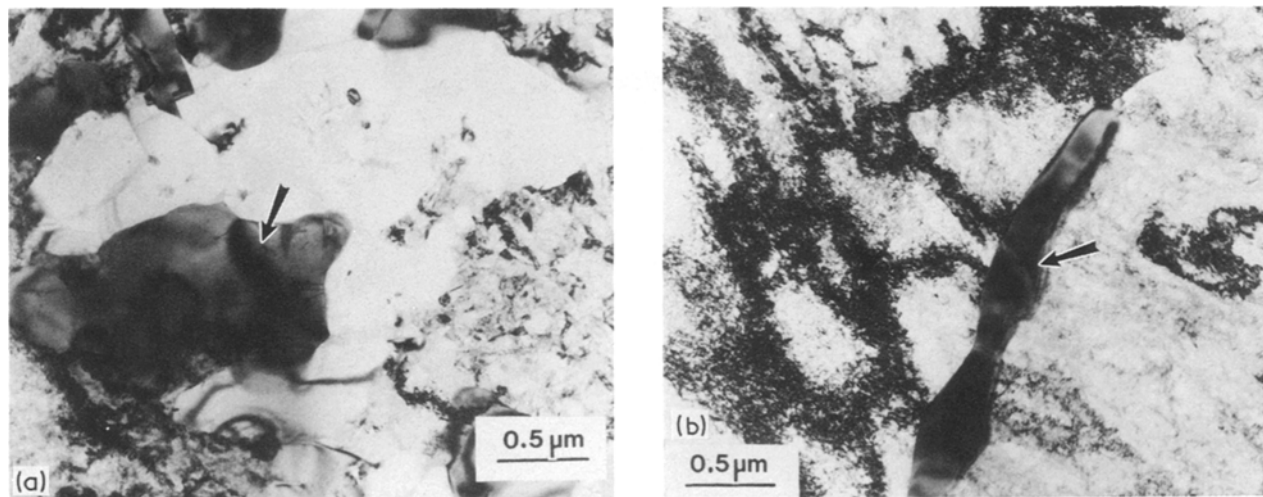


Figure 1 (a) Sigma-phase (arrow) associated with recrystallized austenite in Nitronic 50, CW + 600°C for 96 h. (b) Sigma-phase (arrow) on austenite-austenite grain boundary in the same specimen.

The ingots were annealed at 1200°C, hot forged, and solution annealed at 1120°C per 30 min. Pieces were hot-rolled to 0.25 cm thick, cold-rolled to 0.20 cm, solution-treated, cold-rolled to 0.05 cm thick and then pack-rolled to 0.02 cm thick. This was a total of ~87% cold work. Samples were encapsulated in quartz under vacuum. Half of the samples were solution-annealed at 1120°C per 30 min and water quenched. They were then aged for various times at 600, 700, 800, 900 and 1000°C. The other samples were aged at the same temperatures and times, but in the as-cold-worked condition.

Thin foils were prepared from each sample using a 20% perchloric/80% methanol solution. They were examined in a JEOL JSEM-200 scanning transmission electron microscope, operated at 200 kV. The microscope was equipped with an energy dispersive spectrometer. For spectral acquisition, a beam size of approximately 10 nm was used. Phase chemistries were obtained from spectra taken on austenite and sigma phase using a normalized intensity procedure, described elsewhere [4]. Five spectra were taken in each particle, and from three to five separate particles of each phase were usually examined. The chemistries calculated from normalized intensities were comparable to those calculated using the Cliff-Lorimer method [16]. The 95% confidence level on the precision with which these compositions were measured was $2S \sim 0.25\text{--}0.5 \text{ wt } \%$, where S is one standard deviation.

3. Results

3.1. Microstructure in cold-worked plus aged conditions

Phase transformations observed in the cold-worked and aged samples were similar for both alloys. Ageing for 96 h at 600°C resulted in a small amount of recrystallization, with the recrystallized austenite

grains about 0.5–1.0 μm in size. Associated with these grains were intergranular sigma-phase precipitates, about 0.25–0.5 μm in size (Fig. 1a). The sigma was usually found at the boundaries between recrystallized and unrecrystallized austenite. Occasionally sigma nucleated on grain boundaries between unrecrystallized austenite (Fig. 1b), or within an unrecrystallized austenite grain. Ageing cold-worked samples for 0.25 h at 700°C resulted in some recrystallization and sigma formation, and after 48 h at 700°C the specimen was almost fully recrystallized (Fig. 2a), with a few very small unrecrystallized regions. Sigma-phase was distributed on austenite grain boundaries throughout the microstructure. Numerous small intragranular precipitates were also seen in this sample (Fig. 2b).

In samples aged at 800°C for 0.25 h, most of the areas contained sigma-phase and recrystallized austenite, formed either during heating of the sample to that temperature (approximately 10 min from ambient temperature to 800°C), or during time at temperature. After aging at 800°C for 2 h, only a few small unrecrystallized regions were found, and after 24 h, no unrecrystallized austenite was seen. The microstructure consisted of 0.5–1.0 μm recrystallized austenite grains and 0.25–0.5 μm intergranular sigma precipitates (Fig. 3). Continued ageing at 800°C resulted in some coarsening of the austenite and sigma grains, as seen in Fig. 4. Some intragranular precipitates were observed after ageing and were found to be rich in chromium, with a small amount of vanadium.

Ageing at 900°C for 16 h resulted in a microstructure consisting of recrystallized austenite grains about 2.0–4.0 μm in size, and intergranular sigma-precipitates about 0.25–0.5 μm in size (Fig. 5). Occasional small intragranular ferrite regions were seen in a Nitronic 50 W sample (Fig. 5b). After ageing a Nitronic 50 specimen for 8 h at 1000°C, the recrystallized austenite

TABLE I Heat compositions (wt %)

	Mo	Cr	Mn	Fe	Ni	C	N	Nb	V	Si	S	P
N50	2.05	21.3	5.2	59.5	12.4	0.009	0.30	0.23	0.20	0.008	0.006	0.005
N50 W	2.00	23.0	6.2	58.2	11.3	0.04	0.32	0.24	0.20	0.02	0.006	0.005

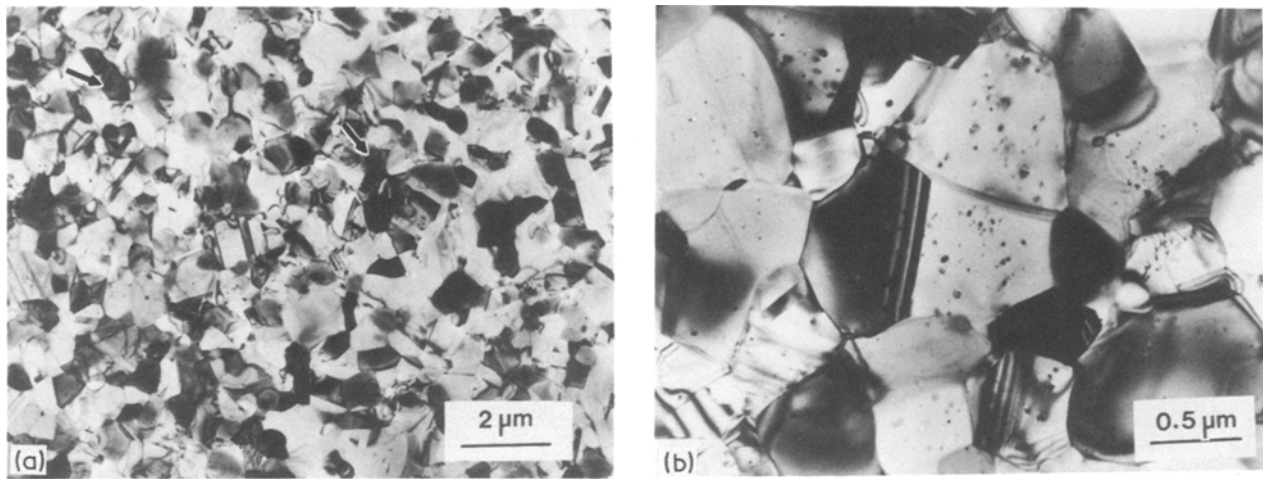


Figure 2 (a) Dispersion of fine recrystallized austenite grains and sigma-phase (arrows) precipitates in Nitronic 50, CW + 700°C for 48 h. (b) Higher magnification of same sample, showing small intragranular precipitates.

grains were 10–20 μm in size, and sigma-phase was infrequently observed (Fig. 6a). In the Nitronic 50 W sample, there was a larger amount of sigma-phase, and the austenite grains were 5–10 μm in size (Fig. 6b). There was a small amount of intragranular ferrite in the Nitronic 50 W, and in both alloys there were rod-shaped intragranular precipitates (Fig. 6a.), which were identified by electron diffraction as Z-phase (NbCrN). This complex nitride [17, 18] has been found in Nitronic 50 heat-treated in the temperature range of 1000–1200°C [4, 5].

In Nitronic 50 W samples aged at all temperatures, the regions which had been ferrite prior to ageing transformed directly to sigma-phase. This resulted in large bands of sigma (Fig. 7) within the recrystallized austenite-plus-sigma matrix. The bands were usually one to two sigma grains wide and many grains long, with a total length of 40–50 μm . The bands developed because ferrite present in the solution-annealed material was elongated during the cold deformation. Rapid nucleation of sigma-phase in the chromium and molybdenum-rich ferrite was followed by rapid growth, resulting in bands wider and more continuous than the original ferrite stringers.

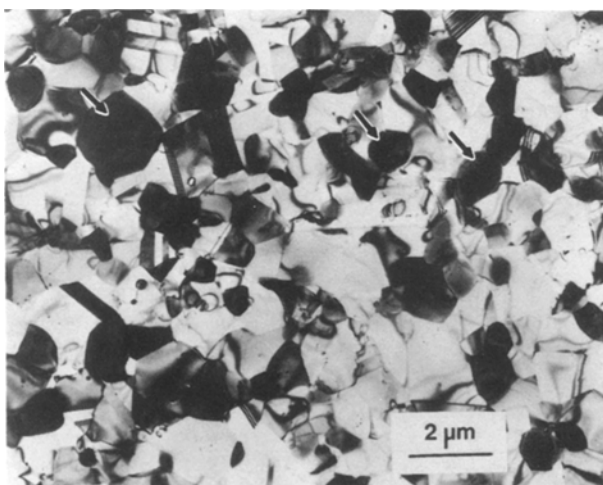


Figure 3 Sigma-phase (arrows) and recrystallized austenite grains in Nitronic 50, CW + 800°C for 24 h.

3.2. Microstructures in solution-annealed plus aged condition

Solution annealing of the cold-worked samples at 1120°C for 0.5 h resulted in complete recrystallization, with austenite grains growing to a size of 10–20 μm . There was some ferrite present in the Nitronic 50 W sample (Fig. 8), while the Nitronic 50 specimen was fully austenitic. Intragranular Z-phase precipitates were present in the solution-annealed samples. Precipitation sequences in the solution-annealed plus aged samples differed considerably in Nitronic 50 and Nitronic 50 W, due to the duplex microstructure of the latter alloy and to the very low carbon content of the former. Ageing at 600°C for 96 h produced no sigma-phase in Nitronic 50, and the microstructure remained indistinguishable from the solution-annealed condition. After 48 h at 700°C, some sigma had formed along the grain boundaries and at triple points (Fig. 9a). Some very small intergranular precipitates were also observed, and have been identified as Z-phase. Ageing at 800°C for 2 h produced a microstructure similar to that in the 700°C for 48 h sample, and continued ageing for 24 h at 800°C resulted in a larger volume fraction of sigma-phase and growth of both the sigma and the small intergranular Z-phase precipitates (Fig. 9b). After 16 h at 900°C, large sigma precipitates were seen on the grain boundaries (Fig. 10), but ageing at 1000°C for 8 h produced no sigma-phase. Intergranular Z-phase precipitates were found in both the 900°C and 1000°C samples.

In the Nitronic 50 W specimen aged at 600°C for 96 h no sigma-phase was seen, but precipitation of intergranular M_{23}C_6 carbides had occurred. At the interface between ferrite and austenite, extensive carbide precipitation was observed (Fig. 11a) and some of the ferrite had transformed to austenite. Similar microstructures were seen in the 700°C for 48 h Nitronic 50 W sample. A small amount of intergranular sigma-phase had formed at this temperature (Fig. 11b). No sigma-phase was seen associated with the transformed ferrite regions in either the 600°C or 700°C sample. After 24 h at 800°C, many of the austenite grain boundaries were covered with nearly continuous

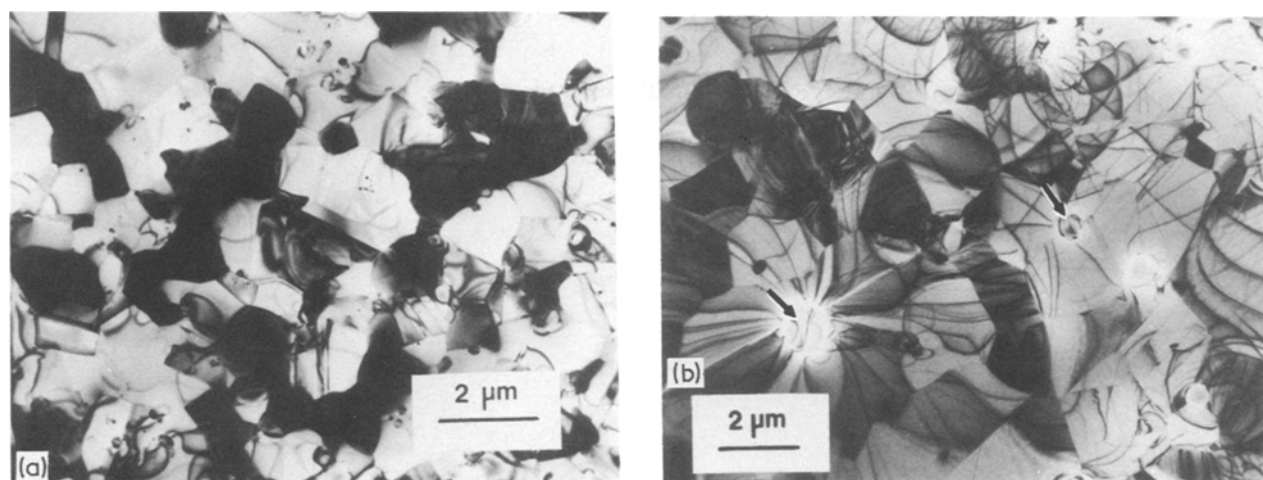


Figure 4 Sigma-phase and recrystallized austenite in (a) Nitronic 50, CW + 800°C for 506 h and (b) Nitronic 50, CW + 800°C for 5500 h. Chromium-rich intragranular precipitate indicated by an arrow.

films of $M_{23}C_6$ carbides (Fig. 12a). Intergranular sigma-phase and Z-phase were also observed in this sample (Fig. 12b). At the ferrite-austenite interfaces, the phase transformations were complex, with sigma, Z-phase and retained ferrite found at these interfaces (Fig. 12c). The central region, which was ferrite prior to ageing, had transformed to austenite.

Ageing for 16 h at 900°C resulted in the precipitation of intergranular sigma and Z-phase (Fig. 13a), but no $M_{23}C_6$ carbides. After 8 h at 1000°C, the Nitronic 50 W sample contained a small amount of intergranular sigma-phase (Fig. 13b), but less than in the 900°C for 16 h specimen. The small intergranular Z-phase precipitates seen at lower temperatures were also found after the 1000°C ageing treatment.

3.3. Phase chemistries

The chemistries of the sigma-phase in the cold-worked

plus aged samples are given in Table II (Nitronic 50) and Table III (Nitronic 50 W). The chemistry of the sigma-phase varied with ageing temperature. There was a measurable increase in molybdenum and a decrease in chromium with increased ageing temperature. The other elements remained essentially constant. Increasing ageing times at 800°C did not affect the sigma chemistry, for the times investigated.

The sigma-phase chemistries in the solution-annealed plus aged conditions are given in Tables IV and V. The sigma chemistries in the latter table are only for intergranular sigma in Nitronic 50 W and do not include data for sigma at the ferrite-austenite interfaces. No clear trend in compositional changes in the sigma-phase was apparent in the solution-annealed plus aged samples. In addition, the elemental concentrations in individual sigma precipitates varied widely within any one sample. For example, the range in molybdenum

TABLE II Nitronic 50: Sigma chemistries in cold-worked plus aged specimens

Ageing treatment	Mo (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)	Ni (wt %)
600°C for 96 h	6.1	33.6	4.7	499	5.5
700°C for 48 h	6.4	32.4	5.4	50.5	5.3
800°C for 1/4 h	6.3	31.7	4.7	51.7	5.4
800°C for 2 h	7.5	31.9	4.6	50.8	5.2
800°C for 24 h	7.2	32.1	4.2	50.9	5.6
800°C for 96 h	6.0	31.8	4.7	51.7	5.7
800°C for 506 h	6.3	31.8	4.7	51.8	5.4
800°C for 5500 h	6.0	33.0	3.6	51.6	5.2
900°C for 16 h	7.6	31.2	4.0	50.7	5.6
1000°C for 8 h	8.3	30.7	3.9	51.2	5.9

TABLE III Nitronic 50 W: Sigma chemistries in cold-worked plus aged specimens

Ageing treatment	Mo (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)	Ni (wt %)
600°C for 96 h	4.4	35.4	4.8	50.9	4.4
700°C for 48 h	4.4	34.3	4.9	52.1	4.2
800°C for 1/4 h	4.7	32.6	6.0	50.8	5.9
800°C for 2 h	4.6	33.2	4.2	52.6	5.4
800°C for 24 h	4.8	32.7	5.5	51.3	5.6
800°C for 96 h	4.7	32.3	6.0	51.3	5.8
800°C for 506 h	5.3	32.6	5.3	51.5	5.1
800°C for 5500 h	5.4	33.2	5.9	50.5	4.9
900°C for 16 h	5.9	32.9	5.3	50.8	5.2
1000°C for 8 h	6.3	32.1	5.5	50.4	5.6

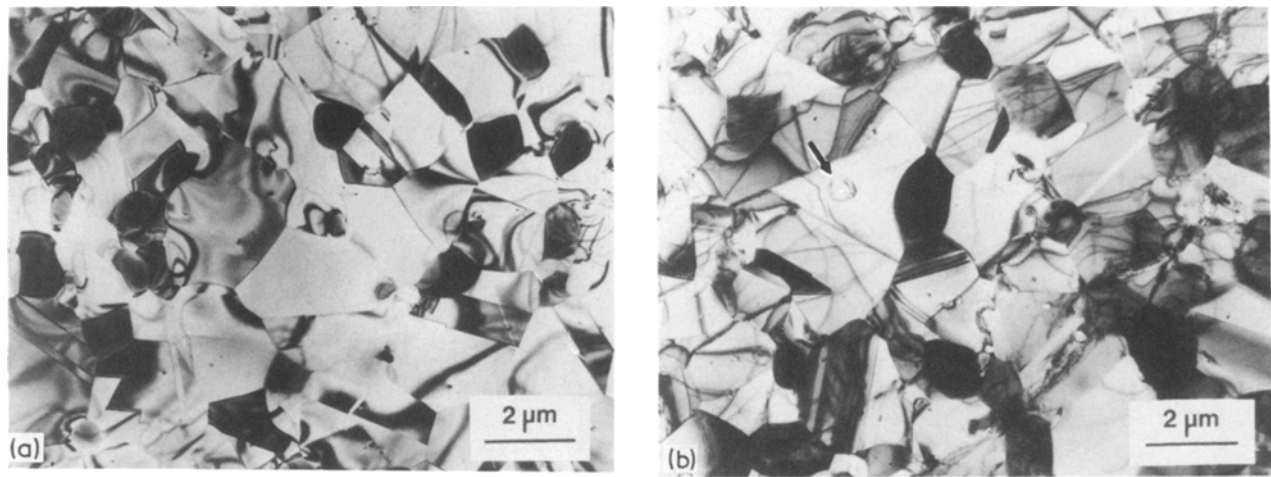


Figure 5 Sigma-phase and recrystallized austenite in CW + 900°C for 16 h samples of (a) Nitronic 50 and (b) Nitronic 50W. Intragranular ferrite indicated by an arrow.

concentrations in the Nitronic 50 W sample solution-annealed and aged at 800°C for 2 h was 6.4–12.9 wt %. By comparison, the variation in molybdenum concentration for sigma-phase in the cold-worked + 800°C for 2 h sample was 4.0–4.9 wt %.

Chemistries were also obtained for phases associated with a transformed ferrite region in the Nitronic 50 W sample solution-annealed and aged for 24 h at 800°C. The region examined is seen in Fig. 12c, and consisted of a central austenite island in a matrix of austenite. Around the perimeter of the island were small ferrite regions, sigma-phase precipitates, and an austenite region separated from the central austenite by a low-angle boundary. The chemistries of the various phases are given in Table VI, with the compositions of the matrix austenite and the intergranular sigma shown for comparison. The variability of the molybdenum content in the sigma at this temperature can be seen.

4. Discussion

This study has considered sigma formation in Nitronic 50 and Nitronic 50 W stainless steels, including the effects of cold work and alloy chemistry on the precipitation sequences and phase chemistries. The primary influence of cold work was to greatly enhance the rate of sigma-phase precipitation at all ageing temperatures studied. This is consistent with work by Nenno *et al.* [19] and Spruiell *et al.* [12], who observed accelerated precipitation of sigma-phase in cold-worked Fe–25 Cr–20 Ni alloys and 316 stainless steel, respectively. Sigma-phase formation in Nitronic 50 and Nitronic 50 W generally occurred in conjunction with recrystallization of the austenite, although some independent nucleation of sigma-phase within the cold-worked austenite and on austenite–austenite grain boundaries in unrecrystallized regions was observed. This is contrary to results in 316 stainless

TABLE IV Nitronic 50: Sigma chemistries in solution-annealed plus aged specimens

Ageing treatment	Mo (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)	Ni (wt %)
700°C for 48 h	8.1	33.8	4.3	48.5	5.3
800°C for 2 h	7.6	31.9	5.1	49.9	5.5
800°C for 24 h	7.6	32.2	3.5	50.7	6.0
900°C for 16 h	8.3	30.9	3.8	51.1	5.9

TABLE V Nitronic 50 W: Sigma chemistries in solution-annealed plus aged specimens

Ageing treatment	Mo (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)	Ni (wt %)
700°C for 48 h	3.5	32.2	5.3	54.3	4.7
800°C for 2 h	7.3	31.4	5.8	49.6	5.7
800°C for 24 h	4.4	33.2	5.3	52.1	5.0
900°C for 16 h	5.8	33.2	5.5	49.8	5.7
1000°C for 8 h	6.3	32.4	5.2	50.6	5.5

TABLE VI Phase chemistries associated with transformed ferrite in Nitronic 50W (SA + 800°C/24 h)

Phase	Mo (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)	Ni (wt %)
Matrix austenite	1.1	22.0	6.4	59.2	11.2
Austenite island	1.7	22.8	6.3	58.5	10.7
Perimeter austenite	0.8	21.5	6.1	60.4	11.2
Perimeter ferrite	1.7	36.5	4.1	54.2	3.5
Perimeter sigma	11.3	29.9	5.9	49.8	3.0
Intergranular sigma	4.4	33.2	5.3	52.1	5.0

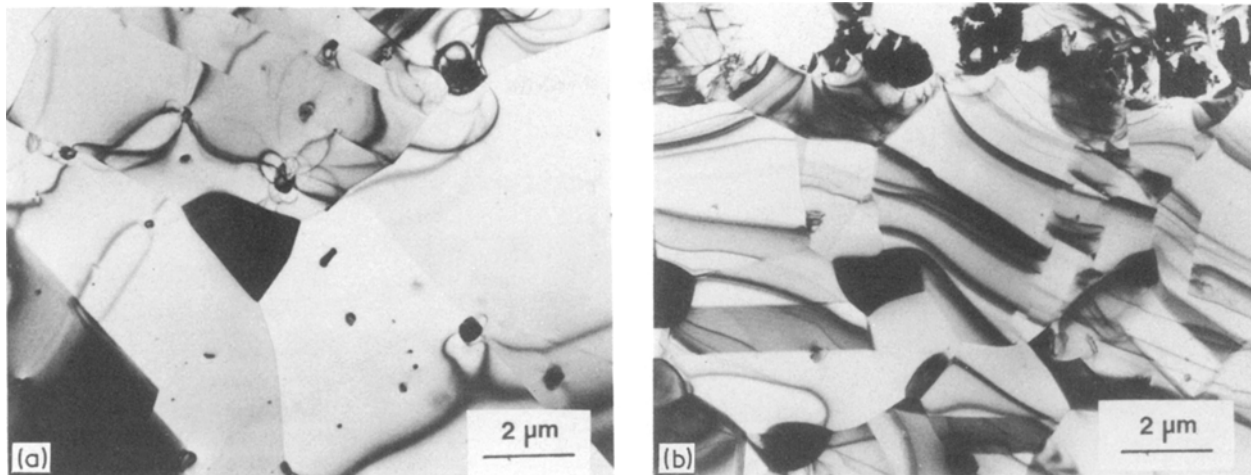


Figure 6 Sigma-phase and recrystallized austenite in CW + 1000°C for 8 h specimens of (a) Nitronic 50 and (b) Nitronic 50 W.

steel [12] and 308 stainless steel [20], where nucleation of sigma-phase was always found to occur within recrystallized regions or at grain boundaries between recrystallized and cold-worked grains. Work on the formation of sigma in a cold-worked Fe-25Cr-20Ni alloy, however, has shown nucleation of sigma precipitates on deformation twins and stacking faults in the unrecrystallized austenite [19]. The interaction between sigma-phase precipitation and recrystallization in Nitronic 50 and Nitronic 50 W is similar to that seen in cold-worked ternary alloys [21]. In both cases, the growth of the recrystallized austenite grains was inhibited by the sigma-phase, resulting in a fine austenite grain size at lower ageing temperatures. Similar retarding of grain growth has been seen to occur due to carbide precipitation during recrystallization of stainless steel [12, 22].

Studies of 316L and 316 stainless steel [12, 13] showed that cold-work enhanced the kinetics of $M_{23}C_6$ formation. In the cold-worked Nitronic 50 W samples, no $M_{23}C_6$ precipitates were observed at any of the ageing temperatures, indicating that the rapid precipitation of sigma-phase suppressed $M_{23}C_6$ formation. This may be a result of either the saturation of available high energy nucleation sites by sigma-phase, or

depletion of chromium in the austenite by sigma precipitation, or a combination of the two effects. The precipitation of intergranular sigma-phase in the low-carbon (0.009 wt %) Nitronic 50 samples was similar to that in the higher carbon Nitronic 50 W. The major difference between the microstructures in these alloys was the presence of long sigma-phase bands in Nitronic 50 W. Also, at nearly all times and temperatures, Nitronic 50 W apparently contained a larger amount of sigma-phase than did Nitronic 50. This is a result of the higher chromium and lower nickel contents of Nitronic 50 W relative to Nitronic 50.

Precipitation sequences in the solution-annealed and aged conditions were influenced by the carbon content of the alloys. In the low-carbon Nitronic 50 heat, sigma-phase nucleated at grain boundaries and triple points, while in the higher-carbon Nitronic 50 W heat extensive precipitation of intergranular $M_{23}C_6$ occurred at temperatures from 600–800°C. This resulted in saturation of nucleation sites, and consequently little sigma-phase precipitation. At temperatures where $M_{23}C_6$ did not form (900–1000°C) in Nitronic 50 W, intergranular sigma-phase was observed. In Nitronic 50 W samples aged at 700°C and 800°C, the small amount of intergranular sigma-phase present nucleated

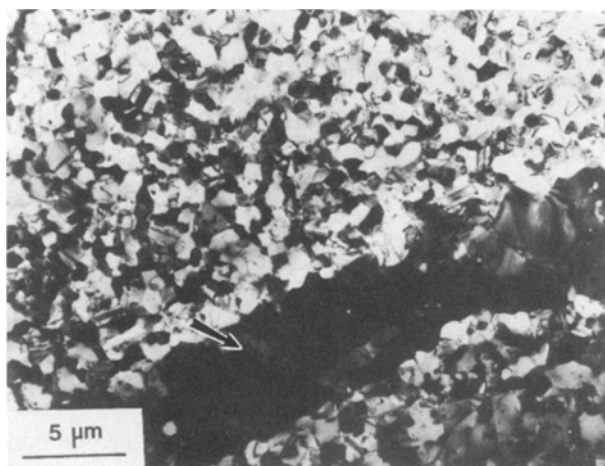


Figure 7 Band of sigma-phase (arrow) in Nitronic 50 W, CW + 800°C for 24 h.

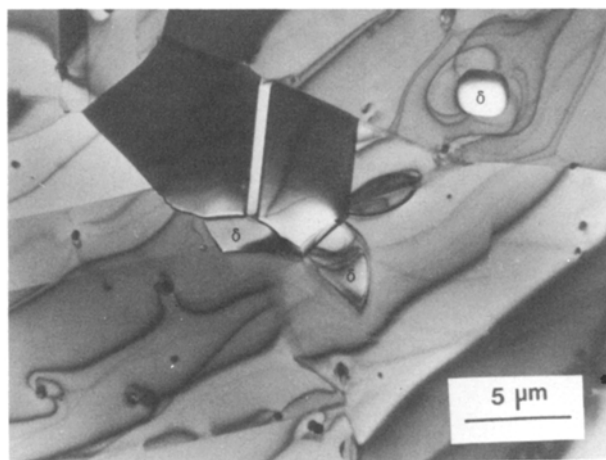


Figure 8 Nitronic 50 W, solution-annealed at 1120°C for 0.5 h. Small intragranular precipitates are Z-phase.

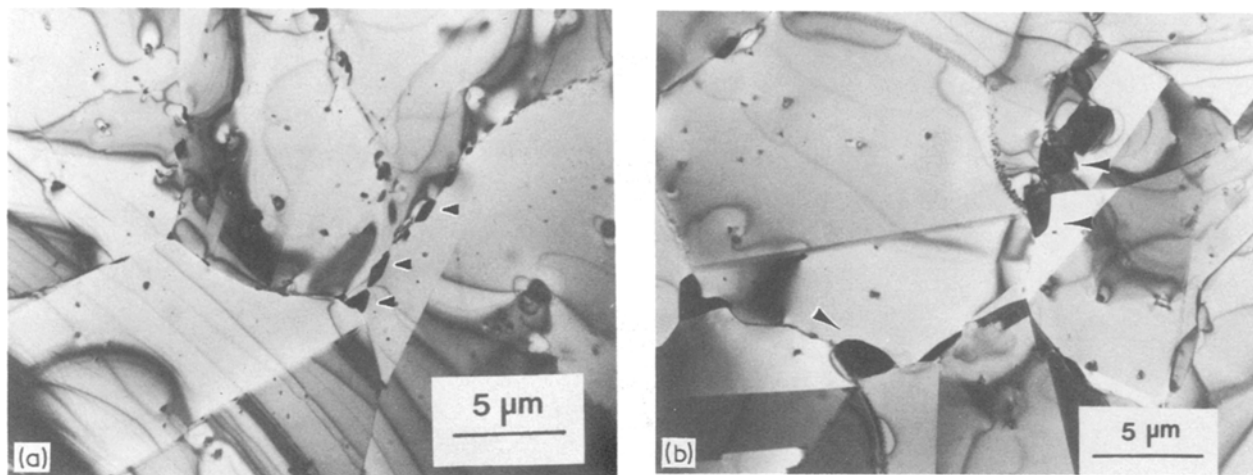


Figure 9 Intergranular sigma-phase (arrow) in Nitronic 50 specimens (a) SA + 700°C for 48 h, and (b) SA + 800°C for 24 h. Very small intergranular precipitates are Z-phase.

on grain boundary segments free of carbides. This observation is similar to results reported for some other steels [13, 23–25]. Nucleation of sigma-phase on intergranular carbides has been seen [9], and was observed in a high-carbon heat (0.055 wt %) of solution-annealed Nitronic 50, aged at 675°C [4]. This indicates that the carbon content of the alloy also influences the preferred site for sigma nucleation.

Precipitation associated with retained ferrite in the solution-annealed Nitronic 50 W samples aged at 600 and 700°C was generally similar to that occurring on austenite–austenite grain boundaries at the same temperature. Precipitation of $M_{23}C_6$ was favoured, and the rapid growth of this phase at ferrite–austenite interfaces depleted the ferrite of the chromium necessary for sigma-formation. At 800°C, the austenite–austenite grain boundaries contained $M_{23}C_6$ and sigma-phase, and the ferrite–austenite interfaces contained sigma-phase and Z-phase. Precipitation of sigma-phase resulted in chromium-depletion of the central ferrite region, with consequent transformation of the ferrite to austenite. The eutectoid decomposition of ferrite to sigma plus austenite, which has been observed in other duplex stainless steels [26], was not seen in Nitronic 50 W. It is apparent from these results that the presence of 0.04 wt % carbon in solution-annealed

Nitronic 50 W retarded sigma-phase formation only at the lower temperatures, where precipitation of $M_{23}C_6$ saturated the high energy nucleation sites. This is similar to observations [13, 14] in other solution-annealed stainless steels, where precipitation of sigma-phase occurred only after $M_{23}C_6$ had lowered the carbon content of the austenite.

One effect of rapid nucleation and growth of sigma in the cold-worked and aged samples was to achieve an equilibrium sigma-phase chemistry early in the ageing sequence. Consideration of the sigma-phase chemistries in the 800°C specimens aged up to 5500 h showed that the equilibrium composition was established after about 0.25 h. It is likely, therefore, that the sigma-phase precipitates in cold-worked specimens aged at the other temperatures are also of the equilibrium chemistry. The small variation in compositions between sigma-phase precipitates within a specific cold-worked and aged specimen tends to support this. By comparison, sigma-phase chemistries within any one solution-annealed and aged sample varied, and non-equilibrium phase chemistries were observed (Tables III, VI).

The sigma-phase chemistries in the cold-worked and aged samples varied with temperature, with chromium decreasing and molybdenum increasing as the ageing temperature increased. A similar trend has been observed in a 316 stainless steel solution-annealed prior to ageing [27]. Increasing molybdenum contents with long ageing times have been reported for 316 stainless steel [27], but this was not seen in Nitronic 50 and Nitronic 50 W, cold-worked and aged at 800°C. It appears that systematic changes in sigma-phase chemistry are a point of controversy [27, 28]. The variation among observations may have resulted from the different treatment prior to ageing (solution-annealed or cold-worked), the specific steel chemistry, or the method used to analyse sigma compositions (chemical or energy dispersive analysis of extracted residue, or analytical electron microscopy on thin foils). It is certainly well established [10] that molybdenum stabilizes sigma-phase, requiring less chromium for the phase to form. The presence of increasing amounts of molybdenum in the sigma formed at higher temperatures may result in the higher solvus tem-

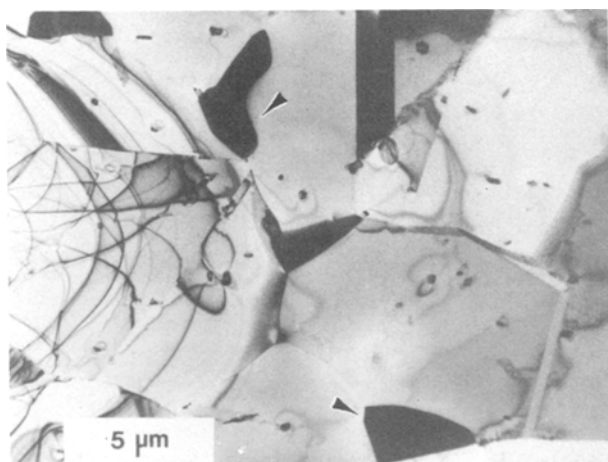


Figure 10 Intergranular sigma-phase (arrow) in Nitronic 50 specimens solution-annealed and aged for 900°C for 16 h.

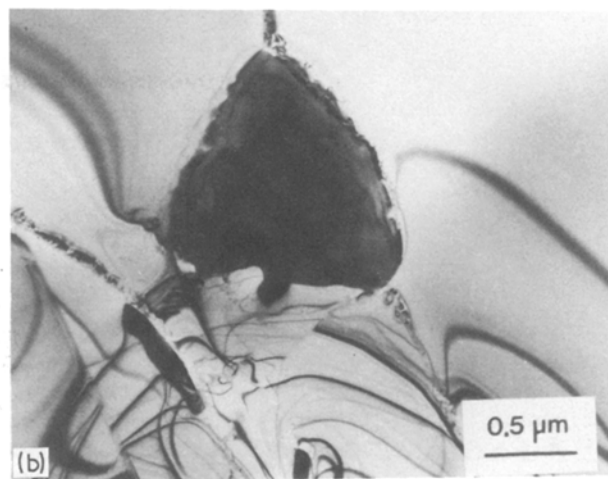
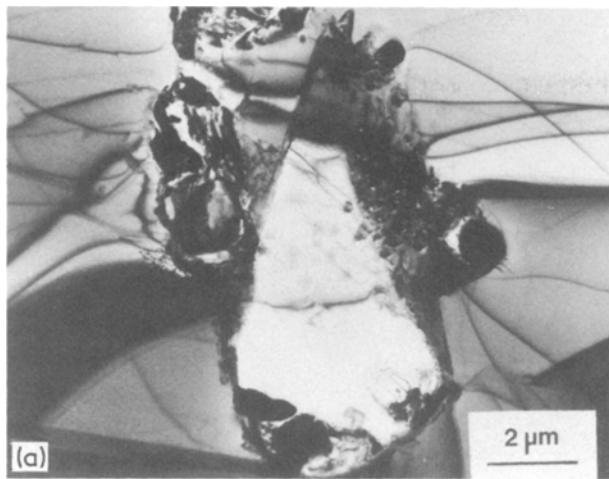


Figure 11 (a) Precipitation of $M_{23}C_6$ carbides at the ferrite-austenite interface in Nitronic 50 W, SA + 600°C for 96 h. (b) Intergranular sigma-phase in Nitronic 50 W, SA + 700°C for 48 h.

perature of sigma in complex steels, compared with Fe-Cr-Ni ternary alloys [14].

It has been observed [14, 28] that the concentration of molybdenum in sigma-phase is a function of the molybdenum content in the steel. In Nitronic 50 and Nitronic 50 W, the molybdenum contents of the alloys were equal. However, consideration of the data in Tables II and III shows that, at all temperatures the sigma-phase in Nitronic 50 was enriched in molybdenum and depleted in chromium relative to

Nitronic 50 W. Since the bulk chromium concentration in Nitronic 50 was less than in Nitronic 50 W, it appears that more molybdenum was necessary to stabilize sigma-phase in Nitronic 50, as has been seen in other steels [14].

5. Conclusions

The phase transformations occurring in Nitronic 50 and Nitronic 50 W aged in the temperature range of 600–1000°C were found to be primarily influenced by

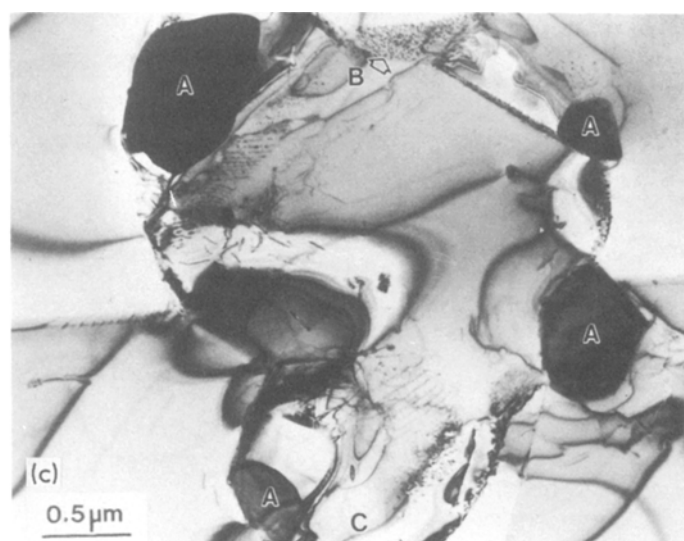
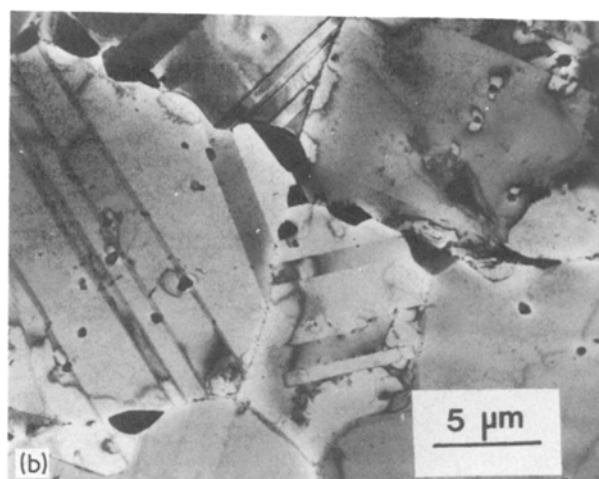
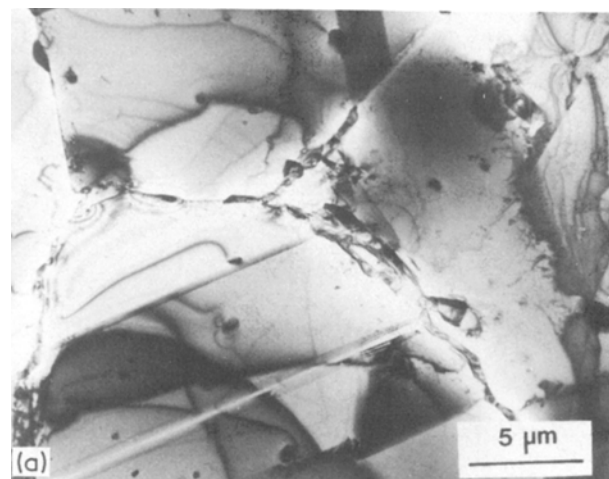


Figure 12 Nitronic 50 W, SA + 800°C for 24 h. (a) Intergranular $M_{23}C_6$ precipitation, (b) intergranular sigma-phase, and (c) sigma-phase (A), Z-phase precipitates (B), and residual ferrite (C) at former ferrite/austenite interface.

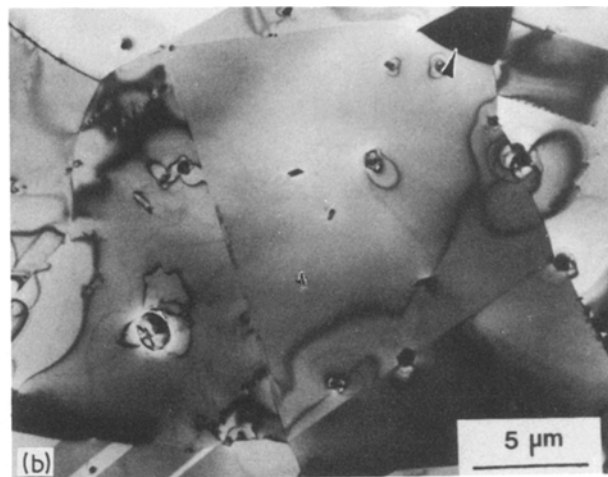
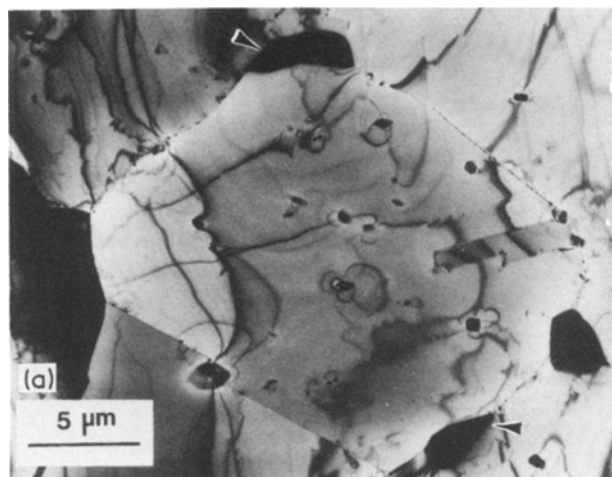


Figure 13 Intergranular Z-phase and sigma-phase (arrow) in Nitronic 50 W specimens (a) SA + 900°C for 16 h and (b) SA + 1000°C for 8 h.

relative carbon and chromium contents and the presence of cold work prior to ageing.

In the low-carbon Nitronic 50 heat solution-annealed before ageing, precipitation of intergranular Z-phase and sigma-phase occurred in the temperature range of 700–900°C. No intergranular precipitation was observed after ageing at 600°C for 96 h. Ageing for 8 h at 1000°C was insufficient to nucleate sigma-phase in this lower-chromium heat.

The presence of 0.04 wt % carbon in the Nitronic 50 W specimens solution annealed before ageing caused rapid precipitation of $M_{23}C_6$ on grain boundary sites, and a consequent retardation of sigma-phase and Z-phase kinetics in the range of 600–800°C. At 900°C and 1000°C the intergranular $M_{23}C_6$ carbides did not form, and intergranular precipitation consisted of Z-phase and sigma-phase.

In both Nitronic 50 and Nitronic 50 W, the effect of cold working prior to ageing was to greatly accelerate the formation of the sigma-phase, which was concurrent with the recrystallization of the austenite. This resulted in a homogeneous distribution of small intergranular sigma particles in a fine-grained austenite matrix. In the higher-carbon heat, all $M_{23}C_6$ precipitation was suppressed in the cold-worked and aged samples, for the ageing times investigated.

The rapid precipitation of sigma-phase in the cold-worked and aged specimens allowed attainment of equilibrium chemistries of this phase after relatively short ageing times.

The equilibrium sigma chemistries were a function of ageing temperature, with chromium decreasing and molybdenum increasing at higher temperatures. Ageing at 800°C showed no changes in sigma-chemistry with time, up to 5500 h at this temperature.

In the solution-annealed and aged samples, much smaller amounts of sigma-phase were observed than in the cold-worked and aged samples. The sigma-phase chemistries in the solution-annealed and aged samples varied widely within any one sample, and differed from the equilibrium chemistries measured in the cold-worked and aged specimens.

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